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LAICM

LATIN-AMERICAN INORGANIC CHEMISTRY MEETING

SANTIAGO DE COMPOSTELA (SPAIN)

13 - 17 September 1993

PROGRAMME


SANTIAGO DE COMPOSTELA

LATIN-AMERICAN INORGANIC CHEMISTRY MEETING

	MONDAY - Sept. 13			TUESDAY - Sept. 14		
9.00	**OPENING CEREMONY** (University Auditorium)					
9.30	*Sir* G. WILKINSON (Ch: *A. Sousa*) (University Auditorium)			J. MOURA (Ch: *R. Delgado*) (University Auditorium)		
10.00						
10.30	Coffee break			Coffee break		
HALL:	A	B	C	A	B	C
CHAIRMAN:	*Costes*	*Tiripicchio*	*C. Otero*	*Pelizzi*	*Süss-Fink*	*Caneiro*
11.00	Weiss	Kroto	Almeida	Ruiz-Azuara	Milstein	Pannetier
11.45	De Castro	Martinho	West	Tudela	Strukul	Flükiger
12.00		Simoes				
12.30	Teixidor	le Bozec	Gatteschi	Lippert	Vargas	Carbonio
13.15	POSTERS SESSION (Hall D)			POSTERS SESSION (Hall D)		
14.00	LUNCH			LUNCH		
HALL:	A	B	C	A	B	C
CHAIRMAN:	*Moreno*	*Lahuerta*	*Gatteschi*	*Davillanova*	*A. Otero*	*Pannetier*
16.30	Rizzarelli	Espinet	Quijano	Balzani	Lugli	Figueiredo
17.15	Delgado	Ephritikhine	García Roja	Costamagna	Riera	Rincón
CHAIRMAN:	*M.R. Bermejo*			*J.S. Casas*		
18.00-19.00	POSTERS SESSION (Hall D)			POSTERS SESSION (Hall D)		
	WELCOMING RECEPTION (20.00-22.00)			CONCERT (20.30-21.30) *Grupo de Cámara*		
				RECEPTION (21.30-22.30)		

Hall A: Chemistry Faculty; Hall B: Pharmacy Faculty

Santiago de Compostela (Spain), 13th-17th September 1993

WEDNESDAY - Sept. 15		THURSDAY - Sept. 16			FRIDAY - Sept. 17
9.00	C. BIANCHINI (Ch: *M. Graziani*) (University Auditorium)				
9.30		R. SANCHEZ-DELGADO (Ch: *P. Dixneuf*) (University Auditorium)			B. MEUNIER (Ch: *E. Carmona*) (University Auditorium)
10.00	A. CANEIRO (Ch: *J. Sordo*) (University Auditorium)				
10 30		Coffee break			Coffee break
		A	B	C	
		Faus	*Royo*	*Rojo*	
11.00	CONFERENCE EXCURSION	Bastida	Paz-Sandoval	Ravaglioli	M.A. ALARIO (Ch: *M. Vallet*) (University Auditorium)
11.45		Vicentini	McAuliffe	Livage	
12.00					CLOSING CEREMONY (University Auditorium)
12.30		Luchinat	Fornies	Planell	
13.15		POSTERS SESSION (Hall D)			*PILGRIMAGE AND OFFERING*
14.00		LUNCH			
		A	B	C	
		McAuliffe	*Strähle*	*Livage*	
16.30		Sadler	Oro	Leyva	
17.15		Chottard	Pombeiro	Oviedo	
		A. Sánchez Díaz			
18.00-19.00		POSTERS SESSION (Hall D)			
		CONCERT (20.00-21.00) *Ultreia*			
		CONFERENCE DINNER (21.30-24.00)			

Hall C: Chemistry Faculty; Hall D: Pharmacy Faculty

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The British Council

Welcome

Dear colleagues and guest,

It is a pleasure for me to welcome you, on behalf of the Organizing Committee to this *Latin-American Inorganic Chemistry Meeting*. We are delighted that so many of you have been able to respond to the appeal of a broad, distinguished scientific programme comprising 7 Plenary Lectures, 45 Session Lectures and 3 Poster Sessions with approximately 375 announced contributions. We trust that the venue of the Meeting in the ancient city of Santiago de Compostela, with its varied surroundings, will prove conductive to fruitful scientific discussion and, together with the Social Programme, provide an opportunity to meet old friends and make new ones.

This brochure contains the Programme of the Meeting together with extensive information on organization, facilities and locations. If you have any problems, do not hesitate to contact organizing staff; it will be our pleasure to help you.

We wish you a pleasant and rewarding stay in Santiago de Compostela.

Antonio Sousa
Chairman,
ORGANIZING COMMITTEE

Honorary Patrons

Excmo. Sr. M. FRAGA IRIBARNE
Presidente da Xunta de Galicia

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Technical Assistance

E. Vázquez López	Software
I.C. Coleman	Translation

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Acknowledgements

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CICYT - *Comisión Interministerial de Ciencia y Tecnología (Spain).*

DGICYT - *Dirección General de Investigación Científica y Técnica (Spain).*

Dirección Xeral de Ordenación Universitaria e Política Científica, Galicia (Spain).

International Centre for Science and High Technology, UNIDO, Trieste (Italy).

CNRC - *Centre National de la Recherche Scientifique (France).*

Junta Nacional de Investigação Científica e Tecnológica (Portugal).

CSIC - *Consejo Superior de Investigaciones Científicas (Spain).*

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ANORSUR, *Sevilla (Spain).*

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Grupo Sargadelos, Galicia (Spain).

Afora S.A. (Spain).

General Information

Reception - Congress Office

The Congress Office is in the entrance hall of the University Auditorium . Opening hours are:

Sunday,	12 September 1993	17.00 to 21.00
Monday,	13 September 1993	09.00 to 13.30 and 16.30 to 19.00
Tuesday,	14 September 1993	09.00 to 13.30 and 16.30 to 19.00
Wednesday,	15 September 1993	09.00 to 11.00
Thursday,	16 September 1993	09.00 to 13.30 and 16.30 to 19.00
Friday,	17 September 1993	09.00 to 13.00

Telephone of the Congress Office: (981) 599255

Full documentation, including invitations and tickets, will be provided upon checking in at reception desk.
Hotel reservations are the responsibility of the official congress agency:

Viajes Atlántico, S.A.
Pl. Fuenterrabía, 3
E-15702 SANTIAGO DE COMPOSTELA (SPAIN)
Tel.: (981) 585899/585189
Fax: (981) 561951

Notices

Notices pertaining to the business of the meeting will be placed on an official board next to the reception desk. Any changes in the scientific programme will be posted on this board, as will official messages for conference participants. For personal messages, a board will be provided at the Meeting Point.

Meeting point

In the reception area there will be a specially designated *meeting point*. There you will find a board for personal messages.

Congress Badge - Admittance to the meeting

You are requested to wear your official Congress badge, which will ensure you admittance to all scientific sessions and exhibitions. For other events, the invitation or admission cards, you will find in your folder must be shown on request.

Coffee, tea

Coffee and tea will be served free of charge in the congress area, after each plenary lecture (from 10.30 to 11.00 a.m.) except on Wednesday.

Meals and Refreshments

There are several cafeterias located within the congress area. Refectories are located in R.U *Monte da Condesa* and C.M. *Fonseca*. Other restaurants and cafeterias can also be found in the neighbourhood.

Photocopying facilities

There are photocopying services in the Chemistry and Pharmacy Faculties.

Bus Service

A special bus service will run from the R.U. *Burgo das Naciόns* to the Congress site 20 min before the first scientific session each morning. The Congress site can also be reached by public transport (for details about routes see the map supplied in your Congress folder).

Taxis

Taxis can be ordered by calling (981) 561028 or (981) 595964.

Sports opportunities

Athletics facilities are available on the University Campus; they include basketball and volleyball, soccer, athletics, swimming and tennis facilities.

Emergencies and first aid

There is a first aid post in the Congress area. In an emergency, please contact the secretariat of the Organizing Committee. Emergency service telephone numbers are:

Fire brigade	080
Police	091/092
Ambulance	222222

Liability

The Organizing Committee declines any responsibility whatsoever for injuries or damages to persons and their property during the LAICM and related events, and reserves the right to cancel, postpone or modify programme points in case of unforeseen circumstances. It accepts no responsibility for travel or accommodation arrangements.
The participant acknowledges that he has no right to lodge damage claims against the organizers should the holding of the Congress be hindered or prevented by unexpected political or economic events or generally by force majeure, or should the nonappearance of speakers or posters or other reasons make programme changes necessary. With his registration, the participant accepts this proviso.

Social Programme

Monday, September 13

09.00-09.30 **University Auditorium**

OPENING CEREMONY

09.30-10.30 **University Auditorium**

OPENING LECTURE

A UNIQUE IRIDIUM(III) CYCLOHEXADIENYL.
NEX IMIDO CHEMISTRY OF MANGANESE AND TUNGSTEN
by Nobel-Laureate *Sir G. Wilkinson*

Chairman: *Prof. A. Sousa*

16.30-19.00 Accompanying Persons
Half-day City Tour (old town).
Departure from the University Auditorium.

20.00-22.00 WELCOMING RECEPTION

Offered by the *Mayor of Santiago de Compostela* and the *Organizing Committee.*

Tuesday, September 14

16.30-19.00 Accompanying Persons
Visit to the City Museums.
Departure from the University Auditorium

20.30-21.30 **Church of San Paio de Antealtares**

CONCERT

Grupo de Camara da Universidade de Santiago de Compostela

21.30-22.30 **Cloisters of the Pazo de Fonseca**

RECEPTION

Offered by the *Rector of the University of Santiago de Compostela.*

Wednesday, September 15

11.00-21.30 (approx.) CONFERENCE EXCURSION

A full day trip to the *Costa da Morte*
During the trip a light meal will be served.
Buses will depart from the University Auditorium.

Thursday, September 16

20.00-21.00 **University Auditorium**

CONCERT

Obradoiro de Cultura Tradicional ULTREIA
Galician Folk Music and Dancing.

21.30 ***LAICM*** CONFERENCE DINNER

Friday, September 17

12.00-12.30 **University Auditorium**

CLOSING CEREMONY

13.00 PILGRIMAGE AND OFFERING TO THE APOSTLE ST. JAMES THE GREAT

FURTHER DETAILS WILL BE GIVEN ON THE ANNOUNCEMENTS BOARD

Scientific Programme

General instructions to chairmen and speakers

Plenary lectures and Session lectures

Plenary lectures are expected to last 60 minutes. The session lectures are scheduled to last 45 minutes, including 5 minutes for discussion.
Chairmen should make appropriate reminders 5 minutes before the end of each lecture.
As the whole programme depends on strict timekeeping, chairmen should insist on absolute adherence to the 60/45 minutes time allotment, and are instructed to terminate any lecture overrunning its time.
Authors shoulds be at their lecture place at least 10 minutes before their session begins and make themselves known to the chairman.

Projection

Slides should be suitably boxed and numbered sequentially in the upper righthand corner when viewed upside down. Each box should be given to the projectionist in the appropriate hall at least 20 minutes before the beginning of the session.

Posters

Authors are requested to mount their poster before 11:00 on the day of presentation and remove them by 19:00 the same day. At least one co-author should be present between 18:00 and 19:00 to discuss the work with interested participants. In the event of unavoidable absence for part of this time, authors should post a notice saying when they expect to return.

Commercial exhibits

The commercial exhibition will be located in the lobby of the Faculty of Chemistry.

Location of Sessions

PLENARY LECTURES: **University Auditorium**

SESSION LECTURES:

1. Coordination and Bioinorganic Chemistry
   Aula Magna (Faculty of Chemistry) **Hall A**

2. Organometallic Chemistry and Catalysis
   Aula Magna (Faculty of Pharmacy) **Hall B**

3. Solid State Chemistry and Inorganic Materials
   Hall of Physical Chemistry (Faculty of Chemistry) **Hall C**

POSTERS: Library (Faculty of Pharmacy) **Hall D**

Monday, September 13

09.00-09.30 **OPENING CEREMONY** **University Auditorium**

09.30-10.30 **OPENING LECTURE** **University Auditorium**

A UNIQUE IRIDIUM(III) CYCLOHEXADIENYL. NEW IMIDO CHEMISTRY OF MANGANESE AND TUNGSTEN.
Sir G. WILKINSON.

Chairman: *A. Sousa*

10.30-11.00 *Coffe Break*

11.00-13.15 **SESSION LECTURES**

1. COORDINATION AND BIOINORGANIC CHEMISTRY **Hall A**

Chairman: *J.P. Costes*

1428S HIGH-VALENT IRON-OXO PORPHYRIN SPECIES: GENERATION AND CHARACTERIZATION OF NEW MODELS FOR PEROXIDASE COMPOUNDS-I.
R. WEISS.

1280S EPR AND VOLTAMMETRIC CHARACTERIZATION OF ELECTROCHEMICALLY GENERATED SCHIFF BASE NICKEL(I) AND NICKEL(III) COMPLEXES WITH CATALYTIC PROPERTIES.
B. de CASTRO.

1496S MODULATION OF THE B(3)-H-Ru DISTANCES IN 7,8-DICARBA-*nido*-UNDECABORATE DERIVATIVES.
F. TEIXIDOR, C. VIÑAS, J.A. AYLLON, R. KIVEKÄS, R. SILLANPÄÄ and J. CASABÓ.

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Chairman: *A. Tiripicchio*

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H.W. KROTO, A.J. STACE, R. TAYLOR, D.R.M. WALTON and M. ENDO.

2091S FROM IONIC SALTS TO EARLY TRANSITON METAL AND ACTINIDE COMPLEXES: THE ENERGETICS OF METAL-OXIGEN BONDS IN LITHIUM, SODIUM, ZIRCONIUM AND URANIUM COMPOUNDS.
J.A. MARTINHO SIMOES.

2321S ACTIVATION OF TERMINAL ALKYNES: NEW ACCESS TO ALKENYL- AND POLYENYL- CARBENE METAL COMPLEXES.
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3. Solid State Chemistry and Inorganic Materials **Hall C**

Chairman: *C. Otero*

3492S SOL-GEL GLASES AND THIN FILMS.
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3495S SOLID STATE CHEMISTRY OF CERAMIC MATERIALS.
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Chairman: *V. Moreno*

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3. SOLID STATE CHEMISTRY AND INORGANIC MATERIALS Hall C

Chairman: *D. Gatteschi*

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1079P SYNTHESIS AND X-RAY DIFFRACTION STUDY OF 1,5-DITHIA-3,7-DIAZA BICICLO[3.3.1]NONANE AND ITS N-BORANE ADDUCT.
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1081P SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CHLORO-BIS(N-PHENYLSALICYLIDE NEAMINATO-O,N)MANGANESE(III).
L. LUACES, M. BERMEJO, J.A. GARCIA-VAZQUEZ, J. ROMERO, J. SANMARTIN, A. SOUSA, C.A. McAULIFFE and R.G. PRITCHARD.

1082P SYNTHESIS AND STRUCTURE OF 1,10-PHENANTROLINE BIS{2-(2-PYRROLE)METHYLIMINO) PHENOLATO}COBALT(II).
J. CASTRO, J. ROMERO, J.A. GARCIA-VAZQUEZ, A. SOUSA and A. CASTIÑEIRAS.

1083P ELECTROCHEMICAL SYNTHESES OF 4,6-DIMETHYLPYRIMIDINE-2-THIOLATO COMPLEXES OF NICKEL AND CADMIUM(II).
R. CASTRO, J.A. GARÇIA-VAZQUEZ, J. ROMERO, A. SOUSA, R. PRITCHARD and C.A. McAULIFFE.

1084P THE SYNTHESIS OF ZINC COMPLEXES OF 4,6-DIMETHYLPYRIMIDINE-2-THIONE BY AN ELECTROCHEMICAL METHOD.
R. CASTRO, J.A. GARCIA-VAZQUEZ, J. ROMERO. A. SOUSA, W. HILLER and J. STRÄHLE.

1085P SYNTHESIS OF BENZOTHIAZOLE-2-THIONATO COMPLEXES OF Ni(II), Zn(II) AND Cd(II).
R. CASTRO, J.A. GARCIA-VAZQUEZ, J. ROMERO, A. SOUSA, R. PRITCHARD and C.A. McAULIFFE.

1086P MANGANESE(II) AND (III) COMPLEXES WITH 2-{2-[(2-PYRIDYL)ETHYL]IMINOMETHYL} PHENOLS (R-SALAEP-H): THE CRYSTAL AND MOLECULAR STRUCTURE OF [Mn(5-NO_2SALAEP)$_2$].
A. SOUSA, L. LUACES, M. BERMEJO, J.A. GARCIA-VAZQUEZ, J. ROMERO, C.A. McAULIFFE, R.G. PRITCHARD and Y. MUGNIER.

1087P CADMIUM(II) COMPLEXES OF 2-(MERCAPTOPHENYL)IMINOMETHYLPHENOLS.
E. LABISBAL, J. ROMERO, J.A. GARCIA-VAZQUEZ, A. SOUSA, C.A. McAULIFFE, R.G. PRITCHARD.

1088P HOMODINUCLEAR (Cu/Cu, Ni/Ni, V/V AND Fe/Fe) AND HETERODINUCLEAR (Cu/Ni, Ni/V AND Fe/Ni) COMPLEXES OF A NOVEL OXAMIDE-TYPE LIGAND COORDINATING IN THE *trans* CONFORMATION.
J.P. COSTES, J.P. LAURENT and G. PRADIE.

1096P ELECTROCHEMICAL SYNTHESIS OF TIN(IV) COMPLEXES OF 2-(2-MERCAPTOETHYL)IMINO PHENOLS.
E. LABISBAL, J. ROMERO, J.A. GARCIA-VAZQUEZ, U. RUSSO, A. CASTIÑEIRAS, M.L. DURAN and A. SOUSA.

1099P BISMUTH(III) DIMETHYLDITHIOPHOSPHINATE: ANOTER DIMER FORMED THROUGH SECONDARY BONDING. THE STEREOCHEMICALLY ACTIVE LONE PAIR REVISITED.
I. HAIDUC, F.T. EDELMANN, C. SILVESTRU and R. CEA-OLIVARES.

1102P LIGAND DESIGN IN PALLADIUM AMIDES SYNTHESIS.
J.V. CUEVAS VICARIO, G. GARÇIA-HERBOSA and A. MUÑOZ SANTAMARIA.

1107P LANTHANIDE PICRATE COMPLEX WITH HEXAMETHYL-PHORPHOROAMIDE (HMPA).
A.G. SILVA, G. VICENTINI, J. ZUKERMAN SCHPECTOR and E.E. CASTELLANO.

1108P SPECTROSCOPIC AND THERMOANALYTICAL STUDIES OF THE TETRAKIS(BENZYL-T-BUTYL SULFOXIDE)EUROPIUM(III) PICRATE.
W.C. MELO, L.B. ZINNER, J.R. MATOS, K. ZINNER, P.C. ISOLANI, M. ZAIN and G. VICENTINI.

1109P CRYSTAL AND MOLECULAR STRUCTURE OF THE SCHIFF BASE COMPLEX N,N'-3,4- TOLUENEBIS(SALICYLIDENEIMINATO) NICKEL(II).
R. HERNANDEZ-MOLINA, A. MEDEROS, S. DOMINGUEZ, P. NUÑEZ, P. GILI, G. GERMAIN and T. DEBAERDEMAEKER.

1110P POLYMER SPECIES IN AQUEOUS SOLUTIONS OF PARA-PHENYLENEDIAMINE-N,N,N',N'- TETRAACETIC ACID IN THE PRESENCE OF COPPER(II).
A. MEDEROS, S. DOMINGUEZ, C.A. GONZALEZ and F. BRITO.

1111P A WAY FOR STUDYING STRONG COMPLEXES OF Fe^{3+} WITH AMINOPOLYCARBOXYLIC LIGANDS. STUDY OF THE COMPLEXES FORMED BY 3,4-TOLUENEDIAMINE-N,N,N',N'- TETRAACETATE WITH Fe^{3+} AND Cu^{2+} IN AQUEOUS SOLUTION.
J. SANCHIZ, F. BRITO, A. MEDEROS and S. DOMINGUEZ.

1112P STRUCTURE OF DIZINC(II)-3,4-TOLUENEDIAMINETETRAACETATE, $[Zn(3,4\text{-}TDTA)\ Zn(H_2O)_4].2H_2O$.
M HERNANDEZ PADILLA, S. DOMINGUEZ, A. MEDEROS and J.M. ARRIETA.

1114P CHLORIDE *vs* WATER IN THE COORDINATION SPHERE OF TIN(IV). THE CRYSTAL STRUCTURE OF THE SALT $[HThiamin][SnMe_2Cl_3.H_2O]Cl$.
Mª.D. COUCE, J.Mª. VARELA, A. CASTIÑEIRAS, J.S. CASAS and J. SORDO.

1116P DIMETHYLTIN COMPLEXES OF VITAMIN B_6. THE CRYSTAL STRUCTURE OF $[SnMe_2(P\text{-}H)]\ (NO_3).2H_2O$ (P = PYRIDIXOL).
J.Mª. VARELA, Mª.D. COUCE, E.E. CASTELLANO, J. ZUKERMAN-SCHPECTOR, J.S. CASAS and J. SORDO.

1125P BIS(MORPHOLINE-1-CARBOTHIOATO) OF CADMIUM(II).
S. GARCIA-FONTAN, P. RODRIGUEZ, J.S. CASAS, A. SANCHEZ and J. SORDO.

1126P THIOSEMICARBAZONE COMPLEXES OF ZINC(II), CADMIUM(II) AND MERCURY(II).
E. BERMEJO, A. CASTIÑEIRAS, h. DOMINGUEZ and C MAICHLE-MÖSSMER.

1128P DIORGANOTIN(IV) DIHALIDE COMPLEXES WITH AZOLES.
Mª.D. COUCE, P. ALVAREZ-BOO, E. FREIJANES, A. SANCHEZ GONZALEZ, J.S. CASAS and J. SORDO.

1129P COPPER. SILVER AND GOLD(I) COMPLEXES WITH BIS(2-DIPHENYLPHOSPHINOETHYL) PHENYLPHOSPHINE.
M. RODRIGUEZ BEIRO, M.E. GARCIA, O.M. NI DHUBHGHAILL, R.E. SUE and P.J. SADLER.

2. Organometallic Chemistry and Catalysis

2002P COMPARATIVE STUDIES ON THE REACTIVITY OF CYCLIC AND ACYCLIC PENTADIENYL CHLORIDE BIS(TRIPHENYLPHOSPHINE) RUTHENIUM COMPLEXES TOWARDS DIPHENYLPHOSPHINE.
M.A. PAZ-SANDOVAL, O. PEREZ-CAMACHO, R. TORRES LUBIAN and R.D. ERNST.

2004P COPPER-CATALYZED CYCLOHEXANE OXIDATION WITH HYDROGEN PEROXIDE AT ROOM TEMPERATURE.
U. SCHUCHARDT and R. PEREIRA.

2005P NEW OXIDE-SUPORTED ZIEGLER CATALYSTS.
U. SCHUCHARDT, S. JERICO, I. JOEKES and W. KAMINSKY.

2015P DEGRADATION OF TRIBUTYLTIN CHLORIDE (TBT) IN WATER BY EITHER ACTIVE CHLORINE OR HYDROGEN PEROXIDE.
J.A. NAVIO and C. CERILLOS.

2018P ALKYNYL-VINYLIDENE COUPLING AS VERSATILE ROUTE TO ENYNYL AND DIENYNYL Ru(II) COMPLEXES.
C. BIANCHINI, M. PERUZZINI, A. PASTOR, A. ROMEROSA and F. ZANOBINI.

2022P COORDINATION OF DIOXYGEN AT A DIHYDROGEN-BINDING SITE: CRYSTAL STRUCTURE OF $[RuH(\eta^2\text{-}O_2)(dippe)_2][BPh_4]$ (dippe = 1,2-BIS(DIISOPROPYLPHOSPHINO)ETHANE).
M. JIMENEZ TENORIO, M.C. PUERTA and P. VALERGA.

2023P THE SYSTHESIS OF *trans*-$[Mo(N_2)_2(dippe)_2]$ (dippe = 1,2-BIS(DIISOPROPYLPHOSPHINO)ETHANE) AND ITS PROTONATION. CRYSTAL STRUCTURES OF $[MoF(NNH_2)(doppe)_2][BF_4]$ AND *trans*-$[MoCl_2(dippe)_2][BF_4]$.
P.P.S. VALERGA.

2024P HALF-SANDWICH HALIDE, ALKYL, HYDRIDE, AND OTHER DERIVATIVES OF IRON CONTAINING THE BULKY DIPHOSPHINE 1,2-BIS(DIISOPROPYLPHOSPHINO)ETHANE (dippe).
M. JIMENEZ TENORIO, M.C. PUERTA and P. VALERGA.

2028P MODELS FOR HDS: REACTIONS OF DIBENZOTHIOPHENE AND DIBENZOTHIOPHENE SULPHONE WITH LOW VALENT PLATINUM METALS.
J.J. GARCIA and P.M. MAITLIS.

2045P SYNTHESIS OF TETRANUCLEAR THIOLATEBRIDGED Fe_3Au CLUSTERS.
E. DELGADO, F. HERNANDEZ, O. ROSSELL, M. SECO and X. SOLANS.

2055P SUPPORTED AND UNSUPPORTED METAL COMPLEXES OF BENZOYLTHIOUREAS.
D. CAUZZI, M. COSTA, G. MARZOLINI, G. PREDIERI, A. TIRIPICCHIO and M. TIRIPICCHIO CAMELLINI.

2461P LITHIATED FLUORENYL ANION COORDINATED TO TWO [Cp*M]⁺ GROUPS, (Cp* = C_6Me_5; M = Fe, Ru). INUSUAL QUENCHING OF ELECTROPHILIC ADDITIONS AND X-ARY CRYSTAL STRUCTURE OF $[(Cp^*Ru)_2\text{-}\eta^6,\eta^6\text{-}C_{13}H_9Li](OSO_2CF_3)_2$.
M. OTERO, E. ROMAN, J.M. MANRIQUEZ and O. WITTKE.

2070P METAL VAPOUR SYSTHESIS OF FLUORENE TRANSITION METAL COMPLEXES.
F.G.N. CLOKE, A.R. DIAS and J.L. FERREIRA DA SILVA.

2075P DIOXOMOLYBDENUM(VI) HALIDES AS OXOTRANSFER CATALYSTS.
F.J. ARNAIZ, R. AGUADO and J.M. MARTINEZ DE ILARDUYA.

2097P ORGANOLEAD DERIVATIVES OF COORDINATIVELY SATURATED PLATINUM(II) OLEFIN COMPLEXES.
V.G. ALBANO, C. CASTELLARI, A. PANUNZI, F. RUFFO and A. SANCHEZ-GONZALEZ.

2098P RHODIUM AND IRIDIUM COMPLEXES WITH α-DIIMINES
M. BIKRANI, M.L. FIDALGO and M.A. GARRALDA.

2100P AN NMR STUDY OF THE DISPROPORTIONATION OF ORGANOLEAD DIORGANODITHIO PHOSPHINATES.
C. SILVESTRU, A. SILVESTRU, R. CEA-OLIVARES and I. HAIDUC

2101P INORGANIC CHELATE RINGS CONTAINING TIN, PHOSPHOROUS, NITROGEN AND OXYGEN/SULFUR. SYNTHESIS AND STRUCTURE.
R. CEA-OLIVARES, C. SILVESTRU, I. HAIDUC and M. GIELEN.

2105P CO_2 LASER INDUCED PHOTODECOMPOSITION OF THIOPHENE, 2-METHYL- AND 3-METHYL-THIOPHENE IN THE PRESENCE OF CHROMIUM HEXACARBONYL.
R. SALGEIRO and A.M. BARRIOLA.

2113P SYNTHESIS OF FUNCTIONAL PHOSPHOLYL ANIONS: AN ACCESS TO THE 3-ETHOXY CARBONYL DERIVATIVE
B. DESCHAMPS, A. ESPINOSA and F. MATHEY

2118P CYCLOMETALLATION REACTIONS OF Pd(II) CYCLOMETALLATED COMPLEXES OF N,N- DIMETHYL-*ter* BUTYLMETHYLHYDRAZONE WITH DIPHOSPHINES.
J.J. FERNANDEZ, J.M. ORTIGUEIRA, M. LOPEZ TORRES, M.T. PEREIRA, J.M. VILA and M. GAYOSO.

2119P CYCLOMETALLATED COMPOUNDS OF Pd(II) WITH DIIMINE LIGANDS.
M. LOPEZ TORRES, J.M. ORTIGUEIRA, A. FERNANDEZ, M.T. PEREIRA, J.M. VILA and M. GAYOSO.

2120P PALLADIUM(II) CYCLOMETALLATED COMPOUNDS VIA OXIDATIVE ADDITION REACTIONS.
A. FERNANDEZ, J.M. ORTIGUEIRA, M. LOPEZ TORRES, M.T. PEREIRA, J.M. VILA and M. GAYOSO.

2121P MIXED $Ph_2PCH_2PPh_2$ (dppm) AND $Ph_2PC(=CH_2)PPh_2$ (vdpp) DICARBONYL COMPLEXES OF GROUP VI METALS. HYDRIDE FORMATION AND MICHAEL ADDITIONS TO THE VINYLIDENE DOUBLE BOND.
J.M. VILA, B.L. SHAW and X.L.R. FONTAINE.

2122P REARRANGEMENT OF A CYCLOMETALLATED Pd(II) COMPOUND IN SOLUTION.
J.J. FERNANDEZ, A. CASTIÑEIRAS, M.T. PEREIRA, J.M. VILA and M. GAYOSO.

2123P CYCLOMETALLATION. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE DINUCLEAR CYCLOMETALLATED COMPOUND $[\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=NCy](Cl)\}_2\{\mu\text{-}Ph_2PC(=CH_2)PPh_2\}]$.
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2131P WATER-SOLUBLE ORGANOMETALLIC COMPLEXES OF TUNGSTEN AND RUTHENIUM. SYNTHESIS, CHARACTERIZATION AND PRELIMINARY STUDIES IN THE HYDROGENATION OF OLEFINS IN A BIPHASIC SYSTEM.
A. ANDRIOLLO, A. BOLIVAR, P. BARICELLI, M. DOMINGUEZ, F. LOPEZ L. and D.E. PAEZ.

2136P REACTIONS OF $[Os_3(CO)_{10}(MeCN)_2]$ WITH ORTO SUBSTITUTED DERIVATIVES OF PYRROLE.
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2137P NEW CARBONYL HYDRIDE CLUSTER DERIVATIVES OF DIPYRIDYLALKANE LIGANDS.
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2148P HOMOGENEOUS CATALYTIC HYDROGENATION OF KETONES BY RHODIUM COMPLEXES.
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2149P DINUCLEAR ORTHOPALLADATED DERIVATIVES WITH MIXED BRIDGES: UNUSUAL *cis-* STRUCTURE.
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2150P CARBONYL MOLYBDENUM(0) AND -(II) COMPLEXES WITH PHENYLBIS(2-PYRIDYL) PHOSPHINE.
P. ESPINET, P. GOMEZ-ELIPE and F. VILLAFAÑE.

2151P DINAMIC BEHAVIOUR IN PALLADIUM COMPLEXES WITH PHENYLBIS(2-PYRIDYL) PHOSPHINESULPHIDE AND TRIS(2-PYRIDYL)PHOSPHINESULPHIDE.
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2152P SYNTHESIS AND CRYSTAL STRUCTURE OF DICHLORODIPHENYLBIS(PYRAZOLE)TIN(IV).
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2153P SYNTHESIS AND CRYSTAL STRUCTURE OF TRICHLOROPHENYLBIS(PIRAZOLE)TIN(IV).
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2154P SYNTHESIS AND CRYSTAL STRUCTURE OF DIBROMODIETHYLBIS(2(3H)-IMIDAZOLINE THIONE)TIN(IV).
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2156P PROTODEMETALATION REACTIONS OF DIPHENYLTHALLIUM(III) COMPOUNDS WITH DICYCLOHEXYLDITHIOPHOSPHINIC ACID. II. CRYSTAL STRUCTURE OF TRIS(DICYCLOHEXYLDITHIOPHOSPHINATO)THALLIUM(III)CHLOROFORM SOLVATE.
J.S. CASAS, A. CASTIÑEIRAS, A. SANCHEZ, J. SORDO and E.M. VAZQUEZ-LOPEZ.

2157P DIPHENYL(DICYCLOHEXYLDITHIOPHOSPHINATO)THALLIUM(III): SYNTHESIS, CRYSTAL STRUCTURE AND SPECTRAL BEHAVIOUR.
J.S. CASAS, E.E. CASTELLANO, A. SANCHEZ, J. SORDO, E.M. VAZQUEZ-LOPEZ and J. ZUKERMAN-SCHPECTOR.

2158P PROTODEMETALATION REACTIONS OF DIPHENYLTHALLIUM(III) COMPOUNDS WITH DICYCLOHEXYLDITHIOPHOSPHINIC ACID. I. CRYSTAL STRUCTURE OF PHENYL[BIS(DICYCLOHEXYLDITHIOPHOSPHINATO]THALLIUM(III).
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2173P TITANIUM μ_3-ALKYLIDYNES.
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2174P CARBONYL INSERTIONS INTO METAL-NITROGEN BONDS OF GROUP 4 DIALKYLAMIDO COMPLEXES.
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2180P REACTIVITY OF TERTIARY SILANES AND STANNANES WITH AN EDGE-BRIDGED TRIRUTHENIUM CARBONYL CLUSTER COMPLEX.
J.A. CABEZA, R.J. FRANCO, A. LLAMAZARES and V. RIERA.

2185P DIFFERENT COORDINATION MODES OF DMIT LIGAND IN GOLD(I) CHEMISTRY.
E. CERRADA, P.G. JONES, A. LAGUNA, M. LAGUNA and R. TERROBA.

2186P TRIGONAL AND TETRAHEDRAL SILVER(I) COMPLEXES WITH DIFFERENT BIDENTATE OR TRIDENTATE PHOSPHINE LIGANDS.
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2187P DINUCLEAR ASYMMETRICAL BRIDGED GOLD(I) AND GOLD(III) COMPLEXES.
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2195P ORTHO METALATION REACTIONS IN DIRHODIUM(II) COMPOUNDS. FURTHER EVIDENCE OF AN EQUILIBRIUM PROCESS INVOLVING METALATION-DEMETALATION REACTIONS OF A P(o-ClC$_6$H$_4$)Ph$_2$ LIGAND. A PRELIMINARY KINETIC STUDY.
A. GARCIA-BERNABE, P. LAHUERTA, E. PERIS, M.A. UBEDA, S. GARCIA-GRANDA, P. PERTIERRA, M. MARTINEZ and G. GONZALEZ.

2201P THE SYNTHESIS AND REACTIVITY OF THE BINUCLEAR RUTHENIUM COMPLEX [Ru$_2$(μ-PPh$_2$) (μ-OH)$_2$(p-cymene)]PF$_6$ WITH VARIOUS POTENTIAL PROTON DONORS.
J. CABEZA, F. MULLA and V. RIERA.

2202P HYDROFORMILATION OF N-ALLYLSUBSTRATES BY RHODIUM CATALYSTS.
A. BERTRAN and J.C. BAYON.

2203P ENANTIOSELECTIVE HYDROFORMYLATION CATALYSTS WITH CHIRAL THIOLATO RHODIUM COMPLEXES.
J.A. PINILLA and J.C. BAYON.

2204P REACTIONS OF β-KETOSULPHOXIDES WITH Pd(OAc)$_2$.
A.I. BARCENA, M.J. CAMAZON, J.L. GARCIA-RUANO, J.R. MASAGUER, C. NAVARRO-RANNINGER and J.H. RODRIGUEZ.

2511P P-C BOND ACTIVATION IN A TETRANUCLEAR IRIDIUM CLUSTER: SYNTHESIS AND X-RAY MOLECULAR STRUCTURE OF Ir$_4$(CO)$_8$(η^1-Ph)(μ_4-η^3-PhPC(H)CPh)(μ-PPh$_2$).
R.M.S. PEREIRA, D.M. VARGAS, F. GREPIONE and D. BRAGA

3. SOLID STATE CHEMISTRY AND INORGANIC MATERIALS

3006P DETERMINATION OF POLYMERIC SULFUR STABILITY BY DSC.
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3017P SURFACE CHARACTERIZATION AND HYDROGENATION PROPERTIES OF SEVERAL POTASSIUM-DOPED NICKEL/α-ALUMINA CATALYSTS.
F. MEDINA, P. SALAGRE, J.E. SUEIRAS and J.L.G. FIERRO.

3020P CRYSTAL FIELD EFFECTS ON THE MAGNETIC SUSCEPTIBILITY OF RARE EARTH (Pr, Nd) MIXED OXIDES.
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3021P SIMPLE AND MULTICOMPONENT IRON OXIDES GENERATION BY THE PYROSOL METHOD.
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3026P STATISTICAL MODEL FOR HYDROGEN SOLUTION IN TiC_z ($z = 0.26$) OF HCP (HEXAGONAL CLOSE PACKED) STRUCTURE.
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3034P SPECTROSCOPIC STUDIES ON FRAGMENTS OF AMPHORAE RECOVERED IN THE SICILIAN AREA.
E. RIVAROLA, G. RUISI, I.D. DONATO and P. MIGLIARDO.

3035P INFRARED CHARACTERIZATION OF ZIRCONIA-SUPPORTED GROUP 6 METAL CARBONYLS.
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3036P FORMATION AND CHARACTERIZATION OF ALKOXY-DERIVED SPINELS.
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3057P STRUCTURAL AND THERMAL STUDY OF NEW PRESEODYMIUM SELENITES.
M. DE PEDRO, A. CASTRO and J.C. TROMBE.

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3069P AN ATTEMP OF COPPER SUBSTITUTION BY MAGNESIUM ON La_2CuO_4.
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3076P SYNTHESIS, SOLID STATE PROPERTIES AND CRYSTAL STRUCTURE OF THE BIS(3-AZA-1,5-PENTAMETHYLENEDIAMONIUM)DISODIUM DIPHOSPHOPENTAMOLYBDATE(VI) PENTAHYDRATE.
P. ROMAN, A. ARANZABE, A. LUQUE and M. MARTINEZ-RIPOLL.

3077P SYNTHESIS AND CRYSTAL STRUCTURE OF THE ISOPOLYVANADATE(V): $[(CH_3)_3CNH_3]_4[H_2V_{10}O_{28}]$.
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3089P CYCLIC VOLTAMMETRY STUDY OF HEXACYANOFERRATE COMPLEX IMMOBILIZED ON SILICA GEL SURFACE CHEMICALLY MODIFIED WITH PYRIDINIUM ION.

L.L.L. PRADO and Y. GUSHIKEM.

3090P CYCLIC VOLTAMETRY STUDIES OF COPPER AND NICKEL HEXACYANOFERRATE IMMOBILIZED ON TITANIUM(IV) OXIDE COATED ON SILICA GEL SURFACE.

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3093P SYNTHESIS, CHARACTERIZATION AND CHEMISOPTION INVOLVING MERCAPTO AND OXIDIZED MERCAPTO SILICA.

C. AIROLDI and A.R. CESTARI.

3104P THERMAL EVOLUTION OF $(Zr,Ti)O_2$ GELS SYNTHESIZED AT DIFFERENT BASIC pH.

J.A. NAVIO, M. MACIAS, P.J. SANCHEZ-SOTO and P. PICHAT.

3115P MICROSTRUCTURAL CHARACTERIZATION OF A 7075 ALUMINIUM ALLOY BY TRANSMISION ELECTRON MICROSCOPY.

M.P. VILLAR, J.M. GERALDIA, J.M. BADIA PEREZ and R. GARCIA.

3117P COMBUSTION SYNTHESIS AND CHARACTERIZATION OF M-TYPE BARIUM HEXAFERRITES.

S. CASTRO, M. GAYOSO, C. RODRIGUEZ, J. MIRA, J. RIVAS and J.M. GRENECHE.

3132P X-RAY PHOTOELECTRON SPECTROSCOPY OF LITHIUM COMPOUNDS.

G. GONZALEZ and H. BINDER.

3134P NEW MOLECULAR MATERIALS BASED ON C_{60}.

A. PENICAUD and A. PEREZ BENITEZ.

3135P EFFECTS OF THE PROCESSING TECHNIQUES ON THE STRUCTURE AND MECHANICAL PROPERTIES OF METALLIC GLASSES.

A.R. PIERNA, A. LORENZO, F. FERNANDEZ, J.C. PRIETO, J. URMENETA and M.L. ESCUDERO.

3167P π-π INTERACTIONS IN COMPLEXES OF THE BIS(1,2-DITHIOOXALATO-S,S')METALLATE(III) ANION CONTAINING PLANAR CATIONS.

P. ROMAN, J.I. BEITIA and A. LUQUE.

3168P ELECTROCHEMICAL STUDIES OF IRON PHTALOCYANINE IMMOBILIZED ON TITANIUM(IV) OXIDE COATED ONTO SILICA GEL SURFACE.

L.T. KUBOTA, Y. GUSHIKEM, J. PEREZ and A.A. TANAKA.

3176P SYNTHESIS OF ZINC FERRITE FROM GOETHITE INDUSTRIAL RED MUDS.

M. ROMERO, P. CALLEJAS and J.Mª. RINÇON.

Tuesday, September 14

09.30-10.30 **PLENARY LECTURE** **University Auditorium**

1052C HOMO AND HETEROMETALLIC CUBANE-TYPE IRON-SULFUR CLUSTERS: STRUCTURE AND REACTIVITY IN RELATION TO BIOLOGY AND CHEMISTRY.
J.J.G. MOURA.

Chairman: *R. Delgado*

10.30-11.00 *Coffee Break*

11.00-13.15 **SESSION LECTURES**

1. COORDINATION AND BIOINORGANIC CHEMISTRY **Hall A**

Chairman: *J. Pedrosa de Jesús*

1378S STUDY OF THE REACTIVITY OF SOME RUTHENIUM(II) AND (III) COMPLEXES CONTAINING TRIPHENYLPHOSPHINE AND MULTIDENTATED LIGANDS.
L. RUIZ AZUARA.

1179S STRUCTURAL INFORMATION FROM ^{119}Sn MÖSSBAUER SPECTROSCOPY.
D. TUDELA.

1171S METALS AND NUCLEOBASES: COORDINATION CHEMISTRY AND BIOLOGICAL RELEVANCE.
B. LIPPERT.

2. ORGANOMETALLIC CHEMISTRY AND CATALYSIS **Hall B**

Chairman: *G. Süss-Fink*

2286S NEW FRONTIERS IN BOND ACTIVATION BY ELECTRON-RICH METAL COMPLEXES.
D. MILSTEIN.

2071S PLATINUN CATALYZED OXIDATIONS WITH HYDROGEN PEROXIDE: THE BAEYER-VILLIGER OXIDATION OF KETONES.
G. STRUKUL.

2381S SOME OF THE CHEMISTRY OF PHOSPHIDO BRIDGED CARBONYL CLUSTERS.
M.D. VARGAS.

3. SOLID STATE CHEMISTRY AND INORGANIC MATERIALS

Chairman: *A. Caneiro*

3497S APPLICATIONS OF SOLID STATE NEUTRON POWDER DIFFRACTION.
J. PANNETIER.

3480S PHASE FORMATION AND CURRENT TRANSPORT IN HIGH Tc SUPERCONDUCTORS.
R. FLÜKIGER.

3278S DESIGN AND SYNTHESIS OF NEW INORGANIC SOLIDS: APPLICATIONS TO THE TAILORING OF SPECIFIC PROPERTIES.
R.E. CARBONIO.

14.00-16.30 *Lunch*

16.30-18.00 **SESSION LECTURES**

1. COORDINATION AND BIOINORGANIC CHEMISTRY

Chairman: *F.A. Devillanova*

1014S PHOTOCHEMICAL MOLECULAR DEVICES BASED ON TRANSITION METAL COMPLEXES.
V. BALZANI.

1010S CHARACTERIZATION AND SOME ELECTROCATALYTIC PROPERTIES OF COMPLEXES WITH AZA-MACROCYCLE LIGANDS.
J. COSTAMAGNA, J. CANALES, J. VARGAS and G. FERRAUDI.

2. ORGANOMETALLIC CHEMISTRY AND CATALYSIS

Chairman: *A. Otero*

2094S ORGANOMETALLIC CHEMISTRY OF LANTHANIDES AND SOME IMPLICATIONS IN DIOLEFINE POLYMERIZATION.
P. BIAGINI, G. LUGLI and P. ANDREUSSI.

2264S BINUCLEAR ORGANOMETALLIC DERIVATIVES: SYNTHESIS AND REACTIVITY.
V. RIERA.

3. SOLID STATE CHEMISTRY AND INORGANIC MATERIALS

Chairman: *J. Pannetier*

3249S CRYSTAL CHEMISTRY IN THE NINETIES: FACTS, FEATURES & PROSPECTIVES.
M.O. FIGUEIREDO.

3175S GLASSES AMD GLASS-CERAMICS CONSIDERED AS BIOMATERIALS.
J.M. RINCON.

11.00-19.00 **POSTERS SESSION** **Hall D**

Chairman: *J.S. Casas*

1. COORDINATION AND BIOINORGANIC CHEMISTRY

1044P C.T.-COMPLEXES OF 1,4,7-TRITHIACYCLONONANE ([9]aneS$_3$) WITH DIIODINE.
F. CRISTIANI, F. DEVILLANOVA, F. ISAIA, V. LIPPOLIS, G. VERANI and F. DEMARTIN.

1133P OXYGEN AND SULFUR TRIPOD MOLECULES. A THEORETICAL STUDY.
R. SALCEDO, R. VILAR and J. GOMEZ-LARA.

1141P N-METHYL-2,2'-BIIMIDAZOLE COMPLEXES OF ORGANOTIN(IV) DIHALIDES.
Mª.D. COUCE, P. ALVAREZ-BOO, E. FREIJANES, J.S. CASAS and J. SORDO.

1142P DIORGANOTIN(IV) COMPLEXES OF BIS(THIOSEMICARBAZONES).
M.C. PEREZ, M.V. CASTAÑO, A. SANCHEZ, J.S. CASAS and J. SORDO.

1143P SYNTHESIS ANS STRUCTURAL STUDY OF DIMETHYL- AND DIPHENYL(2,6-DIACETYLPYRIDINE-BIS-THIOSEMICARBAZONATO)TIN(IV). CRYSTAL STRUCTURE OF [$SnPh_2C_{11}H_{13}N_7S_2$].2DMF.
J.S. CASAS, A. CASTIÑEIRAS, C. MAICHLE-MÖSSMER, M.C. RODRIGUEZ-ARGÜELLES, A. SANCHEZ, J. SORDO and A. VAZQUEZ-LOPEZ.

1144P SYNTHESIS OF (2-THIAZOLIN-2-YL)HYDRAZINE HYDROCHLORIDE AND COORDINATION BEHAVIOUR TOWARDS DIVALENT TRANSITION METAL IONS.
A. BERNALTE, M.A. DIAZ, F.J.G. BARROS, F.J. HIGES, A.M. PIZARRO and C. VALENZUELA.

1145P POTENTIOMETRIC STUDY OF THE COORDINATION OF DIVALENT TRANSITION-METAL IONS TO 2-(BENZYLAMINO)-2-DEOXY-D-GLYCERO-L-GLUCO-HEPTONIC ACID.
M.A. DIAZ DIEZ, F.J. GARCIA BARROS and C. VALENZUELA CALAHORRO.

1146P INVESTIGATION OF MERCURY(II) COMPLEX EQUILIBRIA WITH FOUR SUGAR α-AMINO ACIDS. THE EFFECT OF THE ANION.
A. BERNALTE GARCIA, M.A. DIAZ DIEZ, F.J. GARCIA BARROS and C. VALENZUELA CALAHORRO.

1147P DICHLORODIOXOMOLYBDENUM(VI) COMPOUNDS FROM AQUEOUS MEDIA. CRYSTAL AND MOLECULAR STRUCTURE OF [MoO$_2$(H$_2$O)$_2$](diglyme)$_2$.
F.J. ARNAIZ, R. AGUADO, J. SANZ-APARICIO and M. MARTINEZ-RIPOLL.

1155P THE CRYSTAL STRUCTURE OF TETRAETHYLAMMONIUM TRICHLORODIPHENYL STANNATE(IV).
E. GARCIA MARTINEZ, A. SANCHEZ GONZALEZ, A. CASTIÑEIRAS, J.S. CASAS and J. SORDO.

1162P LANTHANIDE COMPLEXES OF A 15-MEMBERED N$_3$O$_2$ MACROCYCLE LIGAND.
R. BASTIDA, A. DE BLAS, A. MACIAS, R. RIAL, A. RODRIGUEZ and T. RODRIGUEZ.

1163P COMPLEXES OF Mn(III) WITH SCHIFF BASES DERIVED FROM IMIDAZOL-CARBOXALDEHIDE.
M.R. BERMEJO, A. GARCIA DEIBE, L. LUACES, M. REY, J. SANMARTIN, A. SOUSA and C.A. McAULIFFE.

1164P SYNTHESIS AND CHARACTERIZATION OF [MnL]ClO$_4$.nH$_2$O COMPLEXES.
M.R. BERMEJO, A. GARCIA DEIBE, E. GOMEZ FORNEAS, M. REY, J. SANMARTIN, A. SOUSA and C.A. McAULIFFE.

1165P SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW Mn(III) COMPLEXES WITH SYMMETRICAL SCHIFF BASES.
M.R. BERMEJO, A. GARCIA DEIBE, L. LUACES, M. REY, J. SANMARTIN, A. SOUSA and C.A. McAULIFFE.

1166P SYNTHESIS AND CHARACTERIZATION OF HOMO AND HETEROBINUCLEAR PIRAZOLATE- BRIDGED COMPLEXES.
B. FERNANDEZ, M.I. FERNANDEZ, E. GOMEZ FORNEAS, M.R. BERMEJO and J.P. COSTES.

1169P SYNTHESIS, REACTIVITY AND MAGNETIC PROPERTIES OF NEW [Mn$_2$O(RCOO)$_2$]$^{2+}$ CORE.
B. ALBELA, M. CORBELLA and J. RIBAS.

1177P AN ab initio STUDY OF THE SILVER-SILVER INTERACTION IN A DIMER COMPLEX WITH A TRIAZOLE PYRIMIDINE DERIVATIVE.
M.A. ROMERO MOLINA, J.M. SALAS PEREGRIN, M.P. SANCHEZ SANCHEZ, A. RAHMANI, M. QUIROS OLOZABAL and J. MOLINA MOLINA.

1178P 5-METHYL-7-HYDROXY-1,2,4-TRIAZOLO[1,5-a] PYRIMIDINE: A VERSATILE LIGAND. REACTIVITY TOWARDS AG(I)
J. RODRIGUEZ NAVARRO, M.A. ROMERO MOLINA, J.M. SALAS PEREGRIN, M. QUIROS OLOZABAL, M.N. MORENO CARRETERO and F. HUESO UREÑA.

1189P COPPER(I) AND GOLD(I) COMPLEXES WITH DIBASIC NITROGEN AND PHOSPHORUS LIGANDS.
R. TURPIN, A.M. LARSONNEUR, P. FERTE, G. BERNARDINELLI and P. CASTAN.

1190P NEW ν-BONDED TCNQ NICKEL COMPLEXES WITH POLYDENTATE NITROGEN LIGANDS.
M.T. AZCONDO, L. BALLESTER, M.C. BARRAL, A. GUTIERREZ, R. JIMENEZ, M.F. PERPIÑAN and A. SANCHEZ.

1192P CRYSTAL STRUCTURE OF 5-MERCAPTO-1-METHYL-1,2,3,4-TETRAZOLE METHYLMERCURY(II).
J. BRAVO, R. CARBALLO, B. CORDERO and J.S. CASAS.

1193P A STRUCTURAL STUDY OF SOME NEW MANGANESE(III) AND (IV) COMPLEXES.
M.R. BERMEJO, A. GARCIA DEIBE, M. REY, A. SOUSA, C.A. McAULIFFE and R.G. PRITCHARD.

1194P OXYGEN EVOLUTION STUDIES OF Mn(III) SCHIFF BASE COMPLEXES.
M.R. BERMEJO, A. GARCIA DEIBE, E. GOMEZ FORNEAS, M. REY, J. SANMARTIN, A. SOUSA and C.A. McAULIFFE.

1197P COPPER(II) COMPLEX WITH A BINUCLEATING LIGAND DERIVED FROM ISOPHTALDEHYDE AND DI(2-PYRIDYL)METHYLAMINE.
A.M. GARCIA, J. MANZUR, M.T. GARLAND, R. BAGGIO and E. SPODINE.

1198P KINETIC DETERMINATION OF THE Fe-H$_2$ BOND DISSOCIATION ENERGY IN FeH(H$_2$)(Dmpe)$_2^+$.
M.A. MAÑEZ, M.J. FERNANDEZ-TRUJILLO, G.J. LEIGH and M. GARCIA BASALLOTE.

1199P KINETICS OF SUBSTITUTION REACTIONS OF trans-[Mo(N$_2$)$_2$(PPh$_2$Me)$_4$] WITH THE TRIPOD LIGANDS NP$_3$ AND PP$_3$.
M.J. FERNANDEZ-TRUJILLO, M.A. MAÑEZ and M.G. BASALLOTE.

1205P CYCLOMETALLATED Pd(II) AND Pt(II) COMPLEXES OF 2-PHENYLIMIDAZOLINE.
F. ZAMORA, I. LOPEZ-SOLERA, A. MONGE, J.R. MASAGUER and C. NAVARRO-RANNINGER.

1206P PLATINUM(II) AND (IV) SPERMINE COMPLEXES.
P. AMO OCHOA, C. ALONSO, J.R. MASAGUER and C. NAVARRO-RANNINGER.

1207P *In vitro* CYTOSTATIC ACTIVITY OF PLATINUM AND PALLADIUM COMPLEXES WITH BENZOYLBENZYLIDENEAMINES.
I. LOPEZ-SOLERA, J.M. PEREZ, A. ALVAREZ-VALDES, C. NAVARRO-RANNINGER, C. ALONSO and J.R. MASAGUER.

Hall C 1208P ELECTROCHEMICAL INTERACTION: COPPER- HISTIDINE COMPLEXES AND THE TETRATHIO MOLYBDATE ION.
T. HERNANDEZ-PEREZ, C. JUAREZ GORDIANO, A. QUIROZ-GUTIERREZ and I. GONZALEZ.

1214P DI(THIOLATO)AURATE(I) COMPLEXES.
J. VICENTE, M.T. CHICOTE, P. GONZALEZ-HERRERO and P.G. JONES.

1218P CYANAMIDE COMPLEXES OF PALLADIUM AND PLATINUM.
E.M.F.R.M. BRANCO, M.F.C. GUEDES DA SILVA, J.J.R. FRAUSTO DA SILVA, A.J.L. POMBEIRO, R. MICHELIN, R. BERTANI, M. MOZZON and P. BERIN.

1217P SYNTHESIS OF IRON(III) AND COPPER(I OR II) COMPLEXES USING CAMPHOR DERIVATIVES AS LIGANDS.
M.F.N.N. CARVALHO, L.M.G. COSTA, A.J.L. POMBEIRO and R. HERRMANN.

1245P STUDIES ON THE CHELATING BEHAVIOUR OF BISTHIOSEMICARBAZONES IN ZINC COMPLEXES.
M. BELICCHI FERRARI, G. GASPARI FAVA, C. PELIZZI and M.C.
Hall A *RODRIGUEZ-ARGÜELLES.*

1127P COMPLEXES OF THE ANTIHYPERTENSIVE AGENT LISINOPRIL.
E. BERMEJO GONZALEZ, K.B. NOLAN and E. FARKAS.

1242P THE HYPOGLYCEMIC EFFECT OF COPPER(II) COMPLEXES.
A.-S. ABDUL-GHANI, A.L. ABU HIJLEH, N. NAHAS and R. AMIN.

1237P MONONUCLEAR COPPER(II) COMPLEXES CATALYZED OXIDATION OF TMPD AND O-PHENYL ENEDIAMINE AND OXYGEN INSERTION IN THE O-PHENYLEDENEDIAMINE/Ph_3P/COPPER(II) CATALYST SYSTEM.
A.L. ABUHIJLEH.

1230P NEW CHIRAL COPPER COORDINATION COMPOUNDS OF QUINIC
Hall B ACID.
N. BARBA-BEHRENS, A.M. BELLO-RAMIREZ, R. CONTRERAS, A. FLORES-PARRA, M.J. ROSALES-HOZ and F. SALAZAR-GARCIA.

1228P SYNTHESIS AND NMR STUDY OF NEW PENTACYCLIC PHOSPHORANES.
F.J. MARTINEZ-MARTINEZ, N. FARFAN and R. CONTRERAS.

1226P STRUCTURE AND REACTIVITY OF Pd(II) AND Pt(II) ALKYL ESTER AMINO ACID COMPOUNDS.
M. CALAF, A. CAUBET, V. MORENO, X. SOLANS and M. FONT-BARDIA.

1225P ON THE REACTIVITY OF $\{[Pd_2(\mu\text{-dppm})(\mu\text{-}SC_6F_5)](\mu\text{-}SC_6F_5)\}_4 \cdot 2Et_2O$.
Hall C *R. USON, J. FORNIES, M.A. USON and S. HERRERO.*

1221P SYNTHESIS OF THE 20-ELECTRON-DINITROSYL COMPLEX *trans*-$[Re(NO)_2(dppe)_2][BF_4]$ AND ITS REACTIONS WITH ACIDS.
Y. WANG, J.J.R. FRAUSTO DA SILVA and A.J.L. POMBEIRO.

1220P SYNTHESIS AND CHARACTERIZATION OF THE CIS ISOMERS OF THE NITRILE COMPLEXES $[ReCl(NCR)(dppe)_2]$.
M.F.C. GUEDES DA SILVA, J.J.R. FRAUSTO DA SILVA and A.J.L. POMBEIRO.

1257P PINCH PROPHYRINS: A NEW CLASS OF MODEL COMPOUNDS FOR HEME-ENZYMES.
Y. REYES ORTEGA, E. GONZALEZ VERGARA and J. MENDIETA PEREZ.

1258P A NEW MIXED-VALENCE $Fe^{III}Fe^{II}$ COMPLES AS A MODEL FOR THE PINK FORM OF PURPLE ACID PHOSPHATASES.
A. NEVES, M.A. DE BRITO and V. DRAGO.

1259P SYNTHESIS, STRUCTURE, MAGNETIC AND SPECTROELECTROCHEMICAL PROPERTIES OF A NEW IRON(III) COMPLEX AS A MODEL FOR IRON TRANSFERRINS.
S.M.D. ERTHAL, A. NEVES, W. HAASE and H. PAULUS.

1260P SYNTHESIS AND CRYSTAL STRUCTURE AND MAGNETISM OF THE NEW COMPLEX Et_3NH [Fe(TBEN)].1.
I. VENÇATO, A. NEVES, B.R. VINCENT, C. ERASMUS-BUHR and W. HAASE.

1265P SYNTHESIS, CRYSTAL STRUCTURE, ELECTROCHEMICAL AND MAGNETIC PROPERTIES, INFRARED SPECTRA OF $Cu_4[PhN_3C_6H_4N_3(H)Ph]_4(\mu_2\text{-}O)_2$ (1), A TETRANUCLEAR COMPLEX OF COPPER(II) WITH 1-PHENYLTRIAZENO-2-PHENYL TRIAZENIDOBENZENE (2) AS LIGAND.
M. HÖRNER, J. BORDINHAO, A. NEVES, J. BECK and J. STRÄHLE.

1266P TETRAMETHYLUREA ADDUCTS OF BISCYCLOPENTADIENYL COMPLEXES OF Sm(II) AND Yb(II).
M.G. SILVA-VALENZUELA, G. VICENTINI, L. BARBIERI ZINNER, N. MARQUES and A. PIRES DE MATOS.

1269P MONO-, DI- AND TRINUCLEAR IRON COMPLEXES WITH POLYFUNCTIONAL HYDRAZONIC LIGANDS.
M. CARCELLI, F. CAVATORTA, L. MAVILLA, C. PELIZZI, G. PELIZZI and M. SATURI.

1506P SOLUTION STUDY OF THE MIXTURES OF 4,6-DIMETHYL-2-THIOPYRIMIDINE AND THE Zn(II) AND Cd(II) IONS. CRYSTAL STRUCTURES OF $Zn(LH)_2Cl_2$ AND $Cd(LH)_2Cl_2$.
M. GODINO-SALIDO, M.D. GUTIERREZ-VALERO and R. LOPEZ-GARZON.

1514P SYNTHETIC APPROACHES TO ZINC-BINDING DOMAINS. STRUCTURAL AND SPECTROSCOPIC STUDIES ON ZINC(II) THIOLATE COMPLEXES.
X. ALMAGRO, T. ALSINA, A. ALVAREZ, M. BAAMI, J.F. PINIELLA, T. SÁNCHEZ and J. SOLA.

2. Organometallic Chemistry and Catalysis

2209P SYNTHESIS, CHARACTERIZATION, AND SOME CATALYTIC APPLICATIONS OF WATER SOLUBLE RUTHENIUM AND OSMIUM COMPLEXES.
F. LOPEZ-LINARES, M. MEDINA, A. FUENTES and R.A. SANCHEZ-DELGADO.

2213P NEW 3,4,5-TRIMETHOXY-2,6-DINITROPHENYL PALLADIUM(II) COMPLEXES.
J. VICENTE, A. ARCAS and M.A. BLASCO.

2215P VISIBLE LIGHT INDUCED AIR OXIGENATION OF ACETYLACETONATE LIGAND IN CYCLO PALLADATED COMPLEXES TO GIVE C-C BOND CLEAVAGE PRODUCTS.
J. VICENTE, A. ARCAS, D. BAUTISTA and G.B. SHUL'PIN.

2216P INSERTION OF CARBON DISULPHIDE IN AN Fe-H BOND. SYNTHESIS OF THE η^2-DITHIOFORMATE COMPLEX $[Fe(\eta^2\text{-}S_2CH)(dppe)_2][BF_4]$.
L.M.D. RIBEIRO, J.J.R. FRAUSTO DA SILVA and A.J.L. POMBEIRO.

2219P REACTIONS OF PHENYLDIAZENIDE COMPLEXES OF RHENIUM WITH ISOCYANIDES.
M.T.A. RIBEIRO, A.J.L. POMBEIRO and J.R. DILWORTH.

2227P HOMOGENEOUS HYDROGENATION OF THIOPHENE AND BENZOTHIOPHENE AT IRIDIUM.
C. BIANCHINI, V. HERRERA, A. MELI, M. PERUZZINI, R. SANCHEZ-DELGADO and F. VIZZA.

2231P ALKOXYDE DERIVATIVES OF BARIUM AND STRONTIUM.
T.R. BELDERRAIN, L. CONTRERAS, M. PANEQUE, E. CARMONA, A. MONGE and C. RUIZ.

2233P POLYPYRAZOLYL COMPLEXES OF IRIDIUM IN LOW OXIDATION STATE.
E. CARMONA, S. HUDSON, M.C. NICASIO, P.J. PEREZ, M. POVEDA and L. REY.

2234P BINUCLEAR NICKEL COMPLEXES BRIDGED BY PYRAZOLATE AND HYDROCARBON LIGANDS.
J. CAMPORA, P. PALMA, M.L. POVEDA and E. CARMONA.

2235P ACTIVATION OF ORGANIC SUBSTRATES BY Tp^*Ir-DERIVATIVES ($Tp^* = HB(3,5\text{-}Me_2pz)_3^-$).
O. BOUTRY, M. PANEQUE, M.L. POVEDA, S. TABOADA, E. CARMONA, E. GUTIERREZ and A. MONGE.

2238P REACTIONS OF AN ANSA-BRIDGED η^5-CYCLOPENTADIENYL IMIDO DERIVATIVE OF NIOBIUM WITH ALKYLATING AGENTS.
P.T. GOMES, M.L.H. GREEN and P. MOUNTFORD.

2239P Au-Au BONDING IN A PENTANUCLEAR GOLD COMPLEX CONTAINING A LINEAR Au_5 CHAIN.
M.J. CALHORDA and L.F. VEIROS.

2240P ANSA-BRIDGED η^5-CYCLOPENTADIENYL IMIDO AND AMIDO DERIVATIVES OF TITANIUM, ZIRCONIUM AND MOLYBDENUM.
A.M. MARTINS and M.L.H. GREEN.

2241P CATALYTIC HYDROGENATION OF IMINES WITH $[Ir(\mu\text{-}OMe)(COD)]_2/P(O^tBuPh)_3$. STUDY OF THE INVOLVED METALLIC SPECIES.
S. CASTILLON, C. CLAVER, E. FERNANDEZ, A. RUIZ, P.A. CHALONER and P. HITCHCOCK.

2244P MONONUCLEAR PENTACHLOROPHENYL COMPLEXES OF RHODIUM(II).
M.P. GARCIA, M.V. JIMENEZ, L.A. ORO and F.J. LAHOZ.

2250P PREPARATION OF NEW CATIONIC COMPLEXES $[CpFe(dppe)L]PF_6$ WITH SULFUR AND OTHER DONOR LIGAND.
C. DIAZ and A. ARANCIBIA.

2251P HYDROFORMYLATION RHODIUM CATALYSTS WITH S-DONOR CHIRAL LIGANDS.
S. CASTILLON, C. CLAVER, A. RUIZ, A. OREJON and A. MASDEU.

2254P ORGANOMETALLIC NICKEL(II) THIOMOLYBDATES AND THIOTUNGSTATES.
F. MOMBLONA, G. SANCHEZ, G. GARCIA, G. LOPEZ, E. PINILLA and A. MONGE.

2255P SYNTHESIS OF PALLADIUM ENOLATE COMPLEXES.
G. LOPEZ, J. RUIZ, M.T. MARTINEZ, V. RODRIGUEZ, G. GARCIA and F. FLORENCIANO.

2261P C-H CYCLOPENTADIENYL ACTIVATION IN ANIONIC ZIRCONIUM(III) SPECIES $[Cp'_2ZrH_2]^-$ ($Cp' = C_6H_4{}^tBu$, $C_6H_4SiMe_3$).
R. CHOUKROUN.

2262P NEW η^5-MONOCYCLOPENTADIENYLNICKEL(II) DERIVATIVES. SYNTHESIS AND CHARACTERIZATION.
A.R. DIAS, M.H. GARCIA and P.J.G. MENDES.

2267P HIGH VALENT IMIDO VANADIUM COMPLEXES CONTAINING BENZAMIDINATES AS STABILIZING LIGANDS.
M. RIBEIRO DA COSTA, M.T. AVILES and J.H. TEUBEN.

2270P CATALYTIC ACTIVITY OF $[(FeBr_3)_2(DMSO)_3]$ AND $FeBr_3$ AND IN SELECTIVE OXIDATION OF ORGANIC SULFIDES TO SULFOXIDES.
L. ROSSI, A. SUAREZ and S. MARTIN.

2271P REVERSIBILITY FROM OXIDATIVE ADDITION TO β-ELIMINATION IN METAL HALIDES CATALYZED REACTIONS.
S.E. MARTIN, A.R. SUAREZ and M. MARTINELLI.

2272P STRUCTURE AND REACTIVITY OF BROMOMETALATES FORMED IN METAL BROMIDES CATALYZED DEHYDROBROMINATIONS.
A.R. SUAREZ, S.E. MARTIN and M. DOMINE.

2274P SYNTHESIS OF THE PHOSPHINE-THIOLATE METALLOLIGANDS $Cp_2M[S(CH_2)_nPPh_2]_2$ (M = Mo(IV), W(IV), n = 1, 2) AND ITS REACTION WITH Cu(I) AND Rh(I) COMPLEXES TO FORM HETERO BIMETALLIC SYSTEMS.
M.J.A. VILLA DE BRITO, A. ROMAO DIAS and M.H. GARCIA.

2275P SYNTHESIS AND CHARACTERIZATION OF NEW COMPOUNDS WITH BIPYRIDINS AND CYANO PYRIDINS COORDINATED TO MONOCYCLOPENTADIENYLRUTHENIUM(II).
A.R. DIAS, M.H. GARCIA and J.C. RODRIGUES.

2276P NUCLEOPHILIC ADDITION IN TRIPLE BONDS PROMOTED BY PLATINUM(II) COMPOUNDS.
C.L. CASAGRANDE JUNIOR and J. DUPONT.

2283P SYNTHESIS, STRUCTURAL CHARACTERIZATION AND CATALYTIC PROPERTIES OF A NEW SERIES OF MONONUCLEAR AND HETERO-BINUCLEAR METAL COMPLEXES CONTAINING THE SHORT BIT Ph_2PPy LIGAND.
D. DROMMI, C.G. ARENA, F. NICOLO, F. FARAONE and R. GOBETTO.

2285P SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF Re(I) COMPLEXES CONTAINING NITROGEN DONOR LIGANDS DERIVED FROM TERPYRIDINE.
R. SARTORI, R. SARIEGO, R. PASTENE and S.A. MOYA.

2289P ^{19}F AND ^{31}P EVIDENCE FOR SILVER HEXAFLUOROPHOSPHATE HYDROLYSIS IN SOLUTION. SYNTHESIS OF THE FIRST PALLADIUM DIFLUOROPHOSPHATE COMPLEXES.
R. FERNANDEZ-GALAN, B.R. MANZANO, A. OTERO, M. LANFRANCHI and M.A. PELLINGHELLI.

2290P NEW NEUTRAL, ANIONIC AND CATIONIC NIOBIUM(V) ALCOXIDES.
A. ANTIÑOLO, D. CASADO, A. OTERO and E. PALOMARES.

2291P NEW APPROACH TO THE CHEMISTRY OF TRISPYRAZOL-1-YLBORATES RUTHENIUM DERIVATIVES. APPLICATION OF SPECIAL NMR TECHNIQUES TO THE STRUCTURAL ELUCIDATION OF THESE COMPLEXES.
F.A. JALON, A. OTERO and A. RODRIGUEZ.

2292P SYNTHESIS AND REACTIVITY OF RUTHENIUM AND NIOBIUM COMPLEXES WITH POLY (PYRAZOL-1-YL)METHANE LIGANDS.
J. FERNANDEZ-BAEZA, F.A. JALON, A. OTERO, M.E. RODRIGO-BLANCO and A. RODRIGUEZ.

2293P KINETIC STUDIES ABOUT THE SYNTHETIC REACTIONS OF $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(L)$ DERIVATIVES.
A. ANTIÑOLO, F. CARRILLO, M. FAJARDO, S. GARCIA-YUSTE and A. OTERO.

2294P REACTIVITY OF $[(\eta^6\text{-}C_6Me_6)RhCl_2]_2$ TOWARDS SOME 1,2,4-TRIAZINE LIGANDS.
I. SOLANO, G. GARCIA, G. SANCHEZ, G. LOPEZ, J. CASABO, E. MOLINS and C. MIRAVITLLES.

2296P PALLADIUM AND PLATINUM HYDROGENSULFIDO COMPLEXES.
G. LOPEZ, J. RIUZ, V. RODRIGUEZ, J.M. MARTI, C. VICENTE, G. GARCIA and N. CITULLAS.

2301P NEW ARYLOXO COMPLEXES OF PALLADIUM AND PLATINUM.
G. LOPEZ, J. RUIZ, V. RODRIGUEZ, M.T. MARTINEZ, G. GARCIA and J.M. MARTI.

2304P STUDY ON REACTIVITY OF FERROCENE CARBOXALDEHYDE WITH PHENYLENEDIAMINES.
A. BENITO, J. CANO, R. MARTINEZ-MAÑEZ, J. SOTO, M.J.L. TENDERO, J. PAYA and E. SINN.

2311P A STEPWISE SYNTHESIS OF MOLYBDENOCENE, Cp_2MoX_2, AND ANALOGUE MIXED RING SUBSTITUTED DERIVATIVES $CpCp'MoX_2$, ($Cp' = C_5H_4Me, C_9H_7$).
C.G. DE AZEVEDO, I.S. GONÇALVES, E. HERDTWECK, D.S. MORENO, M. PESSANHA, C.C. ROMAO, J. ZUHLKE.

2323P EVIDENCE FOR A THREE-COORDINATE PALLADIUM(II) SPECIES.
J.A. CASARES, S. COCO, P. ESPINET and Y.-S. LIN.

2333P INSERTION REACTIONS OF $SnCl_2$ ON Pt-Cl BONDS.
R. USON, J. FORNIES, L.R. FALVELLO, I. USON and I. ARA.

2341P A STEPWISE SYNTHESIS OF MOLYBDENOCENE, Cp_2MoX_2 AND ANALOGUE MIXED RING SUBSTITUTED DERIVATIVES $CpCp'MoX_2$, ($Cp' = C_5H_4Me, C_9H_7$).
C.G. DE AZEVEDO, I.S. GONÇALVES, E. HERDTWECK, D.S. MORENO, M. PESSANHA, C.C. ROMAO and J. ZÜHLKE.

2346P CATIONIC DI-, TRI- AND TETRANUCLEAR ARENE-RUTHENIUM COMPLEXES CONTAINIG HYDRIDO OR CHLORO LIGANDS: CLUSTER BUILD-UP IN AQUEOUS SOLUTION.
G. MEISTER, G. RHEINWALD, H. STOECKLI-EVANS and G. SÜSS-FINK.

2347P NEW RUTHENIUM HYDRIDES WITH DIPHOSPHINES AND ITS REACTIVITY WITH ALKYNES.
J. LOPEZ, J. MONTOYA, A. SANTOS, P. NOHEDA and A.M. ECHAVARREN.

2357P SYNTHESIS AND ELECTROCHEMICAL STUDY OF $(\eta^6\text{-}C_6Ph_4H)Co(CO)_2$ AND $CH_2[(C_6Ph_4)Co(CO)_2]_2$.
S. DELGADO, J. GONZALEZ-VELASCO, M.J. MACAZAGA, Mª.L. MARCOS, R.M. MEDINA and C. MORENO.

2361P URACIL AND THIOURACIL COMPLEXES OF DICYCLOPENTADIENYL MOLYBDENUM AND TUNGSTEN.
A.R. DIAS, M.H. GARCIA, A. SAUDADE LOPES, M.M. MARQUES, D. MASI, C. MEALI and M.M. SALEMA.

2363P MECHANISM OF THE INSERTION REACTION OF ALKYNES WITH PHOSPHONICKELOCYCLES.
M. MARTINEZ, G. MULLER, D. PANYELLA and M. ROCAMORA.

2364P COMPLEXES OF PLATINUM WITH $PPh_2(ROH)$ LIGANDS. REACTIONS WITH $SnCl_2$.
N. CLOS, G. MULLER and D. SAINZ.

2365P $(PPh_4)[Mn_3(CO)_{12}(\mu\text{-}H)(\mu\text{-}Hg\{Mo(CO)_3Cp\}]$: THE FIRST EXAMPLE OF A MERCURY-CONTAINING PLANAR TRIAGULATED ROMBOHEDRAL METAL CLUSTER.
S. ALVAREZ, O. ROSSELL, M. SECO, G. SEGALES, M.A. PELLINGHELLI and A. TIRIPICCHIO.

3. Solid State Chemistry and Inorganic Materials

3181P BIOGLASS FROM THE $MgO\text{-}CaO\text{-}P_2O_6\text{-}SiO_2$ SYSTEM: MICROSTRUCTURE CHARACTERIZATION AND MICROANALYSIS.
J.C. DOADRIO VILLAREJO, J.Mª. RINCON, C. DIAZ, S. NICOLOPOULOS and M. VALLET REGI.

3182P INFLUENCE OF THE SYNTHETIC METHOD ON THE HYDROXYAPATITE TEXTURE AND MORPHOLOGY.
S. NICOLOPOULOS, M.P. ALONSO, I. DE FRUTOS, M.T. GUTIERREZ-RIOS and M. VALLET-REGI.

3191P STRUCTURAL INCORPORATION OF MnO IN $Ca\text{-}SiO_2$ AND $Al_2O_3\text{-}SiO_2$ SYSTEMS PREPARED BY THE SOL-GEL METHOD.
M.G. FERREIRA DA SILVA.

3211P ELECTRIC PROPERTIES OF MIXED OXIDES WITH SPINEL TYPE STRUCTURE.
C. GONZALEZ, M.L. LOPEZ, M. GAITAN, M.L. VEIGA, C. PICO, E. RUIZ-HITZKY and E. PEREZ-CAPPE.

3212P SYNTHESIS, STRUCTURAL CHARACTERIZATION, MAGNETIC AND ELECTRIC BEHAVIOUR OF $Ti_{3(1-x)}Ni_xM_{2x}O_6$ (M = Sb, Nb) PHASES.
J.M. BELLOCH, J. ISASI, M.L. LOPEZ, E. RAMOS, M.L. VEIGA and M. GAITAN.

3222P SYNTHESIS AND CHARACTERIZATION OF CHROMIUMSILICATE WITH MFI STRUCTURE.
J.S.T. MAMBRIM, H.O. PASTORE and E.J.S VICHI.

3223P THE Immm-R_2BaCoO_6 OXIDES (R = RARE EARTH): STRUCTURAL STABILITY AND MAGNETIC PROPERTIES.
J. HERNANDEZ-VELASCO, A. SALINAS and R. SAEZ-PUCHE.

3224P SYNTHESIS, STRUCTURE AND GAS SENSITIVITY PROPERTIES OF Cu-DOPED SnO_2.
J.C. FABIAN, J. ROMAN, M. LABEAU, G. DELABOUGLISE and M. VALLET-REGI.

3236P ENTHALPIES OF FORMATION OF BUCKMINSTERFULLERENE (C_{60}) AND OF THE PARENT IONS C_{60}^{-}, C_{60}^{2-} AND C_{60}^{+}.
H.P. DIOGO, M.E. MINAS DA PIEDADE, T.J.S. DENNIS, J.P. HARE, H.W. KROTO, R. TAYLOR and D.R.M. WALTON.

3247P V_{4+}-TiO_2 RUTILE SOLID SOLUTIONS AT HIGH TEMPERATURE.
M.A. TENA, G. MONROS, J. CARDA, V. CANTAVELLA and P. ESCRIBANO.

3248P TEOS HYDROLYSIS RATE IN DMSO.
E. CORDONCILLO, S. RODRIGUEZ, G. MONROS, M.A. TENA, P. ESCRIBANO and J. CARDA.

3252P CRYSTAL GROWTH, STRUCTURE AND THERMAL DECOMPOSITION $KLn(CrO_4)_2$ (Ln = Y, Dy-Lu).
I. BUENO, C. PARADA, A. MONGE and C. RUIZ VALERO

3253P SYNTHESIS OF PILLARED CLAYS DERIVED FROM MONTMORILLONITE BY USING CRTA.
Y. LAUREIRO, S. GARCIA-MARTIN, J. ROUQUEROL, F. ROUQUEROL and A. JEREZ.

3256P SYNTHESIS OF TERNARY AND QUATERNARY OXIDES WITH A PEROVSKITE STRUCTURE.
M.E. MELO JORGE and A. CORREIA DOS SANTOS.

3268P LOW TEMPERATURE PREPARATION OF MANGANESE COBALTITE SPINELS $Mn_xCo_{3-x}O_4$, $0 \leq x \leq 1$.
J.L. MARTIN DE VIDALES, O. GARCIA-MARTINEZ, E. VILA, R.M. ROJAS and M.J. TORRALVO.

3273P INCLUSION OF A LITHIUM-AMINE ION IN A NEW MATRIX: THIOUREA-CHLORIDE.
N. YUTRONIC, P. JARA, G. GONZALEZ, V. MANRIQUES and O. WITTKE.

3279P DESIGN AND SYNTHESIS OF SOLID SOLUTIONS $SrTi_{1-x}Ru_xO_3$ PEROVSKITES.
S.L. CUFFINI and R.E. CARBONIO.

3282P PREPARATION AND CHARACTERIZATION OF IRON(III) OXIDE HIGHLY DISPERSED OVER SYNTHETIC HYDROTALCYTE.
E.J.S. VIÇHI and L.A.S. DE ALMEIDA PRADO.

3298P A HREM STUDY OF THE $LnBa_2FeO_x$ SYSTEM.
E. GARCIA, C. PRIETO, M. PARRAS, M. VALLET-REGI and J.M. GONZALEZ CALBET.

3302P ELECTROCHEMICAL LITHIUM INSERTION IN REDUCED TUNGSTEN OXIDES.
A. GARCIA-GARCIA, L.M. TORRES-MARTINEZ, F. GARCIA-ALVARADO, E. MORAN and M.A. ALARIO-FRANCO.

3318P NEW IRIDIUM PEROVSKITE-LIKE MIXED OXIDES Ba_2LnIrO_6 (Ln = Pr, Eu, Ln).
E. RAMOS-CARBONERO, I. ALVAREZ, M.L. VEIGA and C. PICO.

3319P A NOVEL EXAMPLE OF A-CATIONS ORDERING IN THE PEROVSKITES $(MLa)(MgTe)O_6$ FOR M = Na AND K.
M.L. LOPEZ, M.L. VEIGA and C. PICO.

3332P MANGANESE-CONTAINING HYDROTALCITES.
C. BARRIGA, J.M. FERNANDEZ, F.M. LABAJOS, V. RIVES and M.A. ULIBARRI.

3334P SYNTHESIS OF TiO2 BY PYROLYSIS OF AN AEROSOL.
J. PEÑA, A. MARTINEZ, J.M. GONZALEZ-CALBET and M. VALLET-REGI.

3335P DETERMINATION OF THE CARBON IMPURITIES IN THE 2212 Bi-SUPERCONDUCTOR.
J. RAMIREZ, C.V. RAGEL, J.M. GONZALEZ-CALBET and M. VALLET-REGI.

Wednesday, September 15

09.00-10.00 **PLENARY LECTURE** **University Auditorium**

SOLID-GAS REACTIONS OF MOLECULAR ORGANOMETALLIC COMPOUNDS.
C. BIANCHINI.

Chairman: *M. Graziani*

10.00-11.00 **PLENARY LECTURE** **University Auditorium**

OXYGEN CONTENT IN SUPERCONDUCTORS AND RELATED MATERIALS.
A. CANEIRO.

Chairman: *J. Sordo*

Thursday, September 16

09.30-10.30 PLENARY LECTURE **University Auditorium**

COORDINATION AND REACTIVITY OF THIOPHENES ON TRANSITION METAL CENTRES. MOLECULAR ANALOGUES OF SURFACE SPECIES AND REACTIONS RELEVANT TO HYDRODESULPHURISATION.
R.A. SANCHEZ-DELGADO.

Chairman: *P. Dixneuf*

10.30-11.00 *Coffee Break*

11.00-13.15 SESSION LECTURES

1. COORDINATION AND BIOINORGANIC CHEMISTRY **Hall A**

Chairman: *J. Faus*

1025S NEUTRAL DIVALENT TRANSITION-METAL COMPLEXES WITH THIOETHER-IMIDAZOLE- CONTAINING LIGANDS AS MODELS FOR METALLOPROTEINS.
M. BASTIDA.

1106S SOME OPTICAL PROPERTIES OF RARE EARTH COMPOUNDS.
G. VICENTINI.

1494S REDOX PROTEINS IN ENVIRONMENTAL BIOTECHNOLOGY.
C. LUCHINAT.

2. ORGANOMETALLIC CHEMISTRY AND CATALYSIS **Hall B**

Chairman: *P. Royo*

2001S REACTIVITY OF PENTADIENYL TRANSITION METAL COMPLEXES TOWARDS NEUTRAL NUCLEOPHILES.
M.A. PAZ-SANDOVAL.

2498S NOVEL POLYNUCLEAR METALLOCENES SPECIES TO EXPLORE ELECTRONIC DELOCALIZATION, MAGNETIC AND CONDUCTIVE PROPERTIES.
E. ROMAN, J.M. MANRIQUEZ, M. OTERO, Y. CHEVEZ and B. OELCKERS.

2263S RECENT ADVANCES IN THE CHEMISTRY OF PERHALOPHENYL PLATINATE(II) COMPLEXES.
J. FORNIES.

3. Solid State Chemistry and Inorganic Materials **Hall C**

Chairman: *T. Rojo*

3501S SCIENCE, TECHNOLOGY AND APPLICATIONS OF BIOCERAMICS: STATE OF THE ART AND FUTURE PERSPECTIVES.
A. RAVAGLIOLI.

3467S MOLECULAR DESIGN OF ADVANCED CERAMICS.
J. LIVAGE.

3464S BIOMATERIALS FOR HARD TISSUE SUBSTITUTION.
J.A. PLANELL.

14.00-16.30 **Lunch**

16.30-18.00 **SESSION LECTURES**

1. Coordination and Bioinorganic Chemistry **Hall A**

Chairman: *C.A. Mc Auliffe*

1092S NEW CHEMISTRY OF PLATINUM ANTICANCER DRUGS AND THEIR PALLADIUM ANALOGUES.
K.J. BARNHAM, S.J. BERNERS-PRICE, M.I. DJURAN, M.A. MAZID, J.D. RANFORD and P.J. SADLER.

1484S POLYIMIDAZOLE COMPLEXES MODELING THE ACTIVE SITE OF MONONUCLEAR NON-HEME IRON PROTEINS.
E. MULLIEZ, L.M. VAN DER HEIJDT, G. LEMERCIER, S. NAVARATNAM, J.P. TUCHAGUES, G.A. VELDINK and J.C. CHOTTARD.

2. Organometallic Chemistry and Catalysis **Hall B**

Chairman: *J. Strähle*

2027S MOLECULAR DIHYDROGEN COMPLEXES IN HOMOGENEOUS CATALYSIS.
L.A. ORO, M.A. ESTERUELAS and C. VALERO.

2184S PROTONATION AND DEHYDROGENATION OF COMPLEXES WITH SMALL UNSATURATED- CARBON OR -NITROGEN LIGANDS: A CHEMICALAND ELECTROCHEMICAL APPROACH.
A.J.L. POMBEIRO.

3. Solid State Chemistry and Inorganic Materials **Hall C**

Chairman: *J. Livage*

3063S SYSTHESIS, CRYSTAL GROWTH AND CHARACTERIZATION OF SUPERCONDUCTING COMPOUNDS AT THE ARGENTINE ATOMIC ENERGY COMISSION LABORATORIES.
A. LEYVA.

3500S ZEOLITE CHEMISTRY: CATALYTIC APPLICATIONS.
A. OVIEDO.

11.00-19.00 **POSTERS SESSION** **Hall D**

Chairman: *A. Sánchez Díaz*

1. COORDINATION AND BIOINORGANIC CHEMISTRY

1277P NEW HOMO- AND HETEROPOLYNUCLEAR COMPLEXES WITH NITROSO-OXAMIDATE BRIDGING LIGNDS. MAGNETO-STRUCTURAL STUDY.
E. COLACIO, J.M. DOMINGUEZ-VERA, A.M. ROMEROSA, R. KIVEKAS and A. ESCUER.

1281P EPR CHARACTERIZATION OF Ni(I) COMPLEXES WITH PENTADENTATE SCHIFF BASE LIGAND.
B. DE CASTRO, C. FREIRE and M. CORDEIRO.

1284P COORDINATING PROPERTIES OF SYMMETRICALLY DISUBSTITUTED DITHIOOXAMIDES SHOWING AXIAL CHIRALITY.
S. LANZA and G. ROSACE.

1287P CRYSTAL STRUCTURE OF A NEW Co(III) COMPLEX CONTAINING 3-[BIS(2-IMIDAZOLYL)] PROPIONIC ACID.
B. GIMENO, L. SOTO, A. SANCHO, F. DAHAN and J.P. LEGROS.

1295P REACTIVITY OF HYDROXO-NICKEL COMPLEXES TOWARD PHENOLS AND CARBOXYLIC ACIDS.
G. LOPEZ, G. GARCIA, F. RUIZ and G. SANCHEZ.

1297P CHEMICAL MODELS OF THE MOLYBDENUM CENTRE IN NITROGENASE.
D.J. EVANS, G. GARCIA, J.M. PEREZ, M.D. SANTANA and J.M. YAGO.

1299P FIVE-COORDINATE COMPLEXES OF NICKEL(II) BASED ON CYCLIC TRIAMINES AND SALICYLALDIMINES.
G. GARCIA, G. LOPEZ, A. RUFETE, G. SANCHEZ, M.D. SANTANA, J. CASABO, E. MOLINS and C. MIRAVITLLES.

1303P NEW FERROCENE-CONTAINIG LIGANDS:CHIRAL, CHELATING AND MACROCYCLIC LIGANDS.
A. BENITO, J. CANO, R. MARTINEZ-MAÑEZ, J. SOTO, M.J.L. TENDERO and J. PAYA.

1305P INTERACTION OF METAL IONS WITH NEW LIGANDS OBTAINED BY CONDENSATION OF FERROCENE CARBOXALDEHYDE WITH 2-AMINOBENZOIC ACID DERIVATIVES.
A. BENITO, J. CANO, R. MARTINEZ-MAÑEZ, J. SOTO, M.J.L. TENDERO, J. PAYA and F. LLORET and E. SINN.

1306P SYNTHESIS OF IODO URANIUM(IV) COMPLEXES WITH HYDROTRIS(PYRAZOLYL)BORATE LIGANDS.
M.P.C. CAMPELLO, A. PIRES DE MATOS and I. SANTOS.

1307P RHENIUM COMPLEXES WITH TETRAKIS (PYRAZOL-1-YL)BORATE.
M. FERNANDA, N.N. CARVALHO, A. PAULO, A.J.L. POMBEIRO and I. SANTOS.

1308P STRUCTURE OF A SECOND CRYSTALLINE FORM OF TRIS[HYDROTRIS(PYRAZOL-1-YL) BORATO]YTTERBIUM(III).
A. DOMINGOS, N. MARQUES and A. PIRES DE MATOS.

1309P URANIUM(IV)-LIGAND BOND DISSOCIATION ENTHALPIES.
M.P.C. CAMPELLO, J.P. LEAL, N. MARQUES, I. SANTOS, M. SILVA and J.A. MARTIHO SIMOES.

1310P INTERACTION BETWEEN POLYALCOHOLS AND HETEROPOLYTUNGSTATES OF KEGGIN TYPE.
M.C.N. TROVAO, A.M.V.S.V. CAVALEIRO and J.D. PEDROSA DE JESUS.

1312P SPECTROSCOPIC CHARACTERIZATION OF A NICKEL(I) COMPLEX WITH A N_2OS ASYMMETRIC LIGAND.
B. DE CASTRO, E. PEREIRA and L. GOMES.

1313P SYNTHESIS AND CHARACTERIZATION OF COPPER(II) COMPLEXES WITH TETRADENTATE N_2OS LIGANDS.
B. DE CASTRO and E.F.A. PEREIRA.

1314P ELECTROCATALYTIC REDUCTION OF METHYL IODIDE IN THE PRESENCE OF Ni(I) SCHIFF BASES COMPLEXES.
B. DE CASTRO, C. FREIRE and F. AZEVEDO.

1315P INTERACTION OF SQUARE-PLANAR N_4 NICKEL(I) COMPLEXES WITH AXIAL P-DONOR LIGANDS.
B. DE CASTRO, C. FREIRE and M. VALENTE.

1316P EPR CHARACTERIZATION ON NI(III) COMPLEXES WITH N_3O_2 SCHIFF BASE LIGANDS DERIVED FROM NAPHTHALDEHYDE.
B. DE CASTRO, C. FREIRE and P. GOMES.

1324P AZETAZOLAMIDE INTERACTION IN Cu(II), Zn(II) AND Co(II) MODEL COMPLEXES OF THE CARBONIC ANHYDRASE ENZYME.
G. ALZUET, L. CASELLA, J. CASANOVA and J. BORRAS.

1325P CRYSTAL STRUCTURE AND PROPERTIES OF $Cu(Hstz)_2(EtOH)Cl_2$.
J. CASANOVA, G. ALZUET, J. BORRAS, S. GARCIA-GRANDA and R. DIAZ.

1326P EPR SINGLE CRYSTAL OF Cu(sulfathiazole)$_2$ (MeOH)Cl$_2$.

J. CASANOVA, S. FERRER, G. ALZUET, J. BORRAS, D. GATTESCHI and L. DAVID.

1327P HALOCUPRATES(II) OF THE TRIAMTERINIUM, A DIPROTONATED PTERIDINE DERIVATIVE. CRYSTAL STRUCTURE OF (TRIAMTERINIUM)$_2$CuCl$_4$.

G. ALZUET, A. MARTIN, J BORRAS, S. GARCIA-GRANDA and R. DIAZ.

1328P COORDINATION BEHAVIOUR OF SULFATHIAZOLE: CRYSTAL STRUCTURE OF Cu(stz)(py)$_3$Cl.

J. CASANOVA, G. ALZUET, J. BORRAS, S. GARCIA-GRANDA, M. SANAU and J. LATORRE.

1329P METAL COMPLEXES OF SULFACETAMIDE.

F. BLASCO, R. ORTIZ, L. PERELLO and J. BORRAS.

1330P CRYSTAL STRUCTURE OF [Cd$_2$(Cx)$_4$(DMSO)$_2$].2H$_2$O COMPLES; HCx= 1-ETHYL-1,4-DIHYDRO-4-OXO(1,3) DIOXOLO(4,5g) CINNOLINE-3-CARBOXYLIC ACID.

M. RUIZ, R. ORTIZ, L. PERELLO, S. GARCIA-GRANDA and M.R. DIAZ.

1331P COMPLEX FORMATION EQUILIBRIA BETWEEN THE CINOXACIN, AND ANTIMICROBIAL AGENT, AND Co(II), Ni(II) AND Zn(II) IN AQUEOUS SOLUTION.

M. RUIZ, C. RODRIGO, L. PERELLO and R. ORTIZ.

1345P 1-(2-CARBAMYLETHYL)BENZIMIDAZOLE NICKEL(II) COMPLEXES WITH UNUSUAL MAGNETIC BEHAVIOUR.

G.V.A. DA SILVA, M.C.R.M.P. BASTO and A.A.S.C. MACHADO.

1353P PREPARATION, CRYSTAL STRUCTURE AND SPECTRAL BEHAVIOUR OF Cd(S$_2$PPh$_2$)$_2$.

J.S. CASAS, E.E. CASTELLANO, M.S. GARCIA-TASENDE, A. SANCHEZ, J. SORDO, E.M. VAZQUEZ-LOPEZ and J. ZUKERMAN-SCHPECTOR.

1354P COORDINATION AND REACTIVITY OF N-(2-AMINOETHYL)-2-{[(PYRIDINE-2-YL) METHYL]THIO}ACETAMIDE.

R. CARBALLO, A. CASTIÑEIRAS and M.C. GOMEZ.

1369P METAL IONS IN DEMOSPONGIAE OF THE NORTH ATLANTIC.

F. ARAUJO, M.T. LOPES, H.M. GASPAR, M.C. VAZ, M. HUMANES and J.J. FRAUSTO DA SILVA.

1370P SYNTHESIS AND STUDY OF INSULIN MIMICKING VANADIUM.

M. ALMEIDA, L.M.S. LOURA, J.J.R. FRAUSTO DA SILVA, J.A.L. DA SILVA and M.C.T.A. VAZ.

1371P HALOPEROXIDASES FROM THE ALGAE.

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3436P PREPARATION AT HIGH OXYGEN PRESSURES AND STUDY OF $Ln_{1-x}A_xNiO_3$ (A = Ca, Sr; Ln = La, Nd, Sm, Eu).
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3466P SYNTHESIS AND STRCUTURE OF NOVEL CUPRATES IN THE Ba-Ln-M-Cu-O SYSTEMS (Ln: Y, La; M: Ni, Co).
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3485P NEW SPINEL FERRITES OBTAINED BY IONIC EXCHANGUE.
M.C. BLESA, E. MORAN, U. AMADOR, N. MENENDEZ and J.D. TORNERO.

3490P HYDROTERMIC SYNTHESIS OF $M_x(PO_4)_y(OH)_z$ (M = Ca, Mg, Co).
R. GONZALES SANTOS, J. GUERRA-LOPEZ and A. GOMEZ.

3491P EFFECTS OF PHYSICAL-CHEMICAL PROPERTIES OVER THE BEHAVIOR "IN VIVO" OF TWO BIOMATERIALS DERIVED FROM SEA CORALS.
R. GONZALES SANTOS, J. GUERRA-LOPEZ, M.C. MELO and O. PEREDA.

3502P CHARACTERIZATION OF THE ANHYDROUS Cu-Sr AND Cu-Ca FORMATES.
P.K. DE PERAZZO, G. LEYVA, G. POLLA, H. LANZA and M.R. DE BENYACAR.

3503P CRYSTALLINE STRUCTURE OF Cu-Sr AND Cu-Ca FORMATE. Cu-Ca FORMATE SUPERSTRUCTURE ANALYSIS.
A.G. LEYVA, G. POLLA, P.K. DE PERAZZO and F. PARISI.

Friday, September 17

09.30-10.30 **PLENARY LECTURE** **University Auditorium**

CATIONIC MANGANESE PORPHYRINS AS ARTIFICIAL ENDONUCLEASES AND POTENTIAL ANTI-HIV MOLECULES.
B. MEUNIER.

Chairman: *E. Carmona*

10.30-11.00 *Coffee Break*

11.00-12.00 **PLENARY LECTURE** **University Auditorium**

THE MICROSTRUCTURE OF SOME SUPERCONDUCTING MATERIALS.
M.A. SEÑARIS, A. VAREZ, C. RIAL, U. AMADOR, Ph.SAINT-MARD, F. GARCIA ALVARADO, E. MORAN and M.A. ALARIO.

Chairman: *M. Vallet*

12.00-12.30 **CLOSING CEREMONY** **University Auditorium**

ABSTRACTS

(Supplement)

MODULATION OF THE B(3)-H-Ru DISTANCES IN 7,8-DICARBA-*nido*-UNDECABORATE DERIVATIVES

Francesc Teixidor[a], Clara Viñas[a], José A. Ayllón[a], Raikko Kivekäs[b], Reijo Sillanpää[c] and Jaume Casabó[a]
[a]*Institut de Ciència dels Materials (CSIC), Campus UAB Bellaterr, 08193 Barcelona, Spain;* [b]*Depart. Chemistry, Univ. of Helsinki, Vuorikatu 20, SF-00100;* [c]*Department of Chemistry, University of Turku, SF-20500.*

Studies carried on in our group with 7,8-dithio-7,8-dicarba-nido-undecaborate derivatives with S,S' connecting strings have suggested that the length of the string modulates the B(3)...M distance, e.g. the shorter the string the smaller the distance produced. A B(3)-Rh σ interaction had been found in $[NMe_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_9\}]$[1]. In an early report[2] we have presented the first example of a B(3)-H-M interaction. This is unique in the sense that it only involves one boron atom, that this is from the second layer and that it only boron atom in the cage connected to both carborane carbon atoms.
Here we present a way to force and modulate such a bond, which proves the macrocyclic/carborane mutual interaction that permits the, otherwise unlike, formation of rare B(3)-M and B(3)-H-M interactions.

Chem.	Cycle Size	w (°)	B(3)-M (Å)	S-S (Å)
1	8	120.4	2.48	3.21
2	6	110.0	2.41	3.01
3	5	102.7	2.39	2.78

1 $Ru(PPh_3)_2Cl$ (**L8**); 2 $Ru(PPh_3)_2Cl$ (**L6**); 3 $Ru(PPh_3)_2Cl$ (**L5**)

Abreviations: $\{7,8\text{-}\mu\text{-}(SCH_2S)\text{-}7,8\text{-}C_2\text{-}B_9H_{10}\}^-$ (**L5**); $\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2\text{-}B_9H_{10}\}^-$ (**L6**); $\{7,8\text{-}\mu\text{-}(SCH_2CH_2CH_2CH_2S)\text{-}7,8\text{-}C_2\text{-}B_9H_{10}\}^-$ (**L8**).

The analysis of the crystal structures (see table) presented as the *w* angles[2] and the *B(3)-M* distances shows how this can be modulated as a result of the stringlength. This can be of interest in the design of new catalysts, especially when a degree of recognition is desirable.

1. F. Teixidor, A. Romerosa, C. Viñas, J. Rius, C. Miravitlles, J. Casabó; *J. Chem Soc., Chem. Commun.*, **1991**, 192.
2. F. Teixidor, J.A. Ayllon, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó; *J. Chem. Soc., Chem. Comm.*, **1992**, 1281.

DESIGN OF NEW OPTO/MICRO-ELECTRONIC DEVICES: III-V SEMICONDUCTOR HETEROSTRUCTURES.

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In order to fabricate any chosen device structure commercial producers of devices would ideally like to be able to control

1) the band gap,
2) the refractive index,
3) the lattice parameter,
4) the thickness, and
5) the dopant concentration

of the crystalline material in each layer. A futher desirable feature would be the use of a cheap and strong defect-free single crystal substrate. Silicon is the obvious choice. The growth of III-V compound semiconductors with direct bandgaps on a substrate with an indirect gap also offers the possibility of integrating electronic (Si) and optical (GaAs) components on a single chip.

One of the major problems in meeting the above criteria is the difficulty of growing defect-free layers on a substrate of different lattice parameter. Conventional epitaxial growth techniques tend to introduce crystal defects (dislocations, stacking faults and twins) when the mismatch in lattice parameters is more than 0.1% or so.

For many purposes the preferred substrates would be Si or InP. A so-called "buffer layer" is usually the first layer to be grown on the substrate. Its most important functions are to provide:

a) A clean and defect-free surface for futher growth.
b) The chosen lattice parameter on which subsequent layers are to be grown.

These are not simple conditions to meet. Some of the difficulties are:

x) The persistence of "threading" defects in the buffer layer. These tend to be replicated or even multiplied in subsequent layers.
y) The long-term stability of the buffer layer (and hence other more functionally important layers) if it has not fully relaxed to its natural lattice parameter.

We are suggesting that a wide range of materials can be combined monolithically with silicon or with each other, despite lattice or thermal expansion coefficient mismatch, to attain the desired combinations of electrical and optical properties, thus enabling the formation of advanced optoelectronic integrated circuits and other structures.

E. G. Bauer et al. *Fundamental issues in heteroepitaxy -A Department of Energy, Council on Materials Science Panel Report* , J. Mater. Res. 5, 852-894 (1992).

A NOVEL ROUTE TO KNOWN AND UNPREDICTED COMPLEXES BY METAL ACTIVATION WITH R_3EX_2 (E = P, As, Sb)

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UMIST, Department of Chemistry, PO Box 88, Manchester M60 1QD, United Kingdom.

The oxidation of course metal powders by R_3EX_2 compounds leads to

a) Known metal complexes.
b) Isomers of known complexes.
c) One-step 3-electron oxidation of metals, e.g.

$$Ni + 3Me_3PI_2 \dashrightarrow Ni(PMe_3)_2I_3 + 1/2I_2$$

d) Complexes not thought capable of existence, e.g. $Co(SbPh_3)I_3$, an example of extreme symbiosis, and a rare example of a paramagnetic Co(III) complex.

Unusual intermediates have been isolated which give a "snapshot" of the chemistry involved in these processes.

SYNTHESIS AND STRUCTURAL STUDIES OF THE $Ni_{(1-X)}Cu_{(x)}Nb_2O_6$ SYSTEM

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Rua Ernesto Vasconcelos, C1 5º, 1700 Lisboa, PORTUGAL

The columbite niobate $NiNb_2O_6$, has been studied as a good example of a mixed metal oxide ,which structure may contain two different metal ions , each one occupying one sublattice. So, this niobate presented the principal requisites of a promising compound in the field of photoelectrochemistry. Considering the structural similarity of copper niobate, in order to study the effect of the substitution of nickel by copper ions on the photocorrosion, the main problem of nickel niobate, we prepared some samples of $Ni_{(1-x)}Cu_{(x)}Nb_2O_6$ with $0 < x < 1$.

The samples were prepared by the standard ceramic method . The structural characterization was done by XRD, using copper Kα radiation and the electrical behaviour was tested by four probe method .

The effect of a reduction treatment in a controlled hydrogen flux was studied for two samples.

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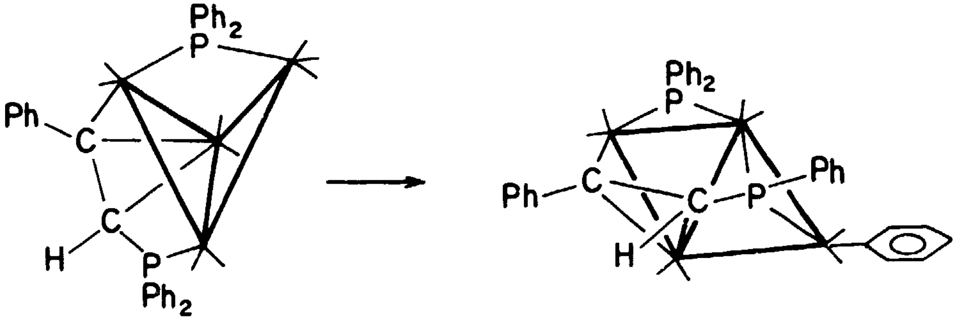
LAICM2511P **127, Mon. 13**

P-C BOND ACTIVATION IN A TETRANUCLEAR IRIDIUM CLUSTER: SYNTHESIS AND X-RAY MOLECULAR STRUCTURE OF $Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)$

R. M. S. Pereira, M. D. Vargas (Instituto de Química, UNICAMP, CP 6154, Campinas, Brazil)

F. Grepioni, D. Braga (Dipartimento di Chimica "G. Ciamician", Universitá di Bologna, 40126, Bologna, Italy)

The butterfly species $Ir_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (1) undergoes an extremely selective rearrangement (80 %) when heated in toluene (70 °C, 48 h) to give $Ir_4(CO)_8(\eta^1\text{-}Ph)(\mu_4\text{-}\eta^3\text{-}PhPC(H)CPh)(\mu\text{-}PPh_2)$ (2), whose molecular structure has been established by an X-ray analysis, as shown below.



(1) (2)

Cleavage of P-C(Ph) bonds in phosphorus ligands coordinated to clusters has been observed previously, but it is only rarely selective. Compound (2) does not react with H_2 under a variety of conditions, but undergoes irreversible carbonylation.

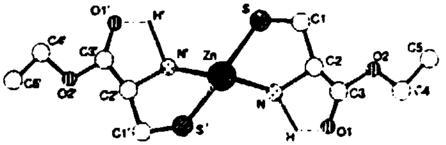
LAICM1514P 128, Tue. 14

SYNTHETIC APPROACHES TO ZINC-BINDING DOMAINS. STRUCTURAL AND SPECTROSCOPIC STUDIES ON ZINC(II) THIOLATE COMPLEXES

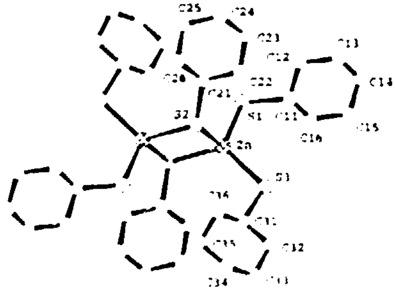
X. Almagro[a], T. Alsina[a], A. Alvarez[b], M. Baumi[a], J.F. Piniella[b], T. Sánchez[a] and Joan Sola[a].
Departaments de Química[a] i de Geologia[b], Universitat Autònoma de Barcelona,
08193 BELLATERRA, Barcelona, Catalunya, Spain

In the past several years it has been revealed the existence of several classes of proteins that contain zinc(II) ions which do not directly participate in any chemical reaction but play fundamental roles in forming structural domains where particular protein conformations are stabilized by coordination. Many of these proteins are involved in nucleic acid binding or gene regulation (1). Some examples include *the transcription factor IIIA*, whose "zinc finger" domains, $[ZnS_2N_2]$, contain two of both cysteine and histidine residues **(A)**, and the *yeast protein GAL4*, where its six cysteine domains **(B)** can be bound to two or three zinc(II) ions.

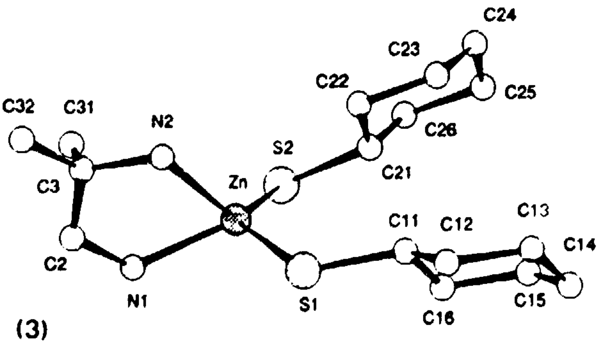
Reaction systems Zn(II)/RSH have led to dinuclear $[Zn_2(SR)_6]^{2-}$ **(2)** and, in the presence of diamines, monomeric $[Zn(SR)_2(H_2NCH_2CMe_2NH_2)]$ **(3)** (SR = cyclohexanethiolate) species, and to the (S,N)-chelate complex $[Zn\{SCH_2CH(NH_2)COOEt\}_2]$ **(1)** with the biotic ligand cysteine ethyl ester. While **(1)** and **(3)** are structural models for **(A)** (ref. 2), complex **(2)** approaches one of those proposed for **(B)**.



(1)



(2)



(3)

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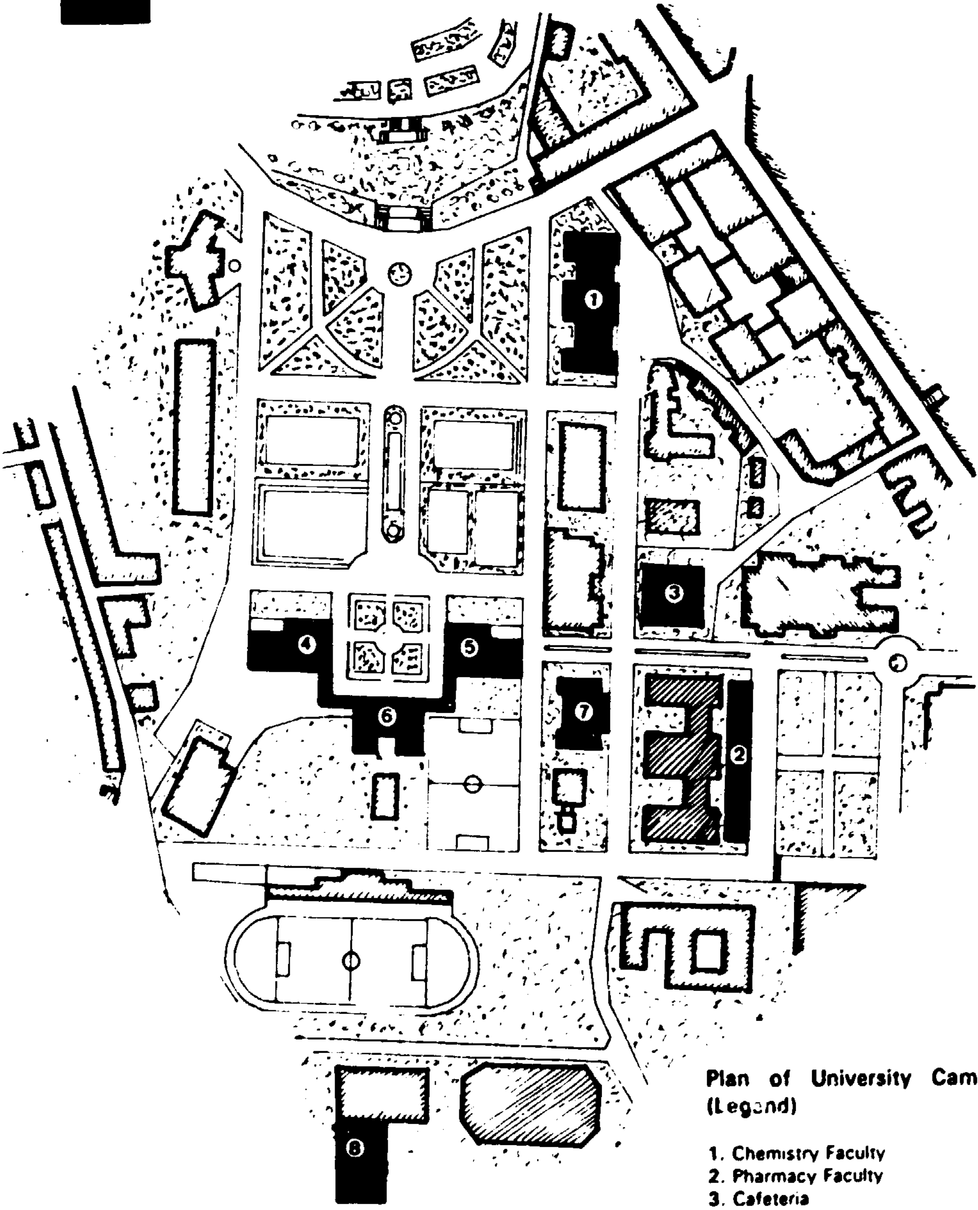
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

SITUACIÓN DAS DEPENDENCIAS UNIVERSITARIAS



Plan of University Campus (Legend)

1. Chemistry Faculty
2. Pharmacy Faculty
3. Cafeteria
4. C.M. *Rodríguez Cadarso*
5. C.M. *San Clemente*
6. C.M. *Fonseca*
   Refectory
   Cafeteria
7. University Auditorium
8. R.U. *Monte da Condesa*
   Refectory
   Cafeteria

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LAICM

LATIN-AMERICAN
INORGANIC CHEMISTRY
MEETING

SANTIAGO DE COMPOSTELA (SPAIN)

13 - 17 September 1993

ABSTRACTS

COLLECTED ABSTRACTS

LATIN-AMERICAN INORGANIC CHEMISTRY MEETING

Santiago de Compostela, Spain
13-17th September 1993

CONTENTS

ABSTRACTS OF PAPERS presented at the *Latin-American Inorganic Chemistry Meeting* held in SANTIAGO DE COMPOSTELA (SPAIN), 13th-17th SEPTEMBER 1993.

These abstracts have been prepared by photographic reproduction of texts submitted by the authors. Underlined names identify the authors presenting the papers.

Each abstract is identified, in the upper left corner, by an alphanumeric code following the initials **LAICM**. The first digit of this code designates the main topic to which the paper has been assigned, while the final letter specifies the presentation mode: **C** = plenary lecture, **S** = session lecture, **P** = poster.

In the upper right corner appear the day of presentation and the hall (for oral contributions) or the panel number (for posters) where the paper will be presented.

PLENARY LECTURES

A UNIQUE IRIDIUM(III) CYCLOHEXADIENYL. NEW IMIDO CHEMISTRY OF MANGANESE AND TUNGSTEN

Geoffrey Wilkinson
Johnson Matthey Laboratory, Imperial College of Science & Technology, London SW7 2AY, England.

The synthesis, structure and nuclear magnetic resonance spectra of [(1,2,3,4,5-η)-6-(1-Ethoxyethyl)-3-Mesityl-2,4,6-Trimethylcyclohexa-2,4-Dienyl]Dimesityliridium(III) will be discussed, in particular the variations on the nature of iridium(III) chlorides that lead to this compound or to $Ir(mes)_4$.

The syntheses of the first non-oxo compounds of manganese(VII) and (VI) with *tert*-butylimido groups, together with new reactions of $Li_2W(NBu^t)_4$.

LAICM1052C **Auditorium, Tue. 14**

HOMO AND HETEROMETALLIC CUBANE-TYPE IRON-SULFUR CLUSTERS: STRUCTURE AND REACTIVITY IN RELATION TO BIOLOGY AND CHEMISTRY

José J.G. Moura
Departamento de Química, Facultade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal.

Iron-sulfur proteins contain prosthetic groups composed of iron and sulfur atoms. They play a diversified functional role in biological systems being involved in electron transfer, in direct interaction with substrates and recently non redox roles have been emphatized. Extensive spectroscopic investigations have been performed on a variety of iron-sulfur proteins and a wealth of information accumulated on their physical properties. Four basic structures have emerged: FeS_4 (S from cysteine) center, [2Fe-2S], [3Fe-4S], and [4Fe-4S] clusters. Cluster ligands are in general, but not exclusively, cyteinyl residues. Recently, higher stoichiometries have been revealed, namely 6Fe and 8Fe cores. A close structural relation is apparent between these clusters and made possible the facile intercorversion between 4Fe and 3Fe clusters that are indicated to be physiologicaly significant.

Incorporation of different metals into the vacant site of a cuboidal [3Fe-4S] core present in simple iron-sulfur proteins results in the formation of heterometallic clusters of the type [M,3Fe-4S], M = Fe, Co, Ni, Zn, Cd, Ga and Tl. A summary of the interconversion pathways, as well as the potentialities of the method for specific labelling an iron-sulfur core will be presented (in particular ^{57}Fe isotopic enrichment and subsite labelling).

These novel heterometal containing clusters show interesting magnetic properties, contain localized and delocalized valences and present a wide range of spin and oxidation states.

Independent inorganic synthesis produced several hetero metal cluster of this type, complenebtibg and extending the work performed using proteins as templates, including the introduction of V, Mo, W, Re, Ni and Co. Se can also be used to replace sulfur.

Naturally occurring hetero metal clusters have also been detected in proteins and will de discussed in this context, in particular the association od Mo and V (nitrogenase) and Ni (CO dehydrogenase) with Fe.

Drs. I. Moura, A.L. Macedo, P.N. Palma, C. Moreno, K.K. Surerus, E. Münck and J. LeGall are aknowledged for many contributions. Work supported by JNICT, NATO and NIH.

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SOLID-GAS REACTIONS OF MOLECULAR ORGANOMETALLIC COMPOUNDS

Claudio Bianchini
ISSECC, CNR Firenze, Italy.

The ability of coordination compounds to undergo thermal reactions in the solid state has been known since many years. Only recently, however, systematic studies have been undertaken to design organometallic complexes capable of reacting in the solid state, at a molecular level, with inorganic and organic gaseous molecules. Solid-gas reactions between transition metal complexes and small organic molecules differ from reactions in solutions essentially in the fact that solid-state reactions occur in the constraining environment of the reactant crystal lattice, which can control both the kinetics and the nature of the products. these may not necessarily be the thermodynamically most stable products available to the system, but may rather be the products of reaction pathways accessible in the constraining environment of the solid. Therefore, as a result of the topochemical control occurring on the solid state, solid-gas reactions may lead to formation of either metal species or organic products not obtainable in analogous fluid solution reactions.

In the lecture, selected examples of molecular solid-gas organometallic reactions will be described including cases of cyclotrimerization of ethyne to benzene (catalytic), of cocylization of ethyne with ethene to cyclohexa-1,3-diene, of reductive dimerization of ethyne to buta-1,3-diene, of dimerization of ethene to butene, of hydrogenation of ethene to ethane (catalytic).

LAICM3095C **Auditorium, Wed. 15**

OXYGEN CONTENT IN SUPERCONDUCTORS AND RELATED MATERIALS

A. Caneiro
Centro Atómico Bariloche, Instituto Balseiro, 8400 S.C. de Bariloche, Argentina.

It is well known that the normal and superconducting properties of the new oxide superconductor materials depend strongly on the oxygen content.

Large variation of the physical properties have been observed within a small range of the oxygen nonstoichiometry. Therefore, in order to found a correlation between oxygen content and physical properties, the former must be well controled. However, the determination of this compositional variable is in many cases very difficult. This is mainly due to the multicompound nature of such systems.

A thermogravimetric equipment, specially developed for thermodynamic measurements of equilibrium oxygen partial pressure as a funstion of the oxygen content in complex oxide systems, will be described. From this measurements the oxygen content of the samples can be controled with high accuracy.

The main results on the correlation between oxygen content, physical and microstructural properties of the La-Sr-Cu-O, La-Sr-Ni-O, Bi-Sr-Ca-Cu-O and Nd-Ce-Cu-O systems will be also discussed.

COORDINATION AND REACTIVITY OF THIOPHENES ON TRANSITION METAL CENTRES. MOLECULAR ANALOGUES OF SURFACE SPECIES AND REACTIONS RELEVANT TO HYDRODESULPHURISATION

R.A. Sánchez-Delgado
Chemistry Centre, Instituto Venezolano de Investigaciones Científicas, IVIC, Apartado 21827, Caracas 1020-A, Venezuela.

In spite of the large scale industrial applications of the hydrodesulphurisation (HDS) process, and of the considerable number of studies of this reaction on heterogeneous catalysts, the mechanisms involved are not yet clearly understood.
In this lecture we will review our work on some aspects of the coordination chemistry of thiophenes pertinent to HDS. In particular, we will describe:

(i) the symnthesis and characterisation of some rhodium and iridium thiophene and benzothiophene complexes containing also phosphine ligands,

(ii) molecular orbital calculations on the structures and bonding of this type of compound for the Co, Rh, Ir triad,

(iii) the reactivity of such derivatives leading to the desulphurisation and/or hydrogenation of thiophenes of rhodium and iridium centres.

The examples to be described constitute excellent molecular analogues of some of the species and reactions that are thought to intervene in heterogeneous catalysis, and thus complement the knowledge obtained from surface studies and contribute to the understanding of this important reaction.

LAICM1008C **Auditorium, Fri. 17**

CATIONIC MANGANESE PORPHYRINS AS ARTIFICIAL ENDONUCLEASES AND POTENTIAL anti-HIV MOLECULES

Bernard Meunier
Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse, France.

Following extensive studies on DNA cleavage by bleomycin, "chemical nucleases" have been developed during the last decade(1,2). All these systems are based on redox-active complexes (copper, iron, ... etc) having a high DNA affinity. In many cases DNA strand breaks result from an oxidative attack on deoxyribose units. Metalloporphyrins, especially those bearing *N*-methylpyridinium groups at *meso* positions, are efficient DNA cleavers when activated by an oxygen atom donor like $KHSO_5$(3). In the case of Mn-TMPyP, the high-valent manganese-oxo complex is able to hydroxylate two C-H bonds accessible from the minor groove: at C1' and at C5'. These two lesions are diagnosed by formation of 5-methylene-2-furanone (5-MF) anf furfural (FUR), respectively.

The tris-pyridiniummetalloporphyrin entity is a suitable DNA cytotoxic cleaver to be attached to a large range of vector (intercalating) agent or oligonucleotide)(4,5).

Since the work of Zamecnik and Stephenson on the inhibition of the replication of Rous sarcoma virus with a 13-mer oligonucleotide, it has been shown that HIV can be inhibited by various chemically modified oligonucleotides(6). We will report that a 3-mer containing the AUG codon of HIV-1 TAT (target = 5'-CAGAGGAGAGCAAGAAATGGAGCCAGTAGATCCTA. This DNA target corresponds to the region containing the initiation codon of TAT 35-mer = nucleotides 5360 to 5394 according to the numbering of ref. 7) is efficiently cleaved *in vitro* by a cationic manganese porphyrin complex vectorised by a 19-mer complementary of the target, Mn-trisMPyP-5'-GGCTCCATTTCTTGCTCTC. Breaks are observed at low concentrations (10 nM) and with only 2.6 molecules of the metalloporphyrin conjugate per molecule of target.

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LAICM3391C **Auditorium, Fri. 17**

THE MICROSTRUCTURE OF SOME SUPERCONDUCTING MATERIALS

M.A. Señarís, A. Várez, C. Rial López, U. Amador, Ph. Saint-Mard, F. García Alvarado, E. Morán and M.A. Alario
Departamento de Química Inorgánica Facultad de Química, Universidad Complutense.
28040 Madrid, Spain.

Real Solids, as opposed to ideal solids -the last ones only existing in books and models- are plagued by a number of defects of various types[1]. The ensemble of these defects which range from so called extended defects to local compositional variations, among others, can be included within the term *MICROSTRUCTURE*. This microstructure often controls the properties, or at least some of the properties characteristic of the solid state.

In the present communication we are going to show a few examples concerning the microstructure of several HTSC materials. We will first discuss the presence of extended defects and intergrowths produced by Li-reduction of the $(RE)Ba_2Cu_3O_{7-\delta}$ materials, where RE stands for a rare earth ion, in particular Y -when we get HTSC properties-, or Pr -when we do not get them-. We will also try to show the evolution of some electric transport properties coupled with simulation studies of the ion responsible for the ionic conductivity.

Secondly, we will consider some superconductors based in the La_2CuO_4-type structure, dealing in particular with two problems:

(*) Local compositional variations and concomitant structural ordering induced by the substitution of La by K.

(**) Structural and SC properties changes produced in the room temperature oxidation of samples of the superconducting solid solution $La_{2-x}Sr_xCuO_4$.

Finally, we will consider the microstructural changes that take place in the electrochemical oxidation of some of the bi-based HTSC materials.

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1 *COORDINATION AND BIOINORGANIC CHEMISTRY*

LAICM1428S **A, Mon. 13**

HIGH-VALENT IRON-OXO PORPHYRIN SPECIES : GENERATION AND CHARACTERIZATION OF NEW MODELS FOR PEROXIDASE COMPOUNDS I.

Raymond Weiss, Laboratoire de Cristallochimie et de
Chimie Structurale (URA-CNRS-424).
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Iron(IV)-oxo porphyrin π-cation radicals are believed to be intermediates in various oxidative pathways catalyzed by hemeproteins. Reaction of the iron(III) resting state of horseradish peroxidase (HRP) with peroxides, peracids, etc gives the so-called compound I having incorporated two oxidizing equivalents above the ferric state. The identity of HRP-I and that of chloroperoxidase compound-I (CPO-I) as oxoferryl porphyrin π-cation radicals has been established. Their iron(IV) center with an S = 1 intermediate-spin state is weakly, but antiferromagnetically, coupled to the S = 1/2 spin state of the porphyrin π-cation radical. In contrast, in the model compounds of several "doubly protected" porphyrins, the ground spin-state of S = 3/2 is indicative of ferromagnetic coupling between the iron(IV) and the porphyrin π-cation radical spins. Thus, the question is : why in the model compounds the spins are ferromagnetically coupled while in the hemeproteins they are antiferromagnetically coupled. In order to understand this question we have investigated the electronic properties of several oxoferryl π-cation radical species with β-pyrrole halogenated porphyrins and with meso-tetraarylporphyrins comprised of three mesityl moieties and one phenyl group in which the ortho positions are occupied by pivalamide, trifluoroamide, ether or other substituents. The results of these studies will be presented.

EPR AND VOLTAMMETRIC CHARACTERIZATION OF ELECTROCHEMICALLY GENERATED SCHIFF BASE NICKEL(I) AND NICKEL(III) COMPLEXES WITH CATALYTIC PROPERTIES

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The less common oxidation states of nickel, Ni(III) and Ni(I), play a vital role in the activity of some enzymes, and the possibility of using nickel complexes in these oxidation states as catalysts in reactions of activation of small molecules and in redox reactions of organic molecules has spurred great interest.

We describe the results obtained for nickel complexes with pseudomacrocyclic tetra- and pentadentate ligands obtained by Schiff condensation. These complexes provided an easy way to control : (a) the coordination sphere (number and type of coordinated atoms); (b) the size of the cavity, and (c) steric effects due to substituents in the equatorial ligand. Relationships between these parameters and oxidation/reduction of the couples Ni(II)/Ni(III) and Ni(II)/Ni(I) are reported.

Reduction of alkyl halides (methyl, *n*-butyl, *i*-butyl and *t*-butyl bromides and iodides) by Ni(I) complexes electrogenerated *in situ* were studied in acetonitrile and $(CH_3)_2SO$ and the kinetics determined. Possible activation of small molecules (H_2) by the corresponding nickel(III) complexes is also described.

LAICM1496S **A, Mon. 13**

CARBORANES AND MACROCYCLES; AN EFECTIVE COOPERATION

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LAICM1416S **A. Mon. 13**

COMPLEXING PROPERTIES OF FUNCTIONALIZED CYCLODEXTRINS

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The appropriate functionalization of cyclodextrins(CD) provides a multisite recognition system capable of improving their usefulness as catalysts, enzyme models and abiotic receptors. While unfunctionalized cyclodextrins form only so-called "second sphere complexes" with metal co-ordination compounds, chemically modified cyclodextrins with substituent groups capable of complexing metal ions have also been used to mimic metal-enzymes and separate enantiomers.

The cooperation between the complexed metal ion and the chiral CD cavity in the chiral resolution of the enantiomeric mixtures of unmodified amino acids containing aromatic side chains has been reported. In particular, the copper(II) complex of CDhm [CDhm = 6-deoxy-6-(N-histamino)-β-cyclodextrin] was used as chiral additive to the mobile aqueous phase with a conventional reverse phase column. The HPLC enantiomeric separation of either D/L-tryptophan, -phenylalanine or -tyrosine was found and we suggested that chromatographic enantioselectivity is mainly due to differential complexation in the mobile aqueous phase. The different formation constants of ternary complexes, which are larger for $[Cu(CDhm)(D\text{-}AaO^-)^+$ than for $[Cu(CDhm)(L\text{-}AaO^-)]^+$, were attributed to the orientation of the aromatic side chain with respect to the cyclodextrin cavity. These promising results prompted us to extend the study of the complexing features of cyclodextrin derivatives. Thus recently, the copper(II) complexes of b-cyclodextrins functionalized in position 6 with ethylenediamine or 2-(amino)methylpyridine or L/D-cysteine were tested as chiral eluents in LEC (ligand exchange chromatography). Chiral discrimination was shown by these CD derivatives which are able to act as abiotic receptors of aromatic amino acids.

More recently, our interest has been attracted by the possible use of the copper(II) complexes of β-cyclodextrin derivatives as SOD-mimicking compounds (SOD = Superoxide Dismutase). We report the O_2^- scavenger activity of some functionalized cyclodextrin copper(II) complexes determined by means of indirect methods. Thermodynamic and spectroscopic measurements were also carried out to find: i) the complex species existing in the experimental conditions of the experimental assay, ii) their stability, iii) the possible correlation between the catalytic activity and the co-ordination features of metal complexes

METAL COMPLEXES OF SOME TETRA-AZA MACROCYCLIC LIGANDS CONTAINING PYRIDINE

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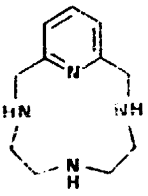
The high stability and great inertness of some metal complexes formed by 12-membered tetra-aza macrocyclic ligands have made them very important in a variety of applications, namely in medicine as diagnostic and therapy agents in Imaging Nuclear Magnetic Resonance spectroscopy (usually the Gd^{3+} complexes) or in nuclear medicine (complexes of ^{99m}Tc, ^{67}Ga, ^{111}In, ^{90}Y, ^{67}Cu) [1]. The principal ligand in this kind of applications is DOTA (1,4,7,10-tetra-azacyclododecane-1,4,7,10-tetracetic acid), which together with some of its derivatives, surpasses classic linear ligands. However, DOTA is not yet the ideal ligand as it forms complexes with similar stability with most metal ions (low selectivity), and presents slow kinetics of formation of some of its complexes [2].
Following our studies with the tetra-aza macrocyclic ligands, we carried out the synthesis of ligands containing pyridine in the ring, **1 - 4**:



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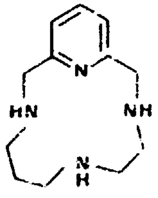
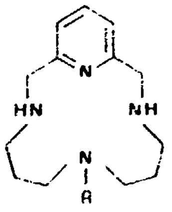


2



3 - R = H

4 - R = CH_3

We have studied the protonation of these ligands and the metal complexation with some divalent first-series transition metal ions and also Cd^{2+} and Pb^{2+}. Our studies have shown that the ligands containing pyridine have faster kinetics in metal complexation, but lower stability constants than the corresponding complexes of the tetra-aza macrocyclic ligands. Trying to understand the behaviour of these two series of metal complexes some structural studies in aqueous solution of the Ni^{2+} and Cu^{2+} complexes were made, namely electronic, NMR and EPR spectroscopies.

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LAICM1378S **A, Tue. 14**

Study of the reactivity of some ruthenium (II) and (III) complexes containing triphenylphosphine and multidentated ligands.

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Abstract

An analysis of the products obtained by the reaction between ruthenium trichloride hidrate and the anhidrous one with triphenilphosphine upon reaction conditions is presented.

The path way to obtained anionic complexes of ruthenium (II) containing triphenylphosphine is also discoused.

The synthesis and characterization of octahedral ruthenium (III) Schiff base complexes obtained from the interaction of RuCl2(PPh3)3 is discused.

Also the synthesis and characterization of a series of octahedral ruthenium (II) Schiff base complexes obtained from the interaction of RuCl$_2$(PPh$_3$)$_3$ to with N,N'-ethylenebis(5-R-salicyldeneimine) are presented.

The red-ox properties and the stability towards oxidaton of Ru(II)(5R-sal2en)(PPh3)2 complexes, (R= H-, Cl-, Br-, CH3O-, NO2-) were related to electron-withdrawing or releasing ability of the substituents in the phenyl ring of the Schiff base.
The results show that electron-withdrawing substituents stabilize Ru(II) complexes, while electron -donating groups favors the oxidation to Ru(III). The changes in E1/2 of complexes, due to remote substituents effect, could be related tochanges in basicity of the phenolic oxygen. This variation has more influence on E1/2 of the complexes than changes in basicity of the phosphorus in the phosphine ligands.

These facts allow us to predict the tendency towards oxidation of the metal in Ru (I)(sal$_2$en)(PPh$_3$)$_2$ complexes, based only in the well known Hammett constants for phenolic substituents.

The possibility to predict and modulate the redox properties of coordination compounds has proved to be useful. For ruthenium-Schiff base complexes this is significant because the catalytic activity of this type of complexes could be related to Ru(IV)/Ru(III) couple and as sugested by Lever , the results obtained for Ru(III)/Ru(II) can be extended to RU(IV)/Ru(III) couple.

Some preliminar results of hidrogenation reaction is presented.

STRUCTURAL INFORMATION FROM
^{119}Sn MÖSSBAUER SPECTROSCOPY

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The principal parameters of a Mössbauer spectrum are the Isomer Shift (IS) and the Quadrupole Splitting (QS). The IS is sensitive to the electronegativity of the atoms bonded to tin. In the case of octahedral tin(IV) halide complexes, SnX_4L_2, the IS increases linearly with decreasing electronegativity of the halogen atoms. Although there is a spread of data, the IS also decreases with increasing electronegativity of the donor atom of the ligand L. Therefore, the IS can be used to get information about the atoms bonded to tin. This is particularly useful in the case of ambidentate ligands.
The QS reflects the symmetry of the charge distribution about the tin atom, and has been widely used to distinguish between different possible isomers of tin compounds. Furthermore, the QS can be used to calculate bond distances because the Sn-X bond distances in octahedral SnX_4L_2 complexes and the partial quadrupole splitting (pqs) of the ligands are linearly related. A similar relationship has been found for $[SnCl_5L]^-$ complexes. Interestingly, the slopes of the plots d(Sn-Cl) *vs* 4pqs for $SnCl_4L_2$ and $[SnCl_5L]^-$ complexes, are in the ratio 2.6(3):1, in good agreement with the ratio 2.5:1 expected from statistical considerations.
Several isomeric pairs of cis and trans-$SnCl_4L_2$ have been characterized by Mössbauer spectroscopy, and the QS values suggest that L is a stronger donor when it coordinates in trans positions. This is supported by the crystal structures of cis and trans-$SnBr_4(Ph_3PO)_2$ which provide the first crystallographically authenticated example of cis-trans isomerism in octahedral tin (IV) halide complexes.

METALS AND NUCLEOBASES: COORDINATION CHEMISTRY AND BIOLOGICAL RELEVANCE

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The systematic study of structural and reactivity patterns of metal-nucleobase complexes provides a wealth of information equally important to the biology of metal-nucleic acid interactions and to coordination chemistry in general. Two topics meeting these criteria will be dealt with in the lecture.

(1) DNA staining. Oligomeric, mixed-valence complexes of cis-$(NH_3)_2Pt$ and pyrimidine nucleobases and related ligands ("platinum pyrimidine blues") have a high affinity for nucleic acids, a property exploited in antitumor activity tests and cytological staining experiments. Even though the nature of this interaction is not fully clear as yet, the understanding of structural aspects of the "blues" is progressing. Two advances, recently made in our laboratory, will be discussed in more detail, viz. formation of cyclic Pt_4 and Pt_8 species of underivatized uracil, and the inability of trans-$(NH_3)_2Pt(II)$ to associate to larger aggregates analogous to those of the cis-isomer.[1]

(2) Selective DNA binding. The base or sequence specific binding of a metal entity to a nucleic acid is a prerequisite for its use as a chemical probe. Two approaches for the development of metal-based probes will be presented: A Au(III) complex has been studied which reacts in a highly preferential fashion with N3 of thymine, and trans-(amine)$_2$Pt(II) modified oligonucleotides are being prepared with the aim to use them as antisense or antigene agents. Possible binding patterns have been established in model nucleobase systems.[2]

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PHOTOCHEMICAL MOLECULAR DEVICES BASED ON TRANSITION METAL COMPLEXES

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A photon is at the same time a quantum of energy and a bit of information. The interaction of light with matter can therefore be used for energy or information purposes The results that can be obtained depend on the degree of organization of the receiving matter. The simplest form of organization is that of a small number of atoms in a molecule. A higher level of organization is the assembly of a discrete number of molecular components to yield supramolecular species. Supramolecular organization can be attained by intermolecular forces or by linking together molecular components by covalent bonds. In this way it is possible to design structurally organized and functionally integrated systems (*photochemical molecular devices*)[1] capable of elaborating the energy and information input of photons to perform complex functions (light harvesting, conversion of light into chemical or electrical energy, etc.).

We are currently investigating the interaction of light with several types of supramolecular systems involving coordination compounds. In this lecture, the photochemical and photophysical properties of some of these systems will be illustrated.

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CHARACTERIZATION AND SOME ELECTROCATALYTIC PROPERTIES OF COMPLEXES WITH AZA-MACROCYCLE LIGANDS

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In the electrochemical reduction of CO_2 over metallic cathodes, the large overpotential required for driving the electrode reaction at an appropriate rate is an unquestionable technical problem which has been addressed by adding catalysts to the reaction.

Tetra- and hexa-azamacrocyclic and related complexes of cobalt and nickel have been successfully used as catalysts in electrochemical and photochemical processes.

Little is known, however, about the properties of macrocyclic compounds derived from 1,10-phenanthroline and related bases(1). Since such compounds are considered to be related to phtalocyanines and porphyrines, they potentially have interesting chemical properties for the catalytic preparations of fuels and/or the storage of solar energy.

The synthesis, characterization and properties of transition metal ion complexes with aza-cyclophanes and related ligands will de discussed in this work. In these preparations, the obtention of the compounds with good yields will be emphasized.

The nature of the redox processes has been established by electrochemical techniques. A number of them have been characterized as multiple electron transfers involving either or both the metal center and the ligand(2). The electrocatalitic reduction of CO_2 in the presence of these compounds is also shown.

The financial aid of FONDECYT/CONICYT, Project 0113/92 and DICYT/USACH, Project 8932CM is acknowledge.

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LAICM1025S **A, Thu. 16**

NEUTRAL DIVALENT TRANSITION-METAL COMPLEXES WITH THIOETHER-IMIDAZOLE-CONTAINING LIGANDS AS MODELS FOR METALLOPROTEINS

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In order to understand the mechanisms that rule the physiological behaviour of metalloproteins it is necessary to know their structures or, at least, the structure of the active site. For several decades single crystal X-ray diffraction has served as the final arbiter for biological structure determination. However, good crystals are often difficult to prepare and the resolution of the structure determination is often limited. As a consequence many inorganic chemists become involved in Inorganic Biochemistry by attempting to devise small molecule models the properties of which can be compared with those of the metalloprotein and hence provide a model compound.

In accordance with the structural, chemical, and spectroscopic characteristics, there are several types of copper(II) ions present in copper proteins, and it is known that the active sites of copper proteins for which X-ray crystal structures are available contain copper(II) bound to two or more histidine imidazole groups,[1] and it may be that the distorted geometry around the metal is of great importance in that it controls the redox properties of the particular protein. From this point of view, a logical step to synthetic models should be to design and synthesise ligands which contain one or more imidazole groups and so might impose a distorted co-ordination around the metal.

Consequently *imidazole-containing ligands* can act as versatile models for copper protein environments. Not only do they give opportunity to study Type 1 copper sites, in which a distorted metal ion environment of low symmetry is present, but also Type 2 copper sites such as that present in bovine erythrocyte superoxide dismutase where an imidazolate bridges the heterobinuclear copper-zinc pair.

To date, several cationic copper, nickel, and cobalt complexes have been synthesised from these type of ligands. We have found that an electrochemical method[2] gives a novel and facile route to the synthesis of neutral complexes by deprotonation of the corresponding ligand and oxidation of a *sacrificial electrode* (Cu, Zn, Ni, Co).

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LAICM1106S **A, Thu. 16**

SOME OPTICAL PROPERTIES OF RARE EARTH COMPOUNDS

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Some 'optical properties,based in the absorption spectra of the Neodymium(III) and emission spectra of Europium(III) compounds,in the solid state,in several conditions at various temperatures and in solution will be considered.Calculations involving spectral,crystal-field and scalar parameters,aspects related to energy transfer mechanisms and some applications will be also considered.

Financial support: CAPES, CNPq, FAPESP,PADCT.

LAICM1494S **A, Thu. 16**

REDOX PROTEINS IN ENVIRONMENTAL BIOTECHNOLOGY

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Understanding the biodegradative pathways for microbial degradation of recalcitrant organic molecules is nowadays an important task. Microorganisms evolve rapidly and, in adverse environmental condictions, develop the ability of using recalcitrant or even toxic organic molecules as source of carbon(1). Once the biodegradation mechanisms are understood one can hope to plan engineered bacteria with improved biodegradation ability, or modified selectivity, or increased resistance. These bacteria can then be used, for instance, bioremediation of polluted sites.

Biodegradation often proceeds through oxidation. There are oxidative pathways for degradation of aromatic as welle as of alifhatic compounds(1). A common initial step seems the oxygenation of the substrate by insertion of two or one oxygen atoms, respectively. Following steps involve further oxidations until carboxylic products are formed.

In most cases the initial oxygenases require electrons together with dioxygen molecules to react with the substrate. Electrons are provided by organic physiological reductants and carried to the oxygenases by iron-sulfur proteins(2). The ubiquitous presence of the latter is due to their versatility in terms of accessible redox potentials, which span more than one volt range. We are beginning to understand the molecular bases for this versatility, i.e., in more general terms, the structure-function relationships in several classes of these proteins(3,4). The insight is provided by coupling complementary information from several spectroscopic techniques. Further insight is expected from molecular dynamics and protein engineering techniques.

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NEW CHEMISTRY OF PLATINUM ANTICANCER DRUGS AND THEIR PALLADIUM ANALOGUES

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Cisplatin, cis-[$PtCl_2(NH_3)_2$], and carboplatin, [$Pt(NH_3)_2$(CBDCA)], where CBDCA is cyclobutane-1,1-dicarboxylate, are widely-used anticancer drugs.

We have used ^{15}N-edited ^{1}H and [^{1}H, ^{15}N] HMQC NMR spectroscopy to demonstrate the special role of Pt-NH H-bonding the 5′-phosphates in stabilizing nucleotide adducts of platinum anticancer complexes in aqueous solution [1]. The application of these techniques to the study of di- and tri-nucleotide GG-Pt adducts will be described.

Direct attack of 5′-GMP on carboplatin occurs without prior hydrolysis or cisplatin formation in chloride solutions [2]. The ring-opened intermediate [$Pt(NH_3)_2$(CBDCA-*O*)(5′-GMP)] has a close hydrophobic contact between the purine and CBDCA rings.

We have separated the *cis* and *trans* isomers of the metabolite [$Pt(Met)_2$] and studied the isomerization reactions in detail [3]. The *cis* isomer predominates in aqueous solution.

The palladium analogues of cisplatin and carboplatin have been synthesized, the latter by a novel route. The properties of these complexes will be described and compared with those of platinum.

We thank the MRC, SERC, Royal Society and Wolfson Foundation for support.

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LAICM1484S **A, Thu. 16**

POLYMIDAZOLE COMPLEXES MODELING THE ACTIVE SITE OF MONONUCLEAR NON-HEME IRON PROTEINS.

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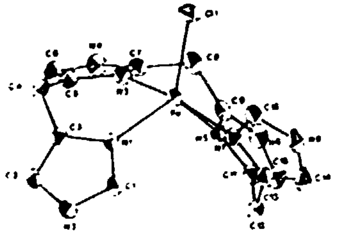
The aim of this work was to model the iron(II) part of the reaction center from *Rhodobacter sphaeroides* (RC) and the iron center of native soybean lipoxygenase (L-1). The X-ray structure of RC shows an hexacoordination by four histidines and one chelating glutamate. EXAFS and MCD studies of L-1 supported a distorted octahedral structure with 4 nitrogens in a plane and 2 oxygens occupying axial sites. Both systems exhibit very similar EXAFS features.

We synthesized the ligand bis[(imidazol-4'-methyl)-4 imidazol-2-yl] methane (TIM) to model the tetraimidazole core.

The following complexes have been fully characterized, including X-ray structure : [Fe(TIM)Cl]Cl **1** and [Fe(TIM)(OCOCH$_3$)](ClO$_4$) **2** .

1 is pentacoordinated (fig) and **2** is either penta or hexacoordinated with a chelating or monodentate acetato ligand (the two structures being *simultaneously* present in the same crystal unit cell).



1

The structure of **2** with the chelating carboxylate is very similar to that of RC. **1** in CH$_3$OH loses the chloride ligand, as shown by comparison with Fe(TIM)(ClO$_4$)$_2$ in the same solvent (NMR, Mossbauer, EXAFS). EXAFS and XANES in CH$_3$OH suggest a change from penta to hexacoordination involving two oxygen atoms and reveal a close similarity between this coordination sphere and that of L-1, in agreement with EPR similar features for the two iron (III) forms.

The different data available, *including the most recent X-ray and EXAFS results,* will be discussed in the perspective of comparing the RC and L-1 iron binding sites and the informations given by the different techniques.

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[1] This work is a cooperative project between [a]URA 400 ; [b]Bijvoet Center for Biomolecular Research Dept of Bioorganic Chemistry, Utrecht, The Netherlands ; [c]Laboratoire de Chimie de Coordination du CNRS, Toulouse.

LAICM1003P **1, Mon. 13**

SYNTHESIS AND NMR CHARACTERIZATION OF NEW AROMATIC PHOSPHORANES.

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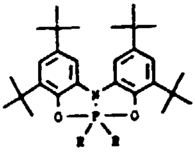
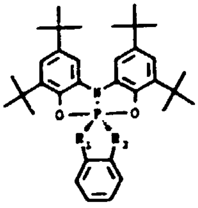
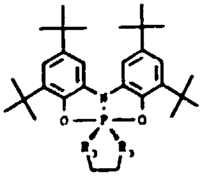
We are interested in developing the chemistry of aromatic phosphorus heterocyclic[1-2]. With this aim we have prepared and characterized by ^{1}H ^{13}C and ^{31}P NMR spectroscopy. A series of new phosphoranes with different functional groups. These compounds have a 10-P-5 bonding system. They have a tetracyclic planar arrangement. Some of the compounds have another rings perpendicular to the tetracyclic plane. These compounds are unusually stable. Substitution reaction are performed on the exocyclic phosphorus substituents.



1) $R = OCH_3$
2) $R = NHiPr$
3) $R = Cl$
4) $R = CH_3$



5) $R_1 = R_2 = O$
6) $R_1 = NH$, $R_2 = O$



7) $R_2 = O$

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LAICM1011P 2, Mon. 13

COMPLEXES OF COPPER(II) AND IRON(III) WITH SCHIFF BASES DERIVED FROM AMINOSUGARS: SPECTROSCOPIC AND ELECTROCHEMICAL CHARACTERIZATION.

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The synthesis of complexes with chiral ligands in order to be used in asymmetric organic synthesis has been a very active area of research in the last years (1,2).

In the present work spectroscopic (ir, uv-visible and Mössbauer) and electrochemical characterization of a new series of complexes prepared by the reaction of copper(II) or iron(III) salts with ligands (**L**) made by the condensation of 2-amino-2-deoxy-D-glucose or 2-amino-2-deoxy-D-galactose and 2-amino-2-deoxy-D-mannose with o-hydroxynaphthaldehyde are informed. Two distinct kind of complexes has been obtained with both metals: they show a different stoichiometry M:**L**, 1:1 and 1:2, respectively. Mossbauer spectra of 1:1, Fe:**L** complexes confirm the presence of high spin Fe(III) species.

Dimethylsulfoxide solutions of the ligands present two tautomeric equilibria: a keto-amine=enol-imine, and an anomeric one as it have been detected by ^{1}H-and ^{13}C-NMR's. The anomeric equilibrium has been confirmed by polarimetry measurements. These measurements also showed that this equilibrium disappeared upon the formation of complexes.

Copper complexes exhibited a similar electrochemical behavior in dimethylsulfoxide and dimethylformamide solutions: the reduction process lead to the irreversible formation a metallic copper. Iron(III) complexes show the formation of stable iron(II) species.

The financial aid of DICYT/USACH, Project 8932CM is acknowledged.

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LAICM1012P **3, Mon. 13**

PREPARATION AND STRUCTURE OF $[Cd(THIAMINE)Cl_3]_2.2H_2O$: A NEW COMPLEX OF CADMIUM(II) AND VITAMIN B_1

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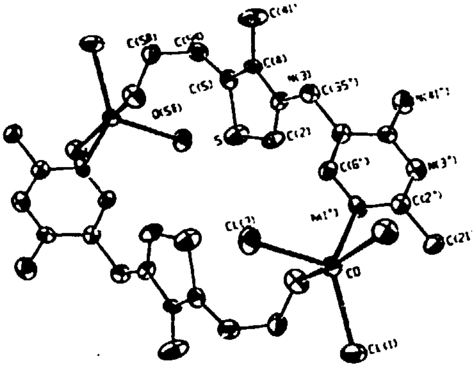
The title compound was prepared by mixing $CdCl_2.H_2O$ with previously neutralized (thiamine)Cl.HCl in a one-to-two molar ratio in water. Its structure was analyzed by X-ray diffraction. The compound is a centrosymetric dimer (see Fig)



and a "true" complex of the vitamin B_1. That is, cadmium(II) form direct bonds with the thiamine cation. As in $Cd(thiamine)Cl_3.0.6H_2O$ [1], the metal atom is coordinated to three chloro ligands and the N(1') atom of the pyrimidine ring, but an additional bond with O(5γ) from a neighbouring molecule expands the cadmium coordination number from four to five and forms the dimeric unit.

[1] R.E. Cramer, R.B. Maynard and J.A. Ibers, *J. Am. Chem. Soc.*, 1981, *103*, 76-81.

DIMETHYL[5-(2'-PYRIDINEMETHYLEN)-2-THIOHYDANTOINATO]THALLIUM(III): AN UNUSUAL CASE OF LINKAGE ISOMERISM

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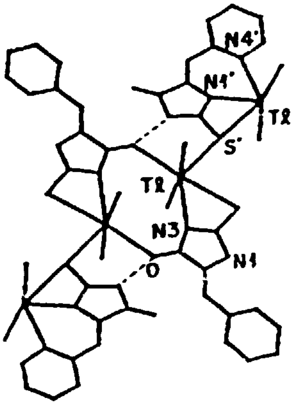
The title compound [TlMe$_2$(PyTd)] was prepared by reacting the neutral form of the ligand (HPyTd) and thallium(III) hydroxide in an aqueous:ethanol mixture.



The two [TlMe$_2$(PyTd)] molecules of each asymetric unit are linkage isomers (see Fig.). In one, the thallium atom (Tl in the Fig) is coordinated to a N(3),S-bonded ligand. In the other, the metallic center (Tl' in the Fig.) is N(1'),N(4'),S'-coordinated to the thiohydantoinate anion. In order to reach this versatile coordinative behaviour, PyTd$^-$ adopts in the complex two isomeric forms with the hydrogen atom of the remaining thiohydantoin N-H group placed at N(1) or N(3') respectively.

LAICM1016P **5, Mon. 13**

SILVER(I), PALLADIUM(II), PLATINUM(II) AND PLATINUM(IV) COMPLEXES WITH ISOOROTATE AND 2-THIOISOOROTATE LIGANDS.

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Isoorotic acid (5-carboxyuracil) is an isomer of orotic acid that exhibits pharmacological properties. In previous papers, we have reported structural and biological studies on several complexes of isoorotato and 2-thioisoorotato ligands mainly with first row transition metal ions. This work describes the results obtained from the study of complexes of isoorotic (H_3CU) and 2-thioisoorotic (H_3CTU) acids with Ag(I), Pd(II), Pt(II) and Pt(IV) ions. Thus, twelve new complexes containing the orotic derived ligand in either monoanionic (H_2L^-) or dianionic ($HL^=$) form have been isolated and studied by conductivity measurements, infrared and nuclear magnetic resonance spectroscopies and thermal methods (TG and DSC). From experimental data, tentative molecular structures are suggested for some of these complexes:

COMPOUND	METAL-LIGAND BINDING SITES
$Ag(H_2CU)$	$Ag_2(O4,O5)_2$
$Ag_2(HCTU)$	...Ag[(S2,N1)(O4,O5)]Ag...
$Ag(H_2CU)(H_3CU)\cdot py$	$[Ag(O4,O5)_2py]$
$Pt(H_2CU)_2\cdot 4NH_3$	$Pt(O4,O5)_2$
$Pt(HCU)\cdot 4NH_3$	*cis*-$[Pt(O4,O5)(NH_3)_2]$
$Pt(HCTU)\cdot 2NH_3\cdot 2H_2O$	...Pt[(S2,N1)(O5,O5')]Pt...
$PtCl_2(H_2CU)_2\cdot 4NH_3$	*trans*-$[PtCl_2(O4,O5)_2]$
$PtCl_2(HL)\cdot 4NH_3$	...(N1)]$Cl_2(NH_3)$Pt[(O4,O5)(N1)]...
$PtCl_2(HCTU)\cdot 2H_2O$	...(S2)]$Cl_2(H_2O)$Pt[(O5,O5')(S2)]...

Also, the antimicrobial activity of these compounds against several bacteria and yeast has been assayed, being noticeable that $PdCl(H_2CU)\cdot py$ complex is active against *Pseudomonas sp* and *Micrococcus sp* at CMI values lower than 50 $\mu g\cdot ml^{-1}$.

LAICM1030P **6, Mon. 13**

EMF and CALORIMETRIC STUDY on H^+/1,10-PHENANTROLINE and H^+ / 2,2'-BIPIRIDYL SYSTEM (0.5 M NaCl, 25 °C).

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While 2,2'-bipyridyl base (B) only form with H^+ the HB^+ complex, there is enough evidence that 1,10-Phenantroline (C) forms beside HC^+, the HC_2^+ specie in aqueous solutions[1].

In this work we study the H^+ /1,10-phenantroline and H^+ / 2,2'-bipyridyl equilibria by emf (glass electrode) and calorimetric measurements in 0.5 M NaCl as ionic medium at 25 °C.

The following table shows the results obtained by application of LETAGROP[2] to the experimental data.

	log β	ΔH° kcal	ΔS° e.u.
$H^+ + B \Leftrightarrow HB^+$	4.34(2)	3.6(1)	7.9(4)
$H^+ + C \Leftrightarrow HC^+$	4.794(4)	-4.3(1)	7.5(4)
$H^+ + 2C \Leftrightarrow HC_2^+$	6.38(3)	-7.4(6)	4(4)
$H^+ + B + C \Leftrightarrow HBC^+$	5.57(7)	-6.1(3)	5(1)
$C + HC^+ \Leftrightarrow HC_2^+$	1.58(2)	-3.1(3)	-3(1)
$B + HC^+ \Leftrightarrow HBC^+$	1.23(5)	-2.6(3)	-3(1)

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LAICM1031P **7, Mon. 13**

EMF STUDY on the COMPLEX FORMATION of ETHYLENEDIAMINE-N,N,N',N'-TETRAACETIC ACID with VANADIUM(V) in 0.5 M NaCl MEDIUM at 25 °C.

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The system $H^+/VO_3^-/H_2C^{-2}$ (H_4C = Ethylenediamine-N,N,N',N'-Tetraacetic Acid, EDTA) was studied by emf (glass electrode) measurements in 0.5 M NaCl as ionic medium at 25 °C, covering the following pH and total concentration ranges: pH = 2 - 9, V(V) and H_2C^{-2} = 5 - 10 (mM)[1].

The data were treated by using LETAGROP[2], according to the reactions:

$$p\,H^+ + 1/q\,(VO_3^-)_q + r\,H_2C^{2-} \Leftrightarrow H_p(VO_2)C_r^{p-3} + H_2O$$

The equilibria analysis indicated the following complexes and stability constants:

(p,q,r)		log β_{pqr} (3σ)
(0,1,1)	VO_2C^{3-}	8.83(1)
(1,1,1)	HVO_2C^{2-}	12.66(1)
(2,1,1)	$H_2VO_2C^-$	15.791(9)

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LAICM1032P **8, Mon. 13**

THERMOCHEMISTRY of REACTIONS in SOLUTIONS.

2. A Thermochemical Study of Hydrolyzed VO_2^+ Solutions (0.5M, NaCl 25°C).

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The enthalpy and entropy changes for the formation of $V_4O_{12}^{4-}$ and the dekavanadate ions $H_xV_{10}O_{28}^{(6-x)-}$, x = 0, 1, 2, 3, from hydrolyzed VO_2^+ solutions in 0.5 M NaCl medium at 25 °C have been determined by means of enthalpy titrations, covering the following pH and total concentration ranges: $1 \leq pH \leq 6.5$ and $0.020\ M \leq V \leq 0.050\ M$ [1].

The experimental data were treated by means of LETAGROP[2], according to the reaction scheme:

$$q\, VO_2^+ + p\, H_2O \Leftrightarrow (OH)_p(VO_2)_q^{p-q} + p\, H^+$$

The following results were obtained:

	ΔG°pqr	ΔH°pqr	ΔS°pqr
$V_4O_{12}^{4-}$	24.3(3)	45.6(4)	71(2)
$V_{10}O_{28}^{6-}$	24.0(1)	28(5)	13(8)
$HV_{10}O_{28}^{5-}$	15.7(3)	33.1(3)	58(2)
$H_2V_{10}O_{28}^{4-}$	11.3(9)	33.7(7)	75(5)
$H_3V_{10}O_{28}^{3-}$	8.7(9)	32.0(8)	78(6)

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LAICM1033P **9, Mon. 13**

SPECTROPHOTOMETRIC STUDY of the AXIAL COMPLEXES of ms-(p-SULFOPHENYL)PORPHINE-Co(III) with PYRIDINE, 4-PICOLINE, IMIDAZOLE and OH$^-$ in 1 M NaClO$_4$ MEDIUM at 25 °C.

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The systems H$^+$ / CoP / L (CoP = ms-IV(4-sulfophenyl)porphine, L = pyridine, 4-picoline and imidazole) were studied by spectrophotometric measurements (400-450 nm) in 1 M NaClO$_4$ as ionic medium at 25 °C, using the following pH and total concentration ranges: $5 \leq pH \leq 11$, CoP 4 µM and $8 \leq L \leq (mM) \leq 55$ [1]. The data were treated by using LETAGROP[2] according to the reaction scheme:

$$p\,H^+ + q\,CoP^{3-} + r\,L \Leftrightarrow H_p(CoP)_qL_r^{p-3q}$$

The equilibria analysis indicated the following complexes and stability constants (log β (3σ)):

(p,q,r)		Pyridine	4-Picoline	Imidazole	OH$^-$
(0,1,1)	CoP.L	6.54(1)	6.97(1)	7.93(1)	
(0,1,2)	CoP.L$_2$	11.84(1)	12.63(1)	14.02(1)	
(-1,1,0)	CoP.OH				-6.91(3)
(-2,1,0)	CoP.(OH)$_2$				-16.68(5)

References.

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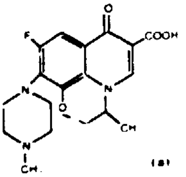
LAICM1039P **10, Mon. 13**

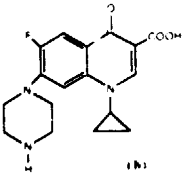
INTERACTION OF CIPROFLOXACIN AND OFLOXACIN WITH POLIVALENT CATIONS

B. Macías Sánchez*, M. Martinez Cabarga, A. Sánchez Navarro** and A. Dominguez-Gil Hurlé**.** (*) Dpto. de Química Inorgánica. (**) Dpto. de Farmacia y Tecnología Farmcéutica. Facultad de Farmacia. Universidad de Salamanca.

Several authors have reported on the interaction between quinolenes and antacids or other drugs which include cations as Al^{3+}, Mg^{2+}, Fe^{2+} or Ca^{2+}. A decrease in the amount of quinolone absorbed after its simultaneous oral administration with the above mentioned cations have been found. In spite of the large number of papers published about this subject, the mechanism of the interaction remains unclear. The aim of the present study is to insight in this interaction from a chemical point of view, in order to extend the conclusions to the reactivity in the gastrointestinal tract under similar experimental conditions. Ofloxacin (**a**) and ciprofloxacin (**b**) have been choosen as quinolones to be studied because they show important differences about its absorption characteristics, either in the absence or the presence of cations.



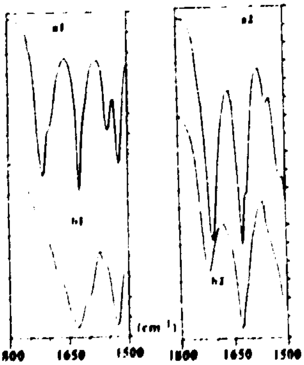
(a)



(b)

Despite the structural analogy between these two molecules, the reactivity with these cations is rather diffrent. Carboxylates are formed with ofloxacin, these salts being more soluble than the quinolone itself, due to its strong ionic character. However, ciprofloxacin does not form salts or non-absorbable complexes with metallic cations, although a crystalline material is formed. Experimental results using FT-IR and ^1H NMR spectroscopies, mass spectrometry and X-ray diffraction indicate that the carboxylic group is unreacted.

FT-IR spectra (1800-1500 cm^{-1}) have been included in the figure: profile **a1** corresponds to starting ofloxacine and **b1** to the solid residue isolated after reaction with different metal cations; **a2** corresponds to starting ciprofloxacin and **b2** to the solid residue isolated after reaction with different metal cations This new product, more stable than the corresponding metallic salts, does no contain any metallic cation.



LAICM1042P **11, Mon. 13**

WATER EXCHANGE REACTIONS ON $[M(CH_3NH_2)_5H_2O]^{3+}$ (M = Co(III), Cr(III), Rh(III) COMPLEXES. ACTIVATION PARAMETERS AND MECHANISTIC IMPLICATIONS

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Following our interest on the reaction mechanism of aminated transition metal complexes we have studied the water exchange reaction

$$[M(CH_3NH_2)_5(H_2{}^{17}O)]^{3+} + H_2O \longrightarrow [M(CH_3NH_2)_5(H_2O)]^{3+} + H_2{}^{17}O$$

The complexes have been prepared in isotopically ^{17}O enriched water and the reactions have been followed using ^{17}O NMR at variable temperature and pressure [1]

From these variable temperature and pressure studies the activation parameters $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta V^{\ddagger}$ have been obtained These. combined with previous data from anation reactions of these complexes [2] enables us to establish the nature of the intimate mechanisms operating for these substitution reactions For M = Cr an associatively activated mechanism seems to operate. while for M = Rh the trend becomes more dissociative

Comparison of $\Delta V^{\ddagger}$ with those for the corresponding ammine complexes. supports a shift towards a more dissociatively activated mechanism as the steric hindrance of the amine ligands increases

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References

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LAICM1043P **12, Mon. 13**

TEMPERATURE, pH, AND PRESSURE DEPENDENCE OF THE OUTER-SPHERE ELECTRON TRANSFER-REACTIONS OF PENTAAMMINE-PHOSPHATOCOBALT(III) TYPE COMPLEXES.

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Continuing our studies on the steric and electronic effects that affect the reactivity and reaction mechanisms of 'simple' transition metal complexes' we have studied the following outer-sphere redox reaction:

$$[Co(NH_3)_5X]^{n+} + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + Co^{2+} + NH_3 + X^{m-}$$

where X^{m-} represents the oxoanions derived from the PO_n, P_2O_7, and P_3O_{10} groups.

Outer-sphere redox reactions are multi-step processes that imply the formation of an intermediate encounter-complex undergoing the rate-determining electron-transfer. We have chosen $[Fe(CN)_6]^{4-}$ as reducing agent because it enables the total separation of these processes represented by *K* and *k* in the derived rate law:

$$k_{obs} = \frac{kK[[Fe(CN)_6]^{4-}]}{1 + K[[Fe(CN)_6]^{4-}]}$$

The thermal and pressure activation parameters for these series of reactions have been determined. A correlation between the electronic and steric nature of the phosphorous oxoanions has been established.

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LAICM1047P 13, Mon. 13

THE SYNTHESIS OF LANTHANUM 6-MOLYBDOMETALLATES

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Heteropoly compounds form a wide variety of coordination compounds, as acids or salts, where one or more central ions coordinate each other in a tetrahedral or octahedral way by octahedrical groups, MoO_6 or WO_6, forming a compact structure named heteropoly anion.

In Anderson-Evans-Perloff's structure ($X\ Mo_6O_{24}H_6$) the six hidrogen atoms bond to oxygen atoms of central octahedron; the central atom could be Al, Cr, Fe, Co, Ga and Rh in oxidation state (III), or Co, Ni and Cu in state (II).

The synthesis of lanthanum salts was made by interaction of ammonium hexamolibdochromate or hexamolibdocobaltate and the stoichiometrically double of lanthanum chloride in aqueous media, by means of the following reaction:

$$X\ H_2O + (NH_4)_3|XMo_6O_{18}(OH)_{16}| + LaCl_3 \longrightarrow La|XMo_6O_{18}(OH)_{16}|\cdot x\ H_2O + 3NH_4Cl$$

The contents of lanthanum, the central atom, as well as molybdenum and water, in the compounds $La|CrMo_6O_{18}(OH)_{16}|\cdot 11\ H_2O$ and $La|CoMo_6O_{18}(OH)_{16}|\cdot 10.5H_2O$ were analysed by standard techniques.

The infrared spectra shows the characteristical vibrations of X-O, Mo-O, Mo-O-Mo and O-M bonds.

Also a thermal analysis was made, which confirmed the different nature of lost water, the "amorphization" of the sample as water was loosing, the recristalization and formation of new cristalline phases.

LAICM1048P **14, Mon. 13**

PREPARATION AND CHARACTERIZATION OF TRINUCLEAR IRON(III) CARBOXYLATE COMPLEXES.

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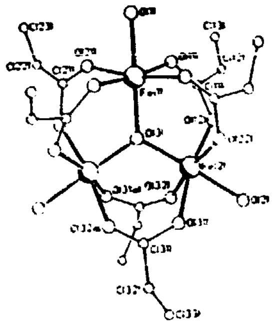
There are few metallic clusters complexes that have yielded more information on the parameters which govern stability within metal-ligand aggregates than the structural variations shown by the triangular μ-oxo centred species $|M_3^{III}O(RCO_2)_6(L)_3|X$. The complexes are able to form with a wide range of metals, carboxylic acids and capping ligand. The flexibility also extend to being able to produce mixed-metal species, as well as to redox chemistry which allow the synthesis of mixed-valence species.



In this work we report new complexes from iron acrylate and crotonate, with water as ecuatorial ligand, with 2,3,4-picoline and 2,3,4-bromopyridine and the mixed metal crotonate complex $|Fe_2CoO(C_4H_5O_2)_6(py)_3|$.

The reactions were carried out with chloroform as solvent and mixing the reactives directly. The reactions with 3-picoline and 3-bromopy yield new complexes with the organic molecule as end ligand from the two procedures, but the another reactions give the complexes in absence of solvent. The metal-mixed complex has been prepared dissolving the aquo complex in pyridine followed by the addition of diethyl ether.

The IR spectra of all complexes show the presence of bridge carboxylates and the bands assigned to pyridine derivatives are shifted in accordance with the new Fe-N bond. The electronic spectrum of the mixed complex confirms the presence of Co(II) octahedrally coordinated. The Fab Mass spectra of the complexes confirm that the basic trinuclear structure remains.

We thank the Dirección General de Investigación Científica y Técnica (Spain) for financial support (project PB90-0227-C02-01).

LAICM1049P **15, Mon. 13**

LEAD(II) COMPLEXES WITH DIAZA AND TETRAAZA LIGANDS CONTAINING TRIAZOL GROUP.

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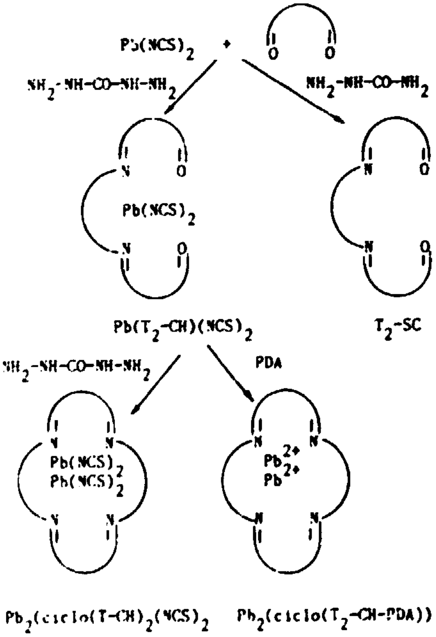
Pilar Souza, Ana Matesanz, Vicente Fernández, Universidad Autónoma de Madrid, Departamento de Química, Cantoblanco. 28049-Madrid, España.

Starting from the results of our previous studies on Schiff-bases, the relationships between the structure and the properties of some carbohydrazones have been investigated because these substances raise interesting structural problems and they have numerous applications.

In the present communication we describe the reactions between 3,5-diacil-1,2,4-triazol and the diammines: thio- and semicarbazide, thio- and carbohydrazide and the role of $Pb(NCS)_2$ as template. Same compounds obtained show their ability of reaction against other diammine molecule to make macrocyclic complexes as show in the scheme. The isolated products were characterized by elemental analyses, melting points, i.r., uv-v., ^1H NMR and mass spectrometry.

We thank the Dirección General de Investigación Científica y Técnica (España) for financial support (PB90-0227-C02-01).



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LAICM1050P **16, Mon. 13**

A CALORIMETRIC STUDY OF THE Ni(II)-5'GMP AND 5'IMP SYSTEMS. A BASE STACKING STABILIZATION.

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The interactions of metallic ions with nucleotides are of great interest owing to the role of metals in the metabolic and carcinogenic processes. In the last decade, new structures of metal-nucleoside complexes have been studied and novel modes of binding illustrated (1). Complexes of purine nucleotides of the type cis $M(NMP)_2$ with 3d metals are known. In a previous calorimetric study (2), the interaction of Ni(II) with 5'AMP was studied.

We present a solution calorimetric study at physiological pH in a wide range of nucleotide concentration (between 3mM and 12mM) for the the Ni(II)-5'GMP and 5'IMP systems, in order to determine the K_2 constant and enthalpies of the following processes:

$$\mathrm{Ni(II)} + \mathrm{NMP}^{2-} = \mathrm{Ni(NMP)} \qquad K_1 \text{ and } \Delta H_1$$

$$\mathrm{Ni(NMP)} + \mathrm{NMP}^{2-} = [\mathrm{Ni(NMP)}_2]^{2-} \qquad K_2 \text{ and } \Delta H_2$$

The values at 25ºC suggest that the stacking interactions, assigned tentatively as ΔH_2-ΔH_1, follow the order AMP> GMP>IMP as it was known by other experimental methods (1,2).

NMP	ΔH_1	ΔS_1	$\log K_2$	ΔH_2	ΔS_2	ΔH_2-H_1
	kJ/mol	e.u.		kJ/mol	e.u	kJ/mol
AMP	-10.0	15	2.34	-21.6	-28	-11.6
GMP	-14.2	20	2.04	-19.2	-25	-5.0
IMP	-12.6	15	-	-	-	-

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LAICM1051P **17, Mon. 13**

NEW OCTAMOLYBDATES CONTAINING ORGANIC BASES CO-ORDINATIVELY BOUND TO MOLYBDENUM.

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Polyoxometalate chemistry includes the study of compounds that are unique because of their topological and electronic versatility and their relevance to several disciplines.

While many octamolybdates of organic bases are known, where the organic base is bonded to $[Mo_8O_{24}]^{-4}$ anion by a hydrogen bond, only two octamolybdates containing an organic base co-ordinatively bound to molybdenum have been decribed (1,2).

In this communication we report new octamolybdates containing imidazole (Him), 1-methyl-imidazole (1-mim) or 2-methylimidazole (2-min), namely $[H_2\ im]_2\ [Mo_8O_{24}\ (Him)_2]$ 1, $[NH_2Me_2]_4\ [Mo_8O_{24}\ (Him)_2]\cdot 3H_2O$ 2, $[1\text{-}Him]_4\ [Mo_8O_{24}\ (1\text{-}mim)_2]\cdot 2H_2O$ 3 and $[2\text{-}Hmim]_4\ [Mo_8O_{24}\ (2\text{-}mim)_2]\cdot 3H_2O$ 4. Compounds 1 and 3 were prepared by the reaction between molybdenum trioxide and imidazole or 1-methyl-imidazole in aqueous medium, whilst 2 and 4 were synthesized by reaction of molybdenum trioxide with imidazole or 2-methyl-imidazole in dmf-H_2O (dmf = dimethylformamide). The compounds have been characterized by elemental analysis, infrared and ^1H and ^{13}C NMR spectroscopies and thermal measurements. The structures of compounds 2 and 3 were determined by X-ray crystallography and showed that both anions are composed of two $NMoO_6$ and six MoO_6 edge-sharing octahedra. The Mo-N and Mo-O bond strengths of both compounds have been calculated.

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CRYSTAL STRUCTURES OF As, Sb AND Bi N,N-DIETHOXYDITHIOCARBAMATE COMPLEXES

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U.Casellato - C.N.R. - ICTIMA - Corso Stati Uniti - Padova (Italy)

Previous studies on complexes of V Group elements with diethyldithiocarbamate ligand have shown different coordination geometries [1]. We report here the crystal structures of the As, Sb and Bi complexes with N,N-diethoxydithiocarbamate (L) [2]

AsL_3, $C_{15}H_{30}N_3O_6S_6As$: triclinic, P$\bar{1}$, a = 8.346(3), b = 11.580(3), c = 15.01[illegible](4)Å, α = 88.62(3), β = 74.44(3), γ = 87.73(3)°. The structure was refined to the final R of 0.056 based on 2820 observed reflections.

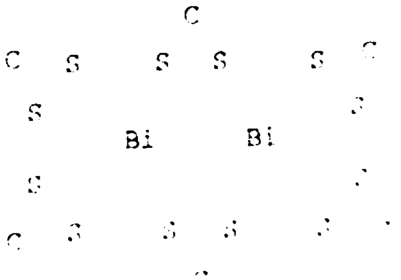
SbL_3, $C_{15}H_{30}N_3O_6S_6Sb$: triclinic, P$\bar{1}$, a = 9.973(3), b = 11.113(3), c = 12.489(4)Å, α = 104.23(3), β = 75.06(3), γ = 85.71(3)°. The structure was refined to the final R of 0.028 based on 3062 observed reflections.

Bi_2L_6, $C_{30}H_{60}N_6O_{12}S_{12}Bi_2$: monoclinic, $P2_1/c$, a = 11.172(3), b = 21.451(3), c = 22.264(4)Å, β = 98.26(3)°. The structure was refined to the final R of 0.062 based on 4100 observed reflections. Two independent molecules of the dimeric compound are present in the asymmetric unit.

The coordination polyhedron in AsL_3 can be described as a distorted trigonal antiprism. Each bidentate ligand is strongly coordinated through the negatively charged sulphur atom [2.33-2.35Å] and forms a relatively weak bond with the other [2.82-2.85Å]. The three strong As-S bonds are nearly at right angles to one another.

The higher atomic dimensions of Sb allows all the six S atoms of the ligands to form comparable coordination bonds with the central ion with small but significant differences between the S atoms of the same ligand. All distances are in the range 2.46 - 2.85Å. The resulting coordination polyhedron is close to a very distorted pentagonal pyramid.

Bi_2L_6, consists of centrosymmetric binuclear molecules where two ligands are chelated to the same ion whereas both S atoms of the third ligand are bridged. Each Bi ion is 8-coordinated and the closest description of the stereochemistry is that of a distorted dodecahedron. The Bi-S(bridged) bonds [3.07-3.14Å] are significantly longer than the others [2.67-2.84Å]



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LAICM1064P **19, Mon. 13**

REMARKS ON RELATIVE CONFORMATION OF THE IMINODIACETATO-COPPER(II) CHELATE RINGS IN COMPLEXES WITH N-HETEROCYCLE SECONDARY LIGANDS.

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Structural, spectral and/or magnetic interest have promoted studies of a variety of mixed-ligand copper(II) complexes with iminodiacetate(2-) ion (IDA) and water or imidazole (ImH) or 4,4'-bipyridine (4,4'-bipy) as secondary ligand. In an attempt to rationalize the nearly perpendicular or coplanar five membered Cu(II)-IDA chelate rings, the compound (2,2'-bipyridine)(iminodiacetato)copper(II) hexa hydrate was prepared and characterized by X-ray crystallography. The crystal consists in asymmetric dinuclear entities $[Cu(IDA)(2,2'\text{-bipy})]_2$ and uncoordinated water molecules. Both Cu(II) atoms exhibit similar flattened square pyramidal coordination. Two interactions between each Cu(II) atom and one O atom from the IDA ligand which chelates the second one make up the dinuclear entity.

The available structural data reveal that complexes with one N-heterocycle per Cu(II) atom have a rather short Cu-N(IDA) bond (<2.000Å) and nearly perpendicular Cu-IDA chelate rings. In contrast, complexes with two N-heterocycle donors per Cu(II) atom have nearly perpendicular Cu-IDA chelate rings but a rather long Cu-N(IDA) bond (>2.000Å).

LAICM1065P **20, Mon. 13**

(N-CARBOXYMETHYL-D,L-THREONINATO)(IMIDAZOLE)COPPER(II): SYNTHESIS, PROPERTIES AND CRYSTAL STRUCTURE.

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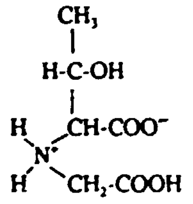
The reaction of N-carboxymethyl-D,L-threonine (H_2CMT) with $Cu_2CO_3(OH)_2$ and imidazole (ImH, 50% in excess) as well as the equimolar addition of ImH to $[Cu(CMT)(H_2O)]$ in aqueous solution yield blue crystal of a new ternary complex. The compound has been characterized by elemental analysis, thermal and spectral methods and X-ray crystallography.



H_2CMT

Analytical data gives the formula $[Cu(CMT)(ImH)]$. The compound is stable under 200°C an decomposes pyrolitically to CuO at 200-457°C. The IR spectrum shows the characteristic bands of carboxylate (CMT) and N-H (CMT and ImH) groups. The d-d band in electronic spectrum has a $\bar{\nu}_{max}$=15.725 cm^{-1}. The ESR spectrum is axial of "reverse" type ($g_\parallel=2.06<g_\perp=2.20$) but with lowest g value>2.05. The crystal of this compound is orthorhombic, space group Pbca. The iminodiacetate skeleton of tridentate CMT (with two nearly coplanar chelate rings) and the hydrogen-free N atom of ImH define the square base of the very flattened pyramidal Cu(II) coordination, which is achieved with the oxygen atom of the CMT side chain from one adjacent complex unit. Both ImH and CMT N-H bonds are involved in hydrogen bonding interactions with two different complex units.

LAICM1066P **21, Mon. 13**

COPPER(II) COMPLEXES WITH N-CARBOXYMETHYL-D,L-THREONINE.

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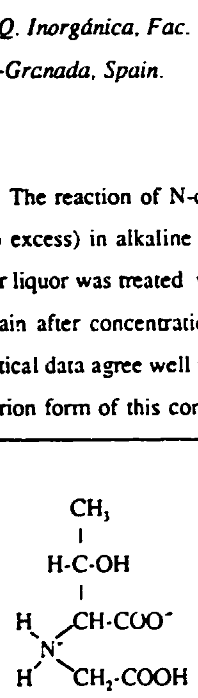
The reaction of N-carboxymethylation of D,L-threonine with chloroacetic acid (100% excess) in alkaline aqueous solution has been carried out. Partially desalinized mother liquor was treated with Amberlite-IR 120(H) in acid form and eluted with water to obtain after concentration the free acid N-carboxymethyl-D,L-threonine (H_2CMT). Analytical data agree well with the anhydrous amino-diacid. Its IR spectrum reveals the zwitterion form of this compound in solid state.



H_2CMT

A series of solutions of H_2CMT with and without Cu(II) nitrate have been titrated (I=0.1M KNO_3, 25°C) against CO_2-free KOH 0.1 M. The poten-tiometric data are actually subjet of computer calculations to fit the best complex formation equilibria for the H_2CMT/Cu(II) system in solution state.

The reaction H_2CMT with $Cu_2CO_3(OH)_2$ in 2:1 molar ratio under vacuum yield blue crystal of $[Cu(CMT)(H_2O)]$, as deduced by the available data of elemental and thermal analysis, as well as IR, reflectance and ESR spectra: Loss of H_2O at 140-175°C, "reverse" axial ESR spectrum ($g_\parallel$=2.06, $g_\perp$=2.19) and $\tilde{\nu}_{max}$=14340 cm^{-1} for the d-d band in electronic spectrum.

LAICM1067P **22, Mon. 13**

DNA-BINDING AND ANTITUMORAL STUDIES ON CIS-DICHLORO-PALLADIUM(II) COMPLEXES WITH MESO-2,3-DIAMINOSUCCINIC ACID AND ITS DIETHYL ESTER.

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Complex formation equilibria of cis-dichloro(meso-diamino-succinic acid)palladium(II) and cis-dichloro(meso-diamino-succinate diethyl ester)palladium(II) have been studied in aqueous solution with high and low chloride ion concentrations. The formations constants were carried out with potentiometric data (E(Cl^-) and/or E(H^+), I=0.15M ($NaCLO_4$), 25°C) with the SUPERQUAD program. This results were applied to explain several biochemical and biological results. Both palladium(II) complexes induce conformational changes in calf thymus DNA and also in the covalently closed circular form of pUC8 plasmid (*E. coli*). The antitumor activity "in vitro" against MDA-MB 468 and HL-60 human cancer cells have been studied. Both palladium(II) complexes have a citotoxicity superior to that of K_2PdCl_4 and the free diaminoacid ligands, but lower than the model anticancer drug cis-$[PtCl_2(NH_3)_2]$.

LAiCM1068P **23, Mon. 13**

OBSERVATION ON THE LIGATING ABILITY OF 2- AND 4-METHYL-IMIDAZOLE AGAINST THE IMINODIACETATO-COPPER(II) COMPLEX UNIT. MOLECULAR AND CRYSTAL STRUCTURE OF THE "REMOTE" ISOMER IMINO-DIACETATO(5-METHYL-IMIDAZOLE)COPPER(II) MONOHYDRATE

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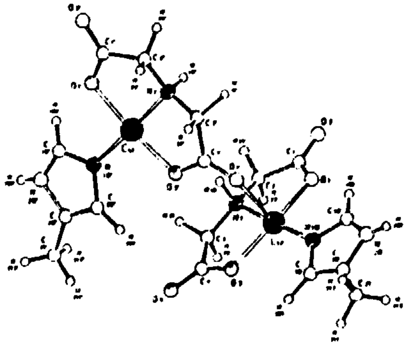
Diaqua(iminodiacetato)copper(II), I = [Cu(IDA)(H_2O)$_2$] reacts with imidazole (ImH) and 2-methyl-imidazole-(2MeImH) to give mixed-ligand complexes with 1:1:1 and 1:1:2 Cu(II)/IDA/ImH or 2MeImH ratios. In clear contrast, the diaqua complex I reacts with 4MeImH (even in excess) only to gives the 1:1:1 related ternary compound. The structural analysis reveals that this compound indeed contains uncoordinated H_2O and the "remote" tautomer complex [Cu(IDA)(5MeImH)] with 5MeImH instead of the "adjacent" tautomer 4MeImH (see figure). The crystal of [Cu(IDA)(5MeImH)].H_2O contains zig-zag chains of this complex with the Cu(II) atom in a flattened square base pyramidal coordination (type 4+1). The available structural, thermal, spectral (IR,NIR-Vis-UV) and magnetic (ESR,μ_{eff}) data suggest that the restricted coordinating ability of 4MeImH against the Cu(II)-IDA unit is due to its tautomeric possibility (which is absent in both ImH and 2MeImH ligands).



LAICM1072P **24, Mon. 13**

DNA INTERACTION AND PRECLINICAL STUDIES OF DIFFERENT Pt(II) COMPOUNDS

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A new series of Pt(II) complexes containing the amino-pyrrolidinic ring and different alkyl groups substituting positions 1 and 2 have been synthesized and studies *in vitro* against RecA$^+$ and RecA$^-$ *E. coli* strains show damage to bacterial DNA and participation of RecA protein in the repair system. Cytotoxicity against L1210 leukemia cells and antitumoral activity on BDF$_1$ male mice bearing L1210 leukemia cells have been carried out. Results from these studies show that these compounds are in the range of cisplatin and carboplatin with the existence of a real antitumoral activity (Table 1).

Table 1. Preclinical studies with different Pt(II) compounds

Product	Viability *E.coli* IC$_{50}$ (µM)		Cytotoxicity IC$_{50}$(µM) L1210	Antitumoral activity BDF$_1$ mice L1210	
	RecA$^+$	RecA$^-$		DL$_{50}$	T/C 100
cisplatin	79.0	17.05	23.0	17.8	164-229*
M-9(Met)	428.14	5.98	78.0	58.0	---
M-9(Et)	1649	57.08	91.0	64.0	167
E-9(Met)	268.4	17.89	98.0	82.7	186
E-9(Et)	672.92	35.57	113.0	117.4	182
carboplatin	>2693	606.0	142.0	117.5	150
HSP-10	----	----	3.0	13.2	200*

* references data.

The CD study of DNA adducts of these series of compounds has allowed the establishment of correlations between their biological activity and the mechanism of interaction to DNA. The CD spectra of the adducts of other Pt(II) complexes with ligands of biological interest, such as amino acids, related compounds or mercaptopurines may be used to predict a possible biological activity.

LAICM1074P **25. Mon. 13**

CYSTINE AND OTHER DITHIO-MOLECULES Pd(II) AND Pt(II) COMPOUNDS. STRUCTURE AND SPECTROSCOPIC PROPERTIES

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The nephrotoxicity of cisplatin is well-know and it is a very important handicap in the use of other Pt(II) drugs. A number of nucleophilic agents, mainly sulphur nucleophiles, have been shown to inhibit these toxic effects[1]. The interaction of cisplatin with several sulphur compounds such as methionine, penicillamine, glutathione, has been studied in recent years by many research groups[2].

To elucidate the mechanisms involved in the toxicity inhibition we studied the behaviour of Pt(II) complexes containing two ligands with -S-S- bonds, dithiosulfiram, (tetraethyldithiouram) and cystine which are able to be used as inhibitors. The study has been extended to the interaction of Pd(II) with both molecules.

In the case of Pd(II) the reaction of $K_2[PdCl_4]$ with cystine (cyt) yields two types of compound: $[Pd_2Cl_2(OH)_2cyt)]$ and $[PdCl(OH)(cyt)_2]$. The first is an orange solid which, in excess of cystine, becomes the second which is a yellow solid. This can also be obtained directly when the cystine:Pd ratio is 2:1. The Pt(II) ion forms only one type of compound, characterized as $[PtCl(OH)(cyt)]$ in which the sites of binding to the metal seem to be one NH_2 group and one sulphur atom. The reactivity of the compounds with 5'-GMP was assayed. Binary and ternary compounds were characterized by elemental analysis, IR and NMR spectroscopies.

The reactions of dithiosulfiram (DTS) with $K_2[MCl_4]$, where M= Pd(II) or Pt(II) gave the compounds$[Pd(OH)_2DTS]$, $[Pd(DTS)_2](OH)_2$ and $[PtCl_2DTS]$. All have been studied by ^{1}H and ^{13}CNMR spectroscopies. The first compound was recrystallized in chloroform giving orange crystals which were studied by X-ray diffraction. It was observed that the -S-S bridge is broken and the two molecules of the thiocarbamate derivative are bound to the Pd(II) by the equivalents sulphur atoms. The reactivity of the compounds with nucleobases such as guanine and 5'-GMP was also assayed.

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LAICM1078P **26, Mon. 13**

SYNTHESIS, CHEMICAL CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NOVEL μ-(OXALATO-O,O,O',O')BIS[BIS(OXALATO-O,O')-NICKELATE(II)] ANION

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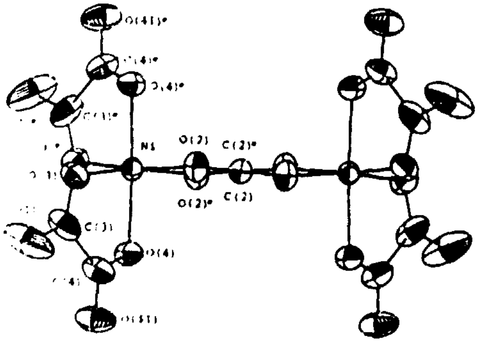
A new dinuclear nickel(II) complex of formula $(H_3dien)_2[(ox)_2Ni\text{-}(ox)\text{-}Ni(ox)_2].12H_2O$ (dien = diethylenetriamine; ox^{2-} = oxalate anion), has been synthesized by adding diethylenetriammonium chloride on an aqueous solution of $K_2C_2O_4.H_2O$ and $NiCl_2.6H_2O$ at room temperature. The compound has been characterized by means of FT–IR spectroscopy, thermal analysis (TG, DTG and DTA), and X-ray single crystal diffraction data. The compound crystallizes in the orthorhombic space group Abnn, $M_r = 986.08$, $a = 15.386(4)$, $b = 15.710(4)$, $c = 17.071(4)$ Å, $V = 4126(2)$ Å^3, $Z = 4$, $D_x = 1.59$, $D_o = 1.60(1)$ $Mg{\cdot}m^{-3}$, $\lambda = 0.71069$ Å, $\mu = 10.199$ cm^{-1}, $F(000) = 2072$, $T = 295$ K. From 4516 reflexions, only 1141 with $I > 2\sigma(I)$ were used for structure solution and refinement. The full-matrix weighted least-squares refinement converged to $R = 0.049$ and $wR = 0.055$ for 148 parameters. Crystal structure is made up of symmetric $[(O_2C_2O_2)_2Ni\text{-}(O_2C_2O_2)\text{-}Ni(O_2C_2O_2)_2]^{6-}$ anions (Figure 1), diethylenetriammonium cations and lattice water molecules held together by electrostatic forces and a hydrogen-bonding network. Each nickel atom of the dinuclear entity shows a distorted octahedral environment: two oxalate bridge oxygen atoms and one oxygen atom from each terminal oxalate form the equatorial plane, whereas the other oxalate terminal oxygen atoms occupy the apical positions. Some nickel and copper dinuclear complexes containing the oxalate as a bis-bidentate ligand have been described in the literature. However, to our knowledge, it is the first time that an anionic dinuclear complex has been found in this type of compounds.



LAICM1079P **27, Mon. 13**

SYNTHESIS AND X-RAY DIFFRACTION STUDY OF 1,5-DITHIA-3,7-DIAZABICICLO[3.3.1] NONANE AND ITS N-BORANE ADDUCT.

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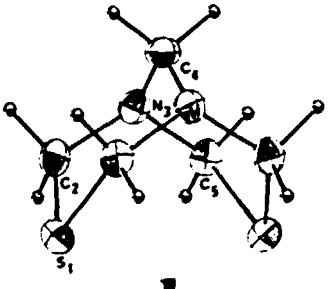
We report the synthesis of the title compound 1, their NMR data and its X-ray diffraction structure and its reactivity with BH_3-THF. We are working in the synthesis of heterocycles rich in lone pairs of electrons ligands[1]. We are interested in studying how the presence of N and S atoms bonded through CH_2 determine the Lewis basic character of these heterocycles. We have prepared 1 from reaction of NH_4OH, NaHS and CH_2O. It was identified by ^1H and ^{13}C NMR and elemental analysis.

The X-ray diffraction study of 1 shows a bicycle with two six membered rings in a chair conformation. The eight membered ring has a saddle conformation with two nitrogen bonded by a CH_2 and its free lone pairs directed to outside and two S atoms at the stirrups. It is a symmetric molecule with a C_2 axis. The N atoms are not completely pyramidal (64% of sp^3 character).

We were interested in knowing if the proximate position of the S atoms could favor their coordination to BH_3-THF over the N. The reaction of 1 with BH_3-THF afforded only the N-BH_3 monoadduct 2. Compound 2 looses by coordination one symmetry plane and the C_2, as observed by ^1H and ^{13}C NMR. Even in an excess of BH_3-THF, we have not observed coordination of a second BH_3 molecule. When the complex is dissolved in DMSO, the heterocycle was open and protonated, *bis*(dimethylamine)methylene was formed.



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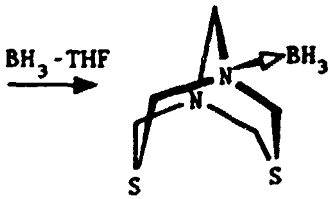

2

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*) The X-ray diffraction structure was obtained by J.C. Daran.

[1] a) A. Flores-Parra, G. Cadenas-Pliego, L.M.R. Marinez-Aguilera, M.L. García-Nares, R. Contreras. *Chem. Ber.* 1993, in press; b) G. Cadenas-Pliego, L.M.R. Martinez-Aguilera, M.-J. Rosales-Hoz, R. Contreras, J.C. Daran, S. Halut, A. Flores-Parra. *Phosphorus, Sulfur and Silicon* 1993, in press.

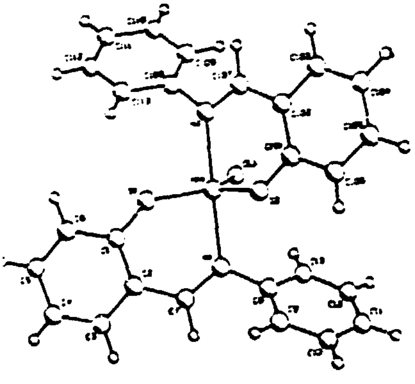
LAICM1081P **28, Mon. 13**

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CHLOROBIS(N-PHENYLSALICYLIDENEAMINATO-O,N) MANGANESE(III)

L. Luaces[a], M. Bermejo[a], J. A. García-Vázquez[a], J. Romero[a], J. Sanmartin[a], A. Sousa[a], C. A. McAuliffe[b], R.G. Pritchard[b]. [a]*Departamento de Quimica Inorganica, Universidad de Santiago de Compostela, 15706 Spain.* [b]*Department of Chemistry, University of Manchester, Institute of Science and Tecnology. Manchester M60 1QD Inglaterra*

The chemistry of manganese has recently attracted considerable attention due to its important role in bioiogical processes such as photosynthesis. This interest has led to structural investigations of several pentacoordinate manganese(III) Schiff-base complexes[1].

Complexes MnL_2 y MnL_2L' (L=anion of Schiff base and L'= phenanthroline or bipyridine) have been obtained by electrochemical oxidation of a manganese anode. These complexes have been used as precursors for the corresponding manganese(III) complexes. The complex MnL_2Cl (L= N-phenylsalicyledeneaminato) was prepared by chemical oxidation of MnL_2phen with ferricinium tetrachloroferrate.



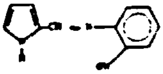
The structure of this compound was determined by X-ray diffraction. The compound consists of discrete neutral molecules with the manganese centre in a distorted trigonal bipyramidal environment $[MnN_2O_2Cl]$; the manganese atom coordinates the chloro and oxygen donors in the equatorial positions, and the iminic nitrogen in apical ones.

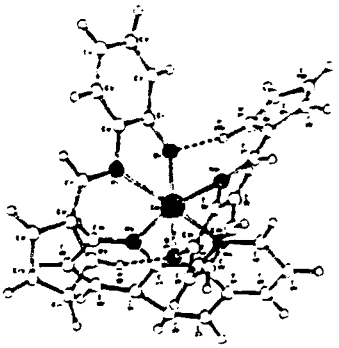
1.- A.K. Oki, F.J. Hodson, *Inorg. Chim. Acta* **170**, 65, (1990)

LAICM1062P 29, Mon. 13

SYNTHESIS AND STRUCTURE OF 1,10—PHENANTROLINE BIS{2—[(2—PYRROLE)METHYLIMINO] PHENOLATO}COBALT(II)

J. Castro, J. Romero, J.A. García-Vázquez, A. Sousa and A. Castiñeiras.
Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela. SPAIN.

The synthesis of metal mixed complexes of Schiff bases containing weakly acid groups can be satisfactorily achieved via an electrochemical procedure, starting from the metal as the anode of an electrolitical cell.[1] Following this method, we have sinthesized the complex [Co(HL)$_2$phen] containing both 2-pyrrole-N—(o-hydroxyphenyl)methylimime] and 1,10—phenantroline (phen). (H$_2$L= )



The cobalt atom is coordinated to the phenolic oxygen and nitrogen atoms of two bidentate monoanionic Schiff bases and to a bidentate phenanthroline molecule. The environment around the cobalt atom is distorted octahedral due to the small bite of the ligands. The N-H group of the pirrole ring is not coordinated but involved in a strong hydrogen bond with the phenolate oxygen atom of the other Schiff base.

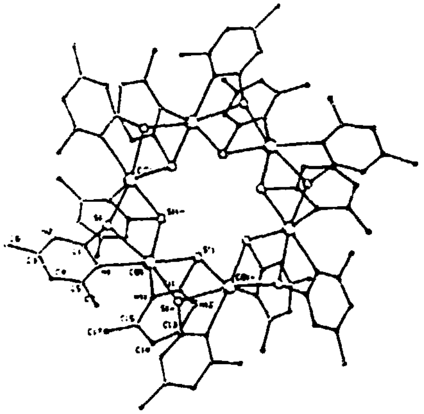
[1] Castro, J.A., Romero, J., García-Vázquez, J.A., Durán, M.L., Castiñeiras, A., Sousa, A. and Fenton, D.E. (1990) *J. Chem. Soc. Dalton Trans.*, 3255.

LAICM1083P 30, Mon. 13

ELECTROCHEMICAL SYNTHESES OF 4,6-DIMETHYLPYRIMIDINE-2-THIOLATO COMPLEXES OF NICKEL(II) AND CADMIUM(II).

R. Castro[a], J. A. García-Vázquez[a], J. Romero[a], A. Sousa[a], R. Pritchard[b] and C. A McAuliffe[b]. [a]*Departamento de Química Inorgánica, Universidad de Santiago, Santiago de Compostela, 15706-Spain.* [b]*Department of Chemistry, University of Manchester, Institute of Science and Technology, PO Box 88; Manchester M60 1 QD, England.*

As part of our continuing interest in the chemistry of metal complexes of heterocyclic thione donors,[1] we report in this communication the electrochemical synthesis of 4,6-dimethylpyrimidine-2-thiolato complexes of nickel(II) and cadmium(II), [M(dmpymt)$_2$], and of their adducts with 1,10-phenanthroline and 2,2'-bipyridine ([M(dmpymt)$_2$phen] or [M(dmpymt)$_2$bipy].



The structure of [Cd(dmpymt)$_2$] determined from X-ray diffraction, consist of cyclic hexameric molecules in which there is a regular non-planar hexagon of six cadmium atoms bridged above and below by the sulphur atoms of twelve thiolate anions.

Each cadmium atom is coordinated to one of the nitrogen and to bridging sulphur atoms of the two thiolate ligands, and to the other two through the bridging sulphur atoms. Therefore, each ligand act as a bridging five electron donor ligand. The environment of each cadmium atom can be described as a distorted octahedral geometry.

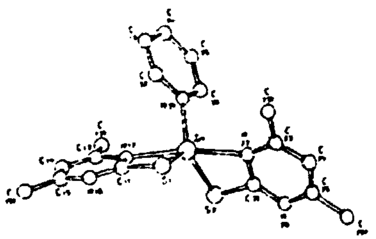
1. R. Castro, M.L. Durán, J. A. García-Vázquez, J. Romero, A. Sousa, E. E. Castellano and J. Zukerman-Schpector, *J. Chem. Soc. Dalton Trans.*, 2559, 1992.

THE SYNTHESIS OF ZINC COMPLEXES OF 4,6-DIMETHYLPYRIMIDINE-2-THIONE BY AN ELECTROCHEMICAL METHOD

R. Castro[a], J. A García-Vázquez[a], J. Romero[a], A. Sousa[a], W. Hiller[b], J. Strähle[b]. [a]*Departamento de Química Inorgánica, Universidad de Santiago, 15706-Santiago de Compostela, Spain.* [b]*Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany.*

The current interest in the coordination chemistry of zinc complexes with ligands bearing sulphur atom is partially due to the zinc(II)-cysteine thiolato interactions are present in a number of DNA and RNA binding proteins[1] and therefore these zinc complexes can be considered as models for zinc-cysteine centres in metalloproteins.[2]

In this communication we described the electrochemical synthesis of the complex of 4,6-dimethylpyrimidine-2-thione (Hdmpymt) with zinc and their adducts with pyridine, 1,10-phenanthroline and 2,2'-bipyridine. These compounds have been investigated by IR and ^{1}H and ^{13}C NMR spectroscopies and the structure of pyridine-bis(4,6-dimethylpyrimidine-2-thiolato)zinc(II) has been determined by a single crystal X-ray structure analysis.



In the crystal structure of the complex, the zinc atom is pentacoordinate to the monodentate pyridine ligand and two bidentate 4,6-dimethylpyrimidine-2-thiolato ligand through sulphur and one of their nitrogen atoms and leaving another nitrogen atom free. The geometry about the zinc atom is best described as distorted trigonal bypiramid.

1.- D.T. Corwin Jr., E.S. Gruff and S.A. Koch, *Inorg. Chim. Acta*, **151** (1988) 5.

LAICM1085P 32, Mon. 13

SYNTHESIS OF BENZOTHIAZOLE-2-THIONATO COMPLEXES OF Ni(II), Zn(II) AND Cd(II).

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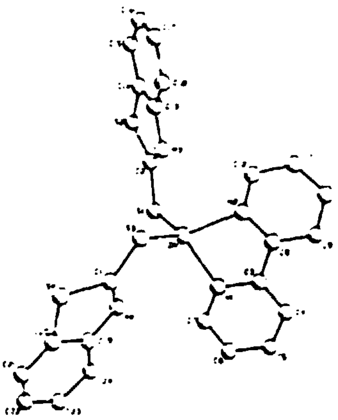
[a]*Departamento de Química Inorgánica, Universidad de Santiago, 15706 Santiago de Compostela, Spain.*

[b]*Department of Chemistry, University of Manchester, Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England.*

Electrochemical procedures have been widely used for the synthesis of metallic complexes, especially those with weakly acid organic ligands, in which the acidic group is usually a hydroxyl or pyrrole NH group.[1] We report its application to the syntesis of nickel(II), zinc(II) and cadmium(II) complexes with benzothiazole-2-thione.

Complexes of formula [M(bztz)$_2$], [M(bztz)$_2$L], where M = Ni, Zn, Cd and L = phen or bipy, were sinthetized following an electrochemical method similar to one the described by Tuck.



These compounds have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR and UV spectroscopies. In the case of [Zn(bztz)$_2$(bipy)] was studied by X-ray difraction. The compound consist of discrete molecules in which the zinc atom is tetracoordinate to the exocyclic sulphur atoms of two monodentate benzothiazole-2-thiolate ligands and to two nitrogen atoms of a bidentate chelating bipyridine molecule. The environment around the metallic atom may be described as a distorted tetrahedral geometry.

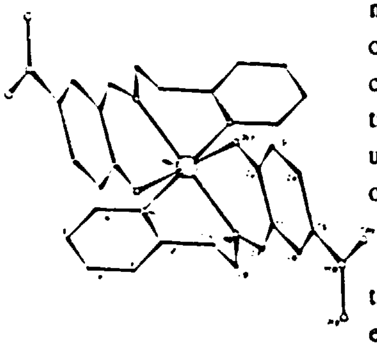
1.- J.A. Castro, J. Romero, J.A. García-Vázquez, A. Castiñeiras and A. Sousa, Z. *Anorg. Allg. Chem.*, **619** (1993) 601.

LAICM1086P **33, Mon. 13**

MANGANESE(II) AND (III) COMPLEXES WITH 2-{2-[(2-PYRIDYL)ETHYL] IMINOMETHYL}PHENOLS (R-SALAEP-H): THE CRYSTAL AND MOLECULAR STRUCTURE OF [Mn(5-NO$_2$SALAEP)$_2$]

A. Sousa[a], L. Luaces[a], M. Bermejo[a], J.A. García-Vázquez[a], J. Romero[a], C.A. McAuliffe[b], R.G. Pritchard[b], Y. Mugnier[c]. [a]*Departamento de Quimica Inorganica, Universidad de Santiago de Compostela, 15706 Spain.* [b]*Department of Chemistry, University of Manchester, Institute of Science and Tecnology. Manchester M60 1QD. England.* [c]*Université de Bourgogne. 21000-Dijon, France.*

The electrochemical oxidation of manganese in a solution of 2-{2-[(2-pyridyl)ethyl]iminomethyl}phenols (R-salaepH) in acetonitrile, with a few mg of Et_4NClO_4 as supporting electrolyte, allows isolation of the compounds [Mn(R-salaep)$_2$] or [Mn(R-salaep)$_2$ClO$_4$]. All compounds were characterized by IR, FAB studies and magnetic measurements.



In the crystal structure of the complex [Mn(5-NO$_2$-salaep)$_2$], the manganese atom is in a distorted octahedral environment, in which it is coordinated meridionally by two tridentate ligands, R-salaep$^-$, each utilizing the pyridine nitrogen, phenolate oxygen and imine nitrogen atoms.

The cyclic voltametry behaviour of this compound has been studied; the electrochemical oxidation in CH_2Cl_2 allows the isolation of [Mn(5-NO$_2$-salaep)$_2$]PF$_6$.

1.- H. Sakiyama, H. Tamaki, M. Kodera, N. Matsumoto and H. Okawa, *J. Chem. Soc. Dalton Trans.*, 591, 1993. 2.- S. M. Abu-El-Wafa and R.M. Isaa, *Bull. Soc. Chim. France*, 595, 1989.

CADMIUM(II) COMPLEXES OF 2-(MERCAPTOPHENYL)IMINOMETHYLPHENOLS.

E. Labisbal, J. Romero, J.A. García-Vázquez, A. Sousa, C.A. McAuliffe* and R.G. Pritchard*. *Departamento de Química Inorgánica, Universidad de Santiago, Santiago de Compostela, E-15706, ESPAÑA.*
** Department of Chemistry, Institute of Science and Technology, University of Manchester, Manchester M60 1QD, U. K.*

We have recently reported the synthesis of tin(IV)[1] and zinc(II)[2] complexes derived from the Schiff bases H_2L_2, (fig 1). In continuation of these works, we have synthesized complexes of cadmium with the same bases.

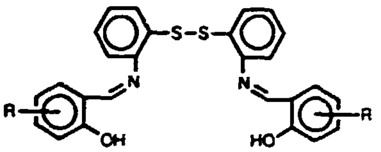


fig 1

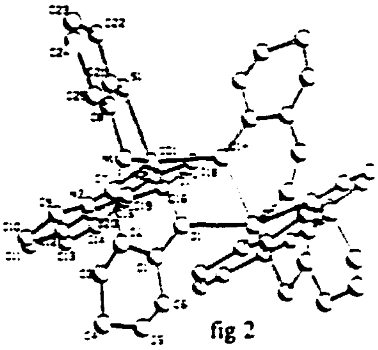


fig 2

The electrochemical method used was similar to those described earlier by Tuck. The complexes are characterized by elemental analyses, IR and NMR spectrocopies. In the case of CdLphen the compound was studied by X-ray difraction. The crystal structure of the complex, (fig 2), shows that the complex is dinuclear through oxygen bridges. The environment around each metallic atom can be described as a very distorted octahedron, the cadmium atom is co-ordinated by one terdentate Schiff base molecule, one bidentate phenanthroline ligand and the oxygen atom of the other Schiff base.

---

[1] E. Labisbal, A. de Blas, J.A. García-Vázquez, J. Romero, M.L. Durán, A. Sousa, N.A. Bailey, D.E. Fenton, P. Leeson and R.V. Parish. *Polyhedron* 1992, **11**, , 227.

[2] E. Labisbal, J.A. García-Vázquez, C. Gómez, A. Macías, J. Romero, A. Sousa, U. Englert and D.E. Fenton. *Inorg. Chim. Acta* 1993, **203**, 67.

LAICM1088P **35, Mon. 13**

HOMODINUCLEAR (Cu/Cu, Ni/Ni, V/V AND Fe/Fe) AND HETERODINUCLEAR (Cu/Ni, Ni/V AND Fe/Ni) COMPLEXES OF A NOVEL OXAMIDE-TYPE LIGAND COORDINATING IN THE *TRANS* CONFORMATION

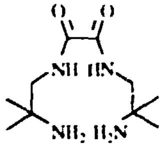
Jean-Pierre Costes, Jean-Pierre Laurent and Gilles Pradie
Laboratoire de Chimie de Coordination du CNRS, UP 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut national Polytechnique. 205 route de Narbonne, 31077 Toulouse Cedex, France.

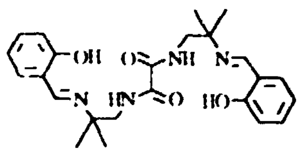
Polymetallic systems are attractive as synthetic models of the active sites of metallobiomolecules and also as materials for studying correlations between structure and cooperative physical properties.

Among the known polynucleating ligands, oxamide derivatives are receiving considerable attention due to their possibilities. Thus, the oxamide bridge is known to be very efficient in transmitting exchange interaction between magnetic ions in favourable geometries [1]. Unfortunately, their N_2O_2 or N_4 coordination sites are only occupied by copper or nickel.

We presently report on the preparation and characterization of an original N,N'-disubstituted oxamide derivative (H_2L_1). This ligand is distinguished by the occurence of substituents with terminal NH_2 groups which can be used in further reactions. Thus by reaction with salicylaldehyde one obtains a new dinucleating ligand (H_4L_2) which affords the first examples of vanadium(IV) and iron(III) oxamido-bridged dinuclear complexes. The spectroscopic characteristics and magnetic properties of these complexes and the related nickel(II) and copper(II) complexes are reported.

H_2L^1





H_4L^2

Although this H_4L_2 ligand presents two identical coordination sites, we have been able to synthesize heterodinuclear complexes (Cu-Ni, Ni-VO, Ni-Fe(III)). Such a reaction pathway results from an application of the cis-trans isomerization of the oxamido group[2]. The spectroscopic characteristics and magnetic properties of these complexes will also be reported. They confirm the existence of these genuine heterodinuclear complexes.

[1] O. Kahn, Structure and Bonding, 68 (1987) 91.
[2] J.P. Costes and J.P. Laurent, Inorg. Chem. 28 (1989) 2234.

LAICM1096P **36, Mon. 13**

ELECTROCHEMICAL SYNTHESES OF TIN(IV) COMPLEXES OF 2-(2-MERCAPTOETHYL)IMINOPHENOLS

E. Labisbal, J. Romero, J. A. García-Vázquez, U. Russo[a]*, A. Castiñeiras, M. L. Durán, A. Sousa.*

Departamento de Química Inorgánica, Universidad de Santiago de Compostela. Santiago de Compostela, E-15706, ESPAÑA.

[a]Dipartimento de Chimica Inorganica, Metallorganica et Analitica, Università di Padova, Padova, ITALIA.

The electrochemical oxidation of anodic tin in acetonitrile solutions of Schiff bases L_2H_2 (Fig. 1), obtained from the condensation of salicylaldehyde derivatives and cystamine yields complexes with formulae SnL_2, where L is the anion which results from the cleavage of a disulphide bond followed by the deprotonation of the phenol group.

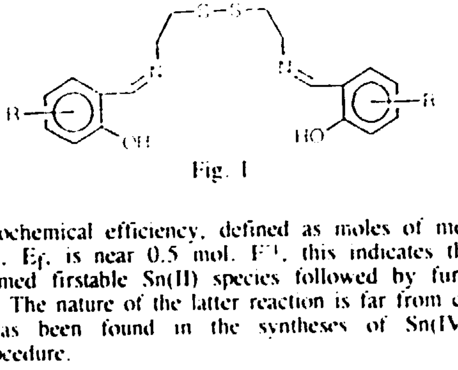
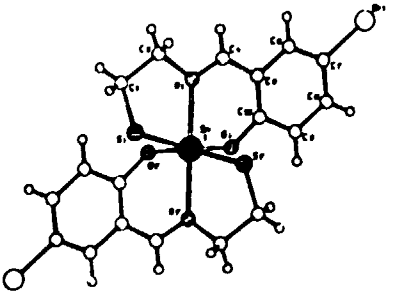


Fig. 1

The electrochemical efficiency, defined as moles of metal dissolved per Faraday of charge, E_f, is near 0.5 mol. F^{-1}, this indicates that in the anodic oxidation was formed firstable Sn(II) species followed by further oxidation in solution to Sn(IV). The nature of the latter reaction is far from clear at this stage. This behaviour has been found in the syntheses of Sn(IV) complexes by electrochemical procedure.

The products were characterized by microanalysis, and by IR, NMR ^1H, ^{13}C, ^{119}Sn and Mossbauer spectroscopies. The crystalline complex SnL^1_2 was suitable for X-ray diffraction studies.



The tin atom is coordinated to the thiophenolate nitrogen and oxygen atoms of the bianionic tridentate ligands. The geometry around the tin can be described as slightly distorted octahedron. The ligands adopt a position such the complex can be described as a meridional isomer.

LAICM1099P **37, Mon. 13**

BISMUTH(III) DiMETHYLDITHIOPHOSPHINATE: ANOTHER DIMER FORMED THROUGH SECONDARY BONDING. THE STEREOCHEMICALLY ACTIVE LONE PAIR REVISITED.

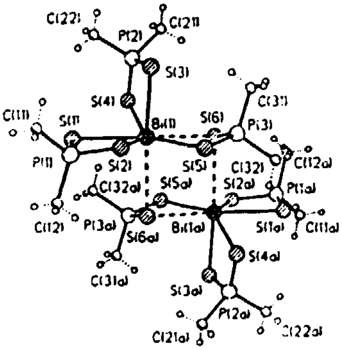
I. Haiduc[a,b], F.T. Edelmann[c], C. Silvestru[a,b] and R. Cea-Olivares[a]

[a] Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 México, D.F.

[b] Facultatea de Chimie, Universitatea Babes-Bolyai, RO-3400 Cluj-Napoca, Romania.

[c] Institut für Anorganische Chemie der Universität Göttingen, D-3400 Göttingen, Germany.

Bismuth(III) dimethyldithiophosphinate, $Bi(S_2PMe_2)_3$, the missing member of the $Bi(S_2PR_2)_3$ family was prepared from $BiCl_3$ and $NaS_2PMe_2.2H_2O$ in benzene. An X-ray diffraction study revealed a dimeric structure A, which is compared with those of monomeric $Bi(S_2PEt_2)_3$[1], $Bi[S_2P(OR_2)]_3$ (R=Et, Pr^i) and dimeric $Bi(S_2PPh_2)_3$.[2]



The possible role of stereochemically active lone pair of electrons is discussed.

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[1] D.B. Sowerby and I. Haiduc, J. Chem. Soc. Dalton Trans., 1987, 1257.
[2] M.J. Begley, D.B. Sowerby and I. Haiduc, J. Chem. Soc. Dalton Trans., 1987, 145.

LAICM1102P **38, Mon. 13**

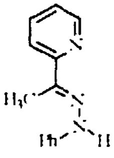
LIGAND DESIGN IN PALLADIUM AMIDES SYNTHESIS.

José V. Cuevas Vicario, Gabriel García-Herbosa, Asunción Muñoz Santamaría.

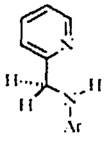
Departamento de Química Inorgánica. Colegio Universitario de Burgos.
Pza. Misael Bañuelos s/n. 09002 Burgos. SPAIN.

In spite of the scarceness of terminal Palladium-Nitrogen amido bonds we have prepared and characterized orthometallated binuclear complexes of Palladium containing amido bonds.[1] The synthesis of two new and stable mononuclear phenylamido complexes of Palladium has recently been published,[2] thus proving that Pd-N amido bonds could be stabilized when both adequate structure and ancillary ligands are present.

One of the reasons for the interest in Palladium amides is the potential use of these complexes to facilitate the formation of Carbon-Nitrogen bonds through the insertion of unsaturated molecules into the Metal-Nitrogen amido bond. To this purpose the lone pair on the Nitrogen should not be involved in π bond formation, thus keeping nucleophilic character enough. Doubtless rich electron late transition metals should be better candidate than early ones.
In addition, oxidation of Palladium or Platinum arylamido complexes allows carbon-carbon coupling, leading to mixed valence redox active complexes which is a further reason to focus attention.

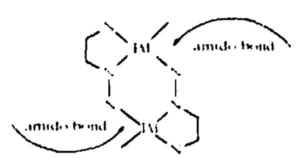


A

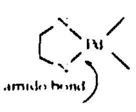


B

Our strategy to obtain complexes containing Pd-N amido bonds is based on ligands A and B as shown above. On a first step, complexes derived from ligands A and B in a N,N´chelate five member ring coordination are expected. Then "N-H" fragments should be close enough to Palladium to allow formation of Pd-N amido bonds after deprotonation. Ligand A should obviously lead to dimeric complexes as previously described [1] and ligand B to mononuclear complexes, in both cases with frameworks as shown above.



A-complexes



B-complexes

Differences between predictions and actual results will be discussed on poster.

1) Espinet, P.; Garcia-Herbosa, G.; Herrero, F. J.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1989**, *28*, 4207
2) Villanueva, I. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2969

LANTHANIDE PICRATE COMPLEX WITH HEXAMETHYL - PHOSPHORAMIDE (HMPA)

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Complexes with composition $Ln(pic)_3.3HMPA$ (pic = picrate, Ln =La-Eu) were prepared by reaction of the hydrated picrates with the ligand in ethanol (molar ratio 1:3). They were characterized by titration of the lanthanide with EDTA, CHN microanalytical procedures and IR spectra. According to X-ray powder patterns they are all isomorphous. They behave as non-electrolytes in acetonitrile. The spectroscopic parameters: nephelauxetic ($\beta = 0.988$) and covalent factor ($b^{1/2} = 0.077$) were obtained from the Nd^{3+} absorption spectrum, are indicative of essentially electrostatic bonds between the ligands and the central ion. The emission spectrum of the Eu^{3+} compound was interpreted in terms of a D_{3h} symmetry distorted to C_{3v} . According to single crystal X- ray-diffraction data for the neodymium compound, the coordination polyhedron is that of an approximate tri-caped trigonal prism. The oxygen atoms of three HMPA are at the vertices of one of the prism bases, while the phenolic oxygens of the three picrate groups are at the vertices of the other prism base. Each picrate acts as a bidentate ligand having an oxygen of an ortho-nitro group, sited at center of square bases of the prism.

Financial Support : CAPES, CNPq, FAPESP, PADCT.

LAICM1108P **40, Mon. 13**

SPECTROSCOPIC AND THERMOANALYTICAL STUDIES OF THE TETRAKIS (BENZYL-T-BUTYLSULFOXIDE) EUROPIUM(III) PICRATE

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The complex of formula Eu(pic)$_3$.4L (pic=picrate, L=benzil-t-butylsulfoxide) was isolated from an aqueous reaction medium.The yellow solid was characterized by usual C,H,N analytical procedures,complexometric titration of europium with EDTA, IR spectrum,emission spectra at room temperature and 77K, TG and DTG analysis.IR spectra of the ligand and of the complex show a shift of vSO to lower frequencies (988 cm^{-1}) as compared to the free ligand (1036 cm^{-1}). The picrate ions bands are suggestive of different coordination modes, envolving the phenolic and the ortho-nitro group oxygens (v$_{as}$NO$_2$ at 1577s and 1543s cm^{-1}, v$_s$NO$_2$ at 1365s and 1328s cm^{-1}, vCO at 1275s cm^{-1}). The emission spectra at room temperature and at 77K are very similar,but the one at low temperature is well resolved.They present a very weak $^5D_0$---$^7F_0$ band, three peaks due to the $^5D_0$---$^7F_1$ transition(one A$_2$ and two due to E species), three peaks due to $^5D_2$---$^7F_0$ transition (one A$_1$ and two due to E species) and were interpreted in terms of a C$_{4v}$ symmetry. TG and DTG in dynamic air atmosphere analysis show that the complex decomposes loosing part of the sulfoxide ligand. At higher temperatures picrate decomposition occurs and oxidation of part of the combined sulfur resulting in sulfate ions. The final residue contains sulfate ions and was interpreted as oxi-dissulfate of di-europium, Eu$_2$O(SO$_4$)$_2$.

Financial support: CAPES, CNPq, FAPESP and PADCT.

CRYSTAL AND MOLECULAR STRUCTURE OF THE SCHIFF BASE COMPLEX N,N'-3,4-TOLUENEBIS(SALICYLIDENEIMINATO) NICKEL (II)

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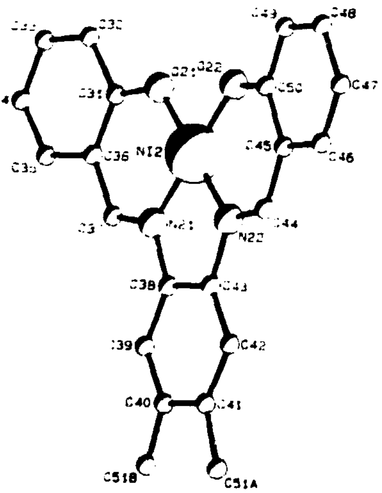
In previous papers[1], the complex of the Schiff base N,N'-3,4-toluenebis(salicylideneimine) with nickel(II) has been prepared. In this work red monocrystals have been isolated from a chloroform solution and its crystal and molecular structure of this complex has been determined by Patterson method and refined by full-matrix least-squares method using SHELX92 computer program.

Formula $(C_{21}H_{18}N_2O_2Ni)_2 \cdot 3HCCl_3$
System Triclinic
Space Group P1
a (Å) = 13.855(3)
b (Å) = 14.591(3)
c (Å) = 15.247(4)
α = 116.24(2)
β = 115.97(2)
γ = 91.30(2)
Z = 2
R = 0.0641
Reflexions number 4017



The crystallographic asymetric unit contains two discrets molecules and three chloroform molecules without hydrogen bonding. Methyl groups are disordered. The coordination around the metallic atom is basically planar square with a N_2O_2 donor set, as it is indicated by others technics[1].

LAICM1110P **42, Mon. 13**

POLYMER SPECIES IN AQUEOUS SOLUTIONS OF *PARA*-PHENYLENEDIAMINE-N,N,N',N'-TETRAACETIC ACID IN THE PRESENCE OF COPPER(II)

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The *para*-phenylenediamine-N,N,N',N'-tetraacetic acid (*p*-PhDTA) with the nitrogen atoms in *para* position can only coordinate one iminodiacetate group to any one metal cation. This ligand can therefore coordinate in two spheres and it is a ligand very versatile for the coordination: in the 1:1 ratio, it can form ML monomer complexes or M_nL_n polimers; with excess of metal it can form M_2L bimetallic species[1], or $M_{n+1}L_n$ polymer species; and with excess of ligand it can form ML_2 monomer species or M_nL_{n+1} polymer species. All these different types of complexes can be protonated, and thus can give rise to a wide variety of complexes.

In this work, a study of the conditions for the formation in aqueous solution (25°C and I=0.5 M in KCl) of polymer species has been made for the Cu(II)-*p*-PhDTA system.

The model that best fits the potentiometric experimental results is that which corresponds to the complex species (H_4L, ligand): H_2CuL, $HCuL^-$, $H_2Cu_2L_2^{2-}$, $HCu_2L_2^{3-}$, $Cu_2L_2^{4-}$, $HCu_3L_3^{5-}$, $Cu_5L_5^{10-}$, $Cu_6L_6^{12-}$, $H_2Cu_2L_3^{6-}$, $H_4CuL_2^{2-}$, $H_3CuL_2^{3-}$, $H_2CuL_2^{4-}$, $HCuL_2^{5-}$, HCu_2L^+ and Cu_2L. The species distribution diagrams indicate that pentamer $Cu_5L_5^{10-}$, is the polymer more stable.

1. C. Ruiz-Pérez, M.L. Rodríguez. F.V. Rodríguez Romero, A. Mederos, P. Gili and P. Martín-Zarza, *Acta Crystallogr.*, C46, 1405 (1990).

LAICM1111P **43. Mon. 13**

A WAY FOR STUDYING STRONG COMPLEXES OF Fe^{3+} WITH AMINOPOLYCARBOXYLIC LIGANDS. STUDY OF THE COMPLEXES FORMED BY 3,4-TOLUENEDIAMINE-N,N,N',N'-TETRAACETATE WITH Fe^{3+} AND Cu^{2+} IN AQUEOUS SOLUTION.

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The complexation of 3,4-toluenediamine-N,N,N',N'-tetraacetate (3,4-TDTA, H_4L) with Fe^{3+} and Cu^{2+} has been studied at 25.0±0.1°C and I=0.5M in KNO_3 by potentiometry. A couple of Ingold L8311 glass-Radiometer K701 Calomel electrode was used to measure the pH($pH=-\log[H^+]$)and the Cu^{2+} ion activity was measured with a F111Cu Radiometer electrode in combination with a Radiometer K701 doubled juntion saturated calomel electrode, with 0.5 M KNO_3 as the bridging solution. Because of the high value of the constants, the usual pH titration did not give any satisfactory results for any system Fe^{3+}/H_4L and Cu^{2+}/H_4L. Therefore metal competition and a copper-selectrode were used(1). The determination of the stability constants for Cu^{2+} was carried out in a ligand buffer containing an excess of Ca^{2+}. When the stability constants for Cu^{2+} are known, potentiometric studies of solutions containing Fe^{3+}, Cu^{2+} and H_4L in appropiate relations and in adecuate pH zone, are able to determine the values of the stability constants for the Fe^{3+}/H_4L system.

	MH_2L	MHL	ML	M(OH)L
Ca^{2+}	-------	4.783(3)	8.607(3)	------
Cu^{2+}	8.953(8)	11.742(5)	15.57(2)	------
Fe^{3+}	--------	16.56(7)	22.06(5)	27.17(5)

LAICM1112P

44, Mon. 13

STRUCTURE OF DIZINC(II)-3,4-TOLUENEDIAMINE-TETRAACETATE, $[Zn(3,4\text{-}TDTA)Zn(H_2O)_4]\cdot 2H_2O$

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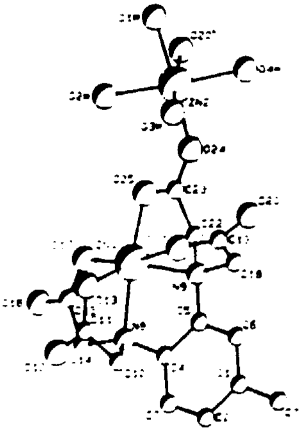
The complex $Zn_2[(3,4\text{-}TDTA)]\cdot 6H_2O$ were prepared by mixing an aqueous solution of the monopotassic salt of 3,4-TDTA (3,4-TDTA= 3,4-toluenediamine-N,N,N',N'-tetraacetic acid) (1) with a concentrated solution of $Zn_2(NO_3)_2\cdot 6H_2O$ in the ratio ligand:metal 1:2. The pH was adjusted to 4 with KOH. Crystal suitable for X-ray crystallography were grown by liquid-vapor diffusion, using isopropilic alcohol as precipitant. The structure was solved by direct methods (SHELX86) and refinement by full-matrix least squares (SHELX76), with anisotropic thermal parameters for all non-H atoms.

Crystallographic data

Formula	$Zn_2C_{15}N_2O_{14}H_{26}$
System	Monoclinic
Space Group	$P2_1/n$
a(Å)	8.140(2)
b(Å)	9.672(3)
c(Å)	27.079(4)
β	94.26(2)
V(Å)^3	2126(1)
Z	4
R	0.0511
R_w	0.0543
Number of Reflexions	6.589



The compound is a binuclear zinc(II) complex bridged by a carboxylate oxygen of the aminopolycarboxylic acid. The molecular geometry of the zinc(II)-3,4-TDTA moiety is close to a trigonal prism, whereas the other metal ion is a nearly Oh environment involving interactions with two oxygen atoms from carboxylate groups of different ligands and four water molecules.

1. A. Mederos, J.V. Herrera, J.M. Felipe and M.L. Quesada, *An.Quím.*, 1984, 80B, 281.

LAICMI114P **45, Mon. 13**

CHLORIDE VS. WATER IN THE COORDINATION SPHERE OF TIN(IV). THE CRYSTAL STRUCTURE OF THE SALT [HThiamin][$SnMe_2Cl_3.H_2O$]Cl

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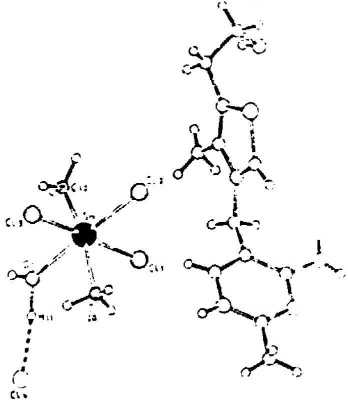
The title compound, synthetized by reacting thiamine chloride hydrochloride with dimethyltindichloride in ethanol/water, consists of protonated thiamine cations and aquotrichlorodimethylstannate(IV) and chloride anions. In the protonated thiamine, as in other salts of chloroanions[1], both the pyrimidine and thiazolium rings are planar and the cation adopts the F conformation.



The stannate anion shows a distorted octahedral structure with the tin atom coordinated to two methyl carbons [Sn-C(10) = 2.092(6); Sn-C(20) = 2.084(6) Å], three chloro atoms [Sn-Cl(1) = 2.690(1); Sn-Cl(2) = 2.486(1); Sn-Cl(3) = 2.562(1) Å] and the oxigen atom of water molecule [Sn-O(1) = 2.418(4) Å]. A strong hydrogen-bond network interlinks the ions in the lattice.

1. R. E. Cramer, R. E. Kirkup and M. J. J. Carrie, *Inorg. Chem.* (1988), 27, 123.

LAICMI116P 46, Mon. 13

DIMETHYLTIN COMPLEXES OF VITAMIN B_6. THE CRYSTAL STRUCTURE OF $[SnMe_2(P-H)](NO_3).2H_2O$ (P = PYRIDOXOL)

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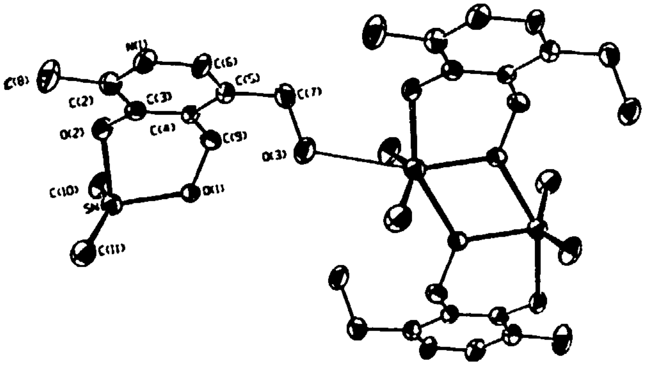
The title compound was prepared by reacting dimethyltin nitrate (from dimethyltin dichloride and silver nitrate) with pyridoxol (from pyridoxol hidrochloride, sodium hydroxide and silver nitrate) in ethanol/water.



As the figure shows, the deprotonated ligand chelates the tin atom via its phenolic and etanolic O-atoms. Simultaneously, the O-etanolic atom acts as a bridge between dimethyltin groups, in which the tin atom reach the hexacoordination via other O-etanolic atoms of neighbouring molecules. An hydrogen bond scheme is present in the structure, interlinking pyridoxol bridges, water molecules and nitrate ions.

LAICM1125P **47, Mon. 13**

BIS(MORPHOLINE-1-CARBOTHIOATO) OF CADMIUM (II).

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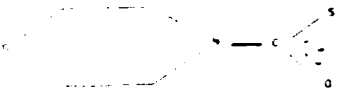
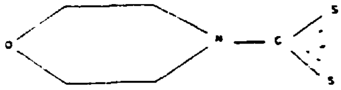
Comparative studies of structural and chemical properties of complexes of monothiocarbamates (SOCNR$_2^-$) and dithiocarbamates (S$_2$CNR$_2^-$) are capable of providing information in relation to the differences between sulfur and oxygen as donors atoms (1).

The present communication is related with the preparation of bis(morpholine-1-carbothioato) of cadmium(II). The corresponding derivative of morpholine-1-carboditioato [Cd(Mdtc)$_2$] has been prepared and studied before (2).



Mmtc



Mdtc

The complex Cd(Mmtc)$_2$ was obtained by reacting the sodium salt of the ligand (from morpholine and SCO in ethanolic NaOH) and cadmium(II) chloride in water, and was characterized by analysis elemental, and IR and NMR (^{13}C, ^{1}H) spectrometry. The coordination of the metallic center is discussed in the light of this information.

(1) J.McCormick, B.P. Stormer. Inorg. Chem. 11, 729-735(1972).

LAICM1126P 48, Mon. 13

THIOSEMICARBAZONE COMPLEXES OF ZINC(II), CADMIUM(II) AND MERCURY(II)

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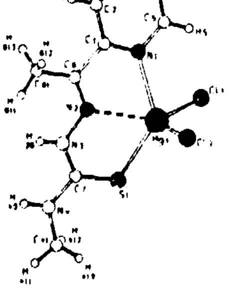
Heterocyclic thiosemicarbazones, as well as their metal complexes, are of interest because of the potentially beneficial biological activity. Although there have been numerous studies involving the isolation of transition metal complexes, comparatively few non-transition metal complexes have been studied.

We prepared the zinc, cadmium and mercury dihalide complexes of ^{4}N-methyl-2-[1-(2-pyridine-2-yl)ethilydene]hydrazinecarbothioamide (L) of general formula $M(L)X_2$ (X = Cl, Br or I), and characterized these complexes by physicochemical and spectroscopic methods (IR and ^{1}H, ^{13}C, ^{113}Cd, ^{199}Hg NMR).

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
$Cd(L)Cl_2$	8.8132	10.0034	13.3437	96.562	104.572	101.160
$Cd(L)Br_2$	8.9450	10.1349	13.5743	96.111	107.838	102.440
$Cd(L)I_2$	9.4002	10.4506	13.6390	93.679	109.480	104.771
$Hg(L)Cl_2$	8.6049	10.1088	13.3751	97.069	104.158	100.605

Crystal structures for cadmium(II) complexes of formula $M(L)X_2{\cdot}2DMSO$ (X = Cl, Br or I) and for $Hg(L)Cl_2{\cdot}2DMSO$ are also presented. The four complexes are isotypical and crystallize in the space group P(-1) with the unit cell dimensions shown in the table.

The metal is pentacoordinated by two halogen atoms and by two nitrogen atoms and one sulfur atom of the ligand (see figure). Distortions of the coordination polyhedra were calculated by the Muetterties and Addison methods and the results obtained are discussed.



DIORGANOTIN(IV) DIHALIDE COMPLEXES WITH AZOLES

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X-ray studies carried out on pyrazole (HL) complexes of the type $[SnR_2X_2(HL)_2]$[1] showed the presence of NH···X inter and intramolecular hydrogen bonds which influence it structure.

Being interested in the preparation of complexes with azoles in which the N-H group is absent, the interaction of $SnMe_2X_2$ with isoxazole, 5-methylisoxazole, 3,5-dimethylisoxazole, 4-methyloxazole, 2-methyl-Δ^2-oxazoline and thiazole was monitored in $CDCl_3$ by using ^1H, ^{13}C and ^{119}Sn NMR spectroscopy. The $[SnR_2X_2L_2]$ adducts (L = 2-methyl-Δ^2 -oxazoline and thiazole; R = Me, Et, Bu, Ph; X = Cl, Br) were isolated and studied in solid state by IR spectroscopy.

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[1] A. Sánchez Gónzalez, J. S. Casas, J. Sordo and G. Valle. *J. Organomet. Chem.* (1992), 435, 29.

COPPER, SILVER AND GOLD(I) COMPLEXES WITH BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE

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The reaction of copper(I) chloride, silver nitrate or tetrachloro auric acide (reduced by thiodiglycol), with bis(2-diphenylphosphinoethyl)phenylphosphine (P_3) in chloroform or acetone, afforded the complexes $Cu(P_3)Cl$, $Ag(P_3)NO_3$ and $Au(P_3)Cl$, with potential antitumour activity [1].

Copper and gold complexes were soluble in the common organic solvents,however, the silver complex was only soluble in dimethylsulfoxide by strong stirring. Molecular weight measurements for copper and gold complexes in $CHCl_3$ solution, show a certain polimerization in $Cu(P_3)Cl$ which increases in $Au(P_3)Cl$.

^{31}PNMR spectra in chloroform, show that the copper complex appears to be quite stable by addition of ligand. The gold complex spectra are more complicate, when ligand is added there are new resonances with exchange reactions. By increasing the amount of ligand, gradually sharp ligand resonances are seen, showing some ligand not exchanging. The complex of silver (a suspension in dmso), eventually dissolved as the ligand was added in $CDCl_3$, show no ligand resonances in any case and so there is probably some exchage going on.

[1] P.J. Sadler; Adv. Inorg. Chem.,36,1 (1991).

LAICM1044P **1, Tue. 14**

C.T.-COMPLEXES OF 1,4,7-TRITHIACYCLONONANE ([9]aneS$_3$) WITH DIIODINE.

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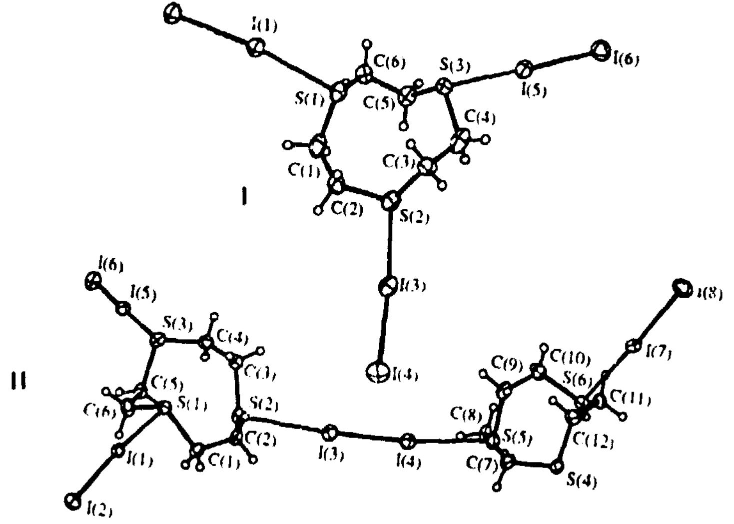
Mesocyclic and macrocyclic polythioethers have been found effective polydentate ligands for complexing a variety of transition metal ions, in spite of their moderately low s-donor and π-acceptor abilities[1]. With the aim of testing the donor ability of thioether macrocyclic ligands with respect to diiodine, we studied the products obtained by reacting 1,4,7-trithiacyclononane ([9]aneS$_3$) with diiodine both in CH$_2$Cl$_2$ solution and in the solid state. In dilute solution, [9]aneS$_3$ reacts with molecular diiodine to form a 1:1 adduct, while at concentrations suitable for ^{13}C-NMR experiments, adducts with higher ligand/diiodine molar ratios are formed. In the solid state three types of compounds were isolated having [[9]aneS$_3$]/[I$_2$] molar ratios of 1:1, 1:2 and 1:3 respectively. The X-ray crystal structures of [9]aneS$_3$·3I$_2$ (I) and 2[9]aneS$_3$·4I$_2$ (II) are reported below. The FT-Raman spectra, carried out on the solid samples, show ν(I-I) frequencies in accordance with the presence of perturbed diiodine molecules, as generally found for I$_2$ weak or medium-weak adducts[2].



1) M N. Bell, A.J. Blake; R.M. Christie; R.O. Gould, A.J. Holder, T I. Hyde, M. Schroder and L.J. Yellowless, *J. Chem. Soc. Dalton Trans.* 1992, 2977 and reference theiren cited.
2) P. Deplano, F.A. Devillanova, J.R. Ferraro, F. Isaia, V. Lippolis and M.L. Mercuri, *Applied Spectr.*, 11, 1992, 1625.

LAICM1133P **2, Tue. 14**

OXYGEN AND SULFUR TRIPOD MOLECULES. A THEORETICAL STUDY.

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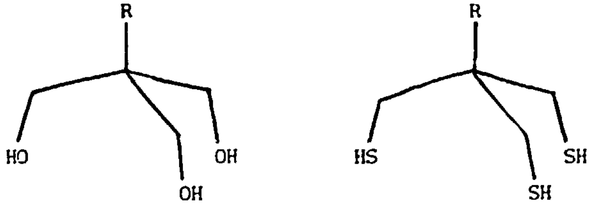
Several AM1 calculations have been performed for systems with the general formula $RC-(CH_2EH)_3$ where E = O or S and R = one of CH_3, NH_2, NO_2, $NHCH_2COOH$, Ph. This general formula we call "tripod molecules", all of which contain the 1,3-propanediol-2-hydroxymethyl group (pdh). AM1 calculations have provided information about the reactivity trends of these molecules as chelating agents towards metallic ions. The results indicate that the trialcohol molecules show different reactivity trends, whereas the trithioalcohols show only one. This agrees well with previously reported experimental results. The results obtained explain satisfactorily several experimental facts already reported and allow us to make some predictions.



R = $-CH_3$, $-NO_2$, $-NH_2$, $-NHCH_2COOH$, -Ph

N-METHYL-2,2'-BIIMIDAZOLE COMPLEXES OF DIORGANOTIN(IV) DIHALIDES.

Mª D. Couce[a], P. Alvarez-Boo[a], E. Freijanes[a], J.S. Casas[b] and J. Sordo[b]

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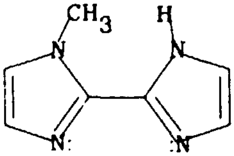
Following our studies on biimidazole derivatives[1], the ligand N-methyl-2,'2-biimidazole (MBIm) was prepared[2] and characterized by chemical analysis and IR and ^1H NMR spectroscopy.



The interaction of MBIm with SnR_2X_2 (R = Me, Et, Bu, Ph; X = Cl, Br) in CH_2Cl_2 affords solids characterized analitically as SnR_2X_2.MBIm, which were studied in solid by IR spectroscopy and by ^1H and ^{13}C NMR in solution.

1. C. López, A. Sánchez-González, M.E. García, J.S. Casas, J. Sordo, R.Graziani and U. Casellato, *J. Organomet. Chem.* 1992, 434, 2612.

2. P. Melloni, E. Dradi and W. Logemann, *J. Med. Chem.*, 1972, 15, 9 .

LAICM1142P 4, Tue. 14

DIORGANOTIN(IV) COMPLEXES OF BIS (THIOSEMICARBAZONES)

M. C. Pérez, M. V. Castaño, A. Sánchez, J.S. Casas and J. Sordo

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Bis(thiosemicarbazones) (H_2BTSC) of composition:

H_2BTSC

reacted with R_2SnO (R = Me, Et) in DMF/H_2O mixtures or in ethanol solution. The reaction afforded solids with [$SnR_2(BTSC)$] stoichiometry, insoluble in water and in organic solvents of low dielectric constant but soluble in DMSO and (partially) in DMF.

The tin coordination is discussed in the light of the spectral properties of the complexes in solid state (IR) and in solution (^1H, ^{13}C and ^{119}Sn NMR).

SYNTHESIS AND STRUCTURAL STUDY OF DIMETHYL- AND DIPHENYL(2,6-DIACETYLPYRIDINEBIS-THIOSEMICARBAZONATO)TIN(IV). CRYSTAL STRUCTURE OF [$SnPh_2C_{11}H_{13}N_7S_2$].2DMF.

J.S. Casas[a], A. Castiñeiras[a], C. Maichle-Mössmer[b], M.C. Rodríguez-Argüelles[c], A. Sánchez[a], J. Sordo[a] and A. Vázquez-López[a]

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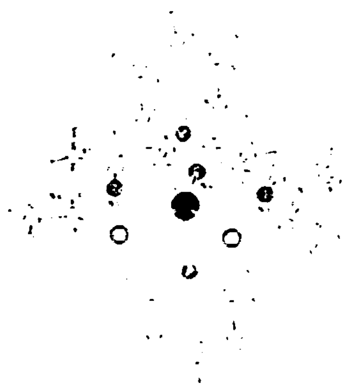
The title compounds were isolated by reacting the neutral ligand with the stoichiometric amount of $SnMe_2O$ or $SnPh_2O$ in DMF. The slow evaporation of the solvent yields monocrystals of the phenyl derivative suitable for X-Ray processing.

Crystal data: $C_{29}H_{37}N_9O_2S_2Sn$, MW=726.5, $P2_1/n$, a= 9.753(1), b= 18.962(1), c= 17,923(3)Å, β= 97,928(5)°, V= 3282.8(6)$Å^3$, Z=4, D(calc)= 1.470 gcm^{-3}, R= 0,034, R_w=0.038, T= 298K.

The coordination sphere of the tin atom can be described as a distorted pentagonal bypiramid with the phenyl groups in the apical positions and the five equatorial positions occuppied by the pentadentate thiosemicarbazonato dianion.



The spectroscopic properties of the compound in the solid state and in solution were explored by IR and NMR spectrometry respectively.

LAICM1144P **6, Tue. 14**

SYNTHESIS OF (2-THIAZOLIN-2-YL) HYDRAZINE HYDROCHLORIDE AND COORDINATION BEHAVIOUR TOWARDS DIVALENT TRANSITION METAL IONS.

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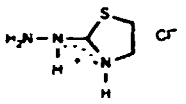
Synthesis of 2-thiazolines han been extensively employed an it is of particular interest, since thiazolines can be easily transformed into thiazoles or penicillin derivatives. Important naturally ocurring derivatives contain the 2-thiazoline ring. Likewise, compounds such as thiazoline-4-carboxilic acid (thiaproline) and 2-amino-2-thiazoline hydrochloride are both capable of inducing "reverse transformation" in tumour cells, they have undergone clinical trials in advanced human cancer and therapeutic activity is reported [1]. In the mechanism of action it is suggested that chelation was involved [2].

We report here the synthesis and characterization of (2-thiazolin-2-yl) hydrazine hydrochloride and its coordination by Co(II), Ni(II), Cu(II) and Zn(II).

The ligand was prepared by reaction of 2-Chloroethylisothiocyanate with hydrazine at room temperature. and was characterized by chemical analysis and IR, ^{1}H and ^{13}C NMR.



Coordination equilibria were investigated by potentiometric titration at 25°C, under nitrogen atmosphere, in aqueous solution of constant ionic strength (0.1 mol dm^{-3} $NaClO_4$). The composition of the various species formed in the systems studied were evaluated from the pH-metric titration data from three independent titrations involving different metal-to-ligand ratios from 1:1 to 1:3, with the MINIQUAD and SUPERQUAD computer programs. The numerical treatment showed the presence of the following species in the above-named systems: Co(II)/L.HCl = ML and MLH, Ni(II)/L.HCl = ML and ML_2, Cu/L.HCl = ML_2 and ML_2H and Zn(II)/L.HCl = MLH and ML_2H_2.

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[1] *Gonsálvez, M.; Vivero, C. and Alvarez, I. (1979) Biochem.Soc.Trans., 7, 191.*

[2] *Huang, Z.X., May, P.M., Williams, D.R. and Gonsálvez, M.; (1981) Inorg.Chim.Acta, 56, 41.*

LAICM1145P **7, Tue. 14**

POTENTIOMETRIC STUDY OF THE COORDINATION OF DIVALENT TRANSITION-METAL IONS TO 2-(BENZYLAMINO)-2-DEOXY-D-GLYCERO-L-GLUCO-HEPTONIC ACID

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Carbohydrates are often highly soluble in water and are usually only weakly immunogenic and of low toxicity. These properties are very useful in developing pharmaceutical agents. Thus, carbohydrate derivatives are useful for the design of new drugs. One such possibility is the development of chelates for the removal of toxic metals or the uptake of essential metals.

The manipulation of the aldehyde group in carbohydrates allowed to obtain carbohydrate α-amino acid derivatives [1], and so we present here a study about the interaction between the metal ions Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and the carbohydrate α-amino acid derived from galactose, 2-benzylamino-2-deoxy-D-glycero-L-gluco heptonic acid (BnGa). This ligand is interesting because it owns a polyhydroxylate chain and a benzyl group which give it a greater ability to interact with membranes cells and a certain lipid solubility, respectively.

The study in aqueous solution was made at 310K and ionic strengh 0.1M in $NaClO_4$. The ratios M(II)/ligand were 1/1, 1/2 and 1/3. The calculation and refinement of the stability constants was carried out by applying the MINIQUAD program to the potentiometric data. The numerical treatment showed that the polynuclear species were not formed. Furthermore, all the systems studied were found to contain complexes of the forms ML and ML_2 which agree with the behaviour of analogous α-amino acids as N-unprotected as N-protected [2].

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1. Galbis, J.; Palacios, J.C. and Roman, E., (1983) *Carbohyd. Res.*, **114**, 158.
2. Kiss,T., in *Biocoordination Chemistry. Coordination Equilibria in Biologically Active Systems*, K. Burger, Ed., 1990, Chap. 3, Ellis Horwood Limited, London.

LAICM1146P **8, Tue. 14**

INVESTIGATION OF MERCURY(II) COMPLEX EQUILIBRIA WITH FOUR SUGAR α-AMINO ACIDS. THE EFFECT OF THE ANION.

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Mercury in water constitutes a real danger for human health. By the action of microorganisms, mercury in the contaminated medium forms alkylmercuric compounds, which may reach man by means of food. The metabolism of these compounds leads to the accumulation of mercury in the brain and kidneys. The final and more important effect is the disfunction of the central nervous system. This persists even when ceasing the exposure to the mercury action, and a cure is not known for the disease [1].

We have recently focused our interest on the study of metal-carbohydrate α-amino acids complexes in solution and in the solid phase [2]. According this line of work, the complex formation of mercury(II) with four carbohydrate α-amino acids derived from glucose and mannose was investigated at 25°C in 0.1 mol dm^{-3} $NaClO_4$ aqueous solution by glass-electrode potentiometry.

From the analysis of the e.m.f. data in the systems by use of computer programs MINIQUAD and SUPERQUAD, it was concluded that the species formed in all the systems are [ML_2] and [ML(OH)]. The formation constants in the systems measured from different salts of mercury(II) show that the values obtained from $HgCl_2$ are extremely less than those observed from $Hg(NO_3)_2$, probably because chloride is bound to mercury(II) with high stability.

It is worth noting that the formation constants for the sugar α-amino acids N-unprotected have somewhat larger values than those for their respective N-protected α-amino acids, with a benzyl protecting group. This tendency may be explained on the assumption of the larger basicity of the former because of the benzyl group exert an electron-withdrawing effect on the amino group which reduces its basicity.

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1. International Inform. in *Boletin Informativo del Medio Ambiente* (1992), **24**, 93
2. Díaz Díez, M.A.; García Barros, F.J.; Sabio Rey, E. and Valenzuela Calahorro, C. (1992) *J. Inorg. Biochem.*, **48**, 129.

LAICM1147P **9, Tue. 14**

DICHLORODIOXOMOLYBDENUM(VI) COMPOUNDS FROM AQUEOUS MEDIA. CRYSTAL AND MOLECULAR STRUCTURE OF $[MoO_2Cl_2(H_2O)_2](diglyme)_2$

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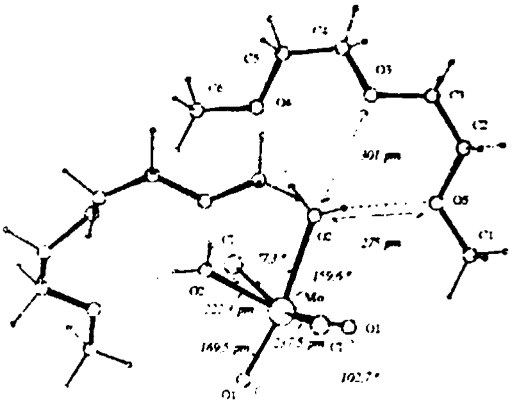
Dpto. de Química Inorgánica, Colegio Universitario de Burgos, 09001 Burgos, Spain.

Juliana Sanz-Aparicio and Martin Martinez-Ripoll
CSIC, UEI Cristalografía, Inst. Rocasolano, Serrano 119, 28006 Madrid, Spain.

Although common molybdates are convenient sources of many dioxomolybdenum(VI) compounds, there is a good number of them that requires starting from MoO_2Cl_2, a material of somewhat tedious preparation in pure form. Some efforts are being directed to develop easier synthetic routes, a good example being the isolation of molybdenum(VI) imidocomplexes[1]. Recently we have described the facile synthesis of $MoO_2Cl_2(DMSO)_2$ starting from hydrochloric solutions of MoO_3 and we report here the behaviour of these solutions with some other common ligands.



Treatment of aqueous hydrochloric solution of MoO_3 with an excess of dmf or hmpa led to the precipitation of the known cis-trans-cis-$MoO_2Cl_2(L)_2$ (L = dmf, hmpa), as microcrystalline solids. The solution obtained with diglyme, upon standing overnight at room temperature, led to a white crystalline mass that analysed as $[MoO_2Cl_2(H_2O)_2]$ $(diglyme)_2$. The ^1H NMR pattern of the diglyme in the compound is closed to that of free diglyme. The broad singlet corresponding to water in acetone-d_6 moves from 6.0 to 3.7 δ growing in intensity as water is being added, showing the labile character of coordinated water in the complex.

This product is stable for weeks at room temperature if stored in the darkness under dry argon. It is very soluble in diethylether, solvent from which it can be recovered unchanged. Treatment of this solution with $SOCl_2$ at room temperature led to a colorless oil whose ^1H NMR in $DCCl_3$ showed no evidence of water and in dmso-d_6 displays the characteristic pattern of free diglyme.

The compound presents two-fold symmetry, the crystallographic two-fold axis passing through Mo atom. The Mo-O bond length and O-Mo-O angle are within the narrow range usually found in dioxomolybdenum compounds. The polyether molecule presents cis-cis conformation stabilised by optimised hydrogen-bonding pattern. Apart from the two hydrogen bonds shown in the Fig. there is some bifurcated interaction between the central O and both hydrogens of the water molecule showing some kind of "molecular recognition" between the diglyme moiety and the $MoO_2Cl_2(H_2O)_2$ unit. In this way, the core defined by the molybdenum coordination sphere is almost buried in a hydrophobic environment which might explain the high solubility of the product in diethylether.

(1) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R.; *Inorg. Chem.* 1992, *31*, 2287

LAICM1155P 10, Tue. 14

THE CRYSTAL STRUCTURE OF TETRAETHYLAMMONIUM TRICHLORODIPHENYLSTANNATE(IV).

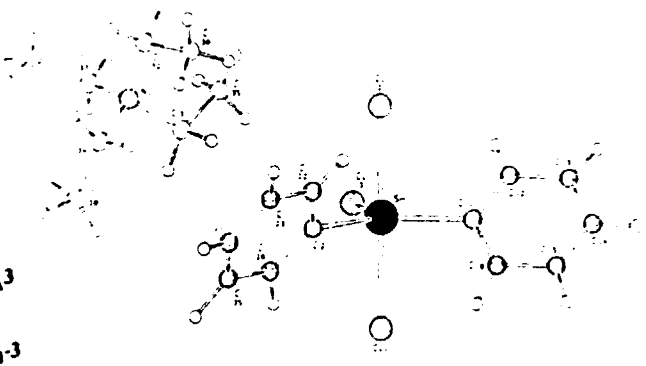
E. García Martínez, A. Sánchez González, A. Castiñeiras, J.S. Casas and J. Sordo.

Departamento de Química Inorgánica, Universidade de Santiago de Compostela, Santiago de Compostela, Galicia (Spain).

Crystallization of $(Et_4N)[SnPh_2Cl_3(Hmimt)]^1$ (Hmimt = 1-methyl-2(3H)-imidazolinethione) unexpectelly gives the tittle compound. Its structure was determined by X-ray diffraction using direct methods.

Crystal data:

$C_{20}H_{30}Cl_3NSn$
M = 509.52
Monoclinic
$P2_1/n$
a = 9.725(1) Å
b = 13.648(1) Å
c = 17.749(2) Å
ß = 101.491(6)°
V = 2308.5(5) $Å^3$
Z = 4
D_x = 1.466 gcm^{-3}
R = 0.025
Rw = 0.025



The crystal consists of isolated $(Et_4N)^+$ cations and $[SnPh_2Cl_3]^-$ anions. The values of bond lengths and angles in the cation are unremarkable. In the sligthly distorted bipyramidal trigonal anion C(11)-Sn-C(21) = 127.51(8), the mean length of the axial Sn-Cl bonds [2.5241(7) Å] is greater than the length of the equatorial Sn-Cl bond [2.3776(7) Å] and the Sn-C bond lengths are close to those found in other diphenyltin pentacoordinated compounds.

LAICM1162P **11, Tue. 14**

LANTHANIDE COMPLEXES OF A 15-MEMBERED N_3O_2 MACROCYCLE LIGAND

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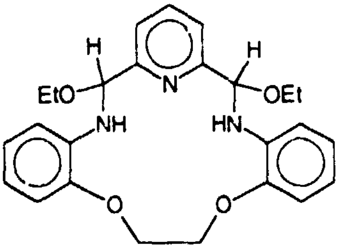
Departamento de Quimica Inorganica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela (España).
[a]Departamento de Quimica Fundamental e Industrial, Universidad de La Coruña, La Coruña (España).

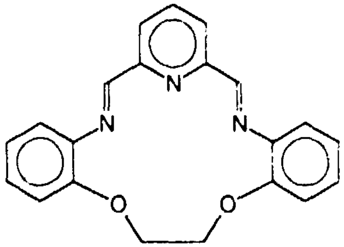
Macrocycles have attracted much attention amongst inorganic chemists in the past decades. An interesting feature of macrocyclic systems is that ligand size can be easily changed by synthesis which have a close impact on the enclosed metal ion.

Condensation reactions between dicarbonyl and primary diamine compounds in the presence of a templating metal ion have played a central role in the preparation of macrocyclic complexes.[1] Reaction of pyridine-2,6-dicarbaldehyde with 1,2-bis(2-aminophenoxy)ethane in EtOH or the use of Mg(II) as the potential template directly lead to the crystallisation of macrocycle (**1**) instead of the corresponding diimine macrocycle (**2**).[2]

In the present communication we report the synthesis of $[Ln(2)](ClO_4)_3$ complexes of the 15-membered pentadentate-N_3O_2 macrocyclic ligand (**2**) by template synthesis using hydrated lanthanide perchlorates. The compounds have been characterised by elemental analysis (C, H, N) and by i.r. and ^1H n.m.r. spectroscopy.



(**1**)



(**2**)

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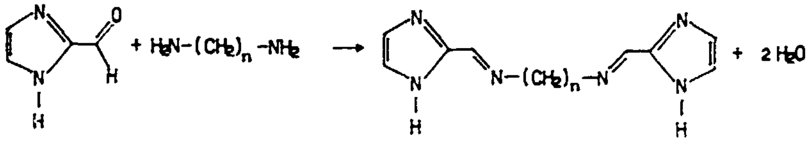
1. M.C. Thompson and D.H. Busch, *J. Am. Chem. Soc.*, (1964) **86**, 3651.
2. D. H. Cook and D. E. Fenton, *Inorg. Chim. Acta*, (1977) **25**, L95.

COMPLEXES OF Mn(III) WITH SCHIFF BASES DERIVED FROM IMIDAZOL-CARBOXALDEHYDE

M.R. Bermejo, A. García Deibe, L. Luaces, M. Rey, J. Sanmartín, A. Sousa, C.A. McAuliffe*.
Departamento de Química Inorgánica. Facultade de Química. Universidade de Santiago de Compostela. E-15706. Galicia.
* Chemistry Department. UMIST. Manchester. M60 1QD. United Kingdom.

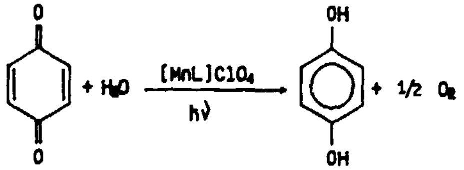
Manganese(III) complexes are inorganic systems of great biological interest because of their essential role in many metalloproteins. In this communication we present the synthesis, structural characterization and photochemical behaviour of some Mn(III) complexes with Schiff bases derived from imidazol-carboxaldehyde.

The Schiff bases were obtained by condensation of imidazol-2-aldehyde and ethylendiamine, 1,3-diaminopropane y 1,4-diaminobutane, respectively, in ethanol, according to the following reaction:



The complexes prepared were characterized by elemental analysis and were studied by electronic and vibrational spectroscopies, as well as by magnetic measurements.

The photochemical studies were performed to follow the process:



a) The O_2 evolution was determined measuring the increasing of O_2 concentration in solution by the using of an oxymeter.

b) The appearing of hydrogen was registered by the variation of the UV-V spectrum of the p-benzoquinone transforming into quinol.

LAICM1164P **13, Tue. 14**

SYNTHESIS AND CHARACTERIZATION OF $[MnL]ClO_4.nH_2O$ COMPLEXES

M.R. Bermejo, A. García Deibe, E. Gómez Fórneas, M. Rey, J. Sanmartín, A. Sousa and C.A. McAuliffe*.
Departamento de Química Inorgánica. Facultade de Química. Universidade de Santiago de Compostela. E-15706. Galicia
* Chemistry Department. UMIST. Manchester M60 1QD. U.K.

During our investigations on the coordination chemistry of Mn(III) with tetradentate dianionic Schiff bases of the type N_2O_2, we have found that many of the studied complexes are capable of decompose water in O_2 and H_2, when irradiated by visible light. This behaviour seems to mimic the WOC (Water Oxidation Complex) of photosystem II (PS II) of the green plants.

We present, in this communication, the synthesis and structural characterization by IR, ^1H NMR, (FAB) mass spectroscopies and magnetic measurements of complexes of the type $[MnL]ClO_4.nH_2O$, being H_2L the Schiff base ligands showed in fig. 1.

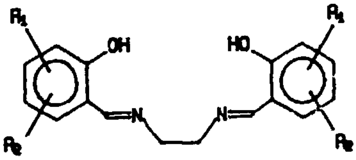
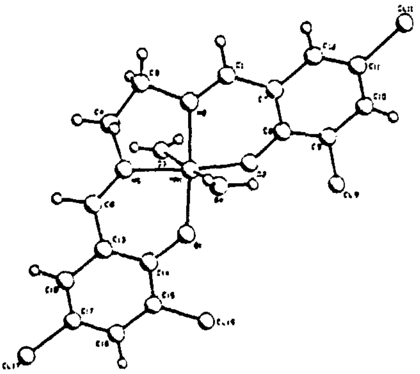


Fig. 1



The crystal structure of the complex [Mn(salen-3,5-Cl]$ClO_4.2H_2O$ has been solved and consists of monomeric octahedrical units, where the Schiff base occupies the equatorial plane and two capping water molecules are on the axial positions.

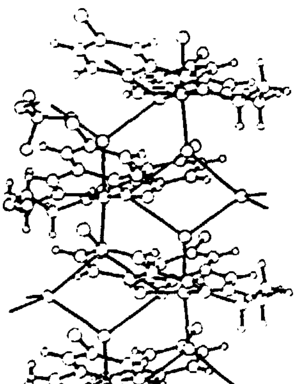
The complexes prepared show photochemical activity and seem to behave like promoters of the water photodecomposition into oxygen and hydrogen.

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW Mn(III) COMPLEXES WITH SYMMETRICAL SCHIFF BASES

M.R. Bermejo, A. García Deibe, L. Luaces, M. Rey, J. Sanmartín, A. Sousa, C.A. McAuliffe*.
Departamento de Química Inorgánica. Facultad de Química. Universidad de Santiago de Compostela. E-15706. Galicia.
* Chemistry Department. UMIST. Manchester. M60 1QD. United Kingdom.

The coordination chemistry of Mn(III) with Schiff bases is of great interest due to the similarity between these complexes and different biological systems, that act as catalysts in the oxidation of organic substracts, mimicing biochemical processes of oxygen transference.

In this communication, we present the synthesis and structural characterization of new Mn(III) complexes with symmetrical Schiff base ligands. These complexes have been characterized by elemental analysis, mass (FAB) and infrared spectroscopies and magnetic measurements. At the same time, we have studied their possible photochemical activity.



The figure shows the structure of the compound $[Mn(salpn\text{-}5\text{-}Br)(OH_2)_2]ClO_4.H_2O$. The x-ray diffraction studies show that the complex is a monomer, where the donor atoms of the tetradentate ligand are in the equatorial plane, occupying the axial positions, two water molecules, complete a distorted octahedrical environment around the metal.

Its macrostructure presents infinite spirals with a helicoidal axis along *c*. This is the result of the formation of hydrogen bonding between the coordinated water molecules and the phenolic oxygen atoms of the next monomeric unit, and the overlapping of the aromatic rings of contiguous units. Besides, hydrogen bonding exits between the oxygen atoms of the perchlorate anion and the coordinated water molecules.

LAICM1166P **15, Tue. 14**

SYNTHESIS AND CHARACTERIZATION OF HOMO AND HETEROBINUCLEAR PIRAZOLATE-BRIDGED COMPLEXES

B. Fernández, M.I. Fernández, E. Gómez Fórneas, M.R. Bermejo* and J.P. Costes**

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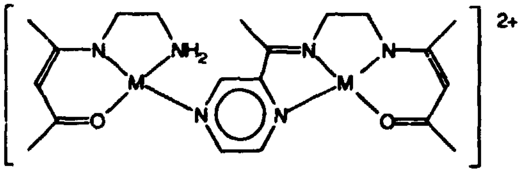
* Departamento de Química Inorgánica. Facultad de Química. Universidad de Santiago de Compostela. E-15706.

** Lab. de Chimie de Coordination du CNRS. Toulouse. FRANCE.

A non-symmetrical tetradentate Schiff base (HAEPyz) has been prepared and characterized. HAEPyz is the result of the condensation of tridentate Schiff base 7-amino-4-methyl-5-aza-3-hepten-2-one (HAE)[1] with 2-acetylpyrazine. This ligand can be monoanionic by deprotonation of the -NH group.

Monometallic complexes were obtained by mixing of the ligand HAEPyz and a metallic salt in ethanol. These complexes have a nitrogen atom of the pyrazine fragment that remains free and therefore, able to link a second metallic ion. Homo and heterobimetallic complexes have been obtained with pyrazine-bridges (fig. 1) $[MLM'L']X_2$, being M,M'= Cu^{2+}, Ni^{2+}; L= AEPyz and L'= AE similar to the complexes already obtained with imidazolate-bridged[2].



$[M(AEPyz)M'(AE)]^{2+}$

Fig. 1

All the complexes have been characterized by elemental analysis, spectroscopic techniques: IR, ^1H NMR and UV-V and magnetic measuremens.

[1] Costes J.P., Cros G.; *C.R. Acad. Sci. Ser. B.* (1982) 173, 294.

[2] Costes J.P., Fernández M.I.; *Inorg. Chim. Acta* (1990) 247-54.

SYNTHESIS, REACTIVITY AND MAGNETIC PROPERTIES OF NEW $[Mn_2O(RCOO)_2]^{2+}$ CORE.

B. Albela, M. Corbella, J. Ribas.

Departament de Quimica Inorgànica. Universitat de Barcelona. Diagonal 647. 08028 -Barcelona. Spain.

There are numerous enzymes that specifically require manganese and some use the redox capabilities of this element as well, i.e. manganese catalases. These enzymes mediate the conversion of H_2O_2 to H_2O and O_2. Mn catalases contain a binuclear manganese site and have at least four accessible oxidation states; the structure is not clear, but it is suspected to have a $[Mn(III)_2O(RCOO)_2]$ core.

We have centered our work on the synthesis of new binuclear Mn (III) complexes with this core: $[L(bipy)Mn\ O\ (RCOO)_2\ Mn(bipy)L]^{+n}$ with R= Ph 1,*o* , *m* -, *p* - ClPh 2-4 and *2,6*- Cl_2Ph 5. The magnetic properties of these compounds are different. Mn(III) Mn(III) are ferromagnetically coupled for 1- 4; while 5 is antiferromagnetic.

The ESR spectra for the binuclear ferromagnetic complexes Mn(III) Mn(III) show a band at low fields characteristic of the compounds with a ground state S=4.

This series of binuclear complexes can oxidize the H_2O_2 into oxygen, giving the corresponding binuclear manganese (II) compounds. This reaction is very fast for the complexes 1 to 4, but the complex 5 is very difficult to reduce.

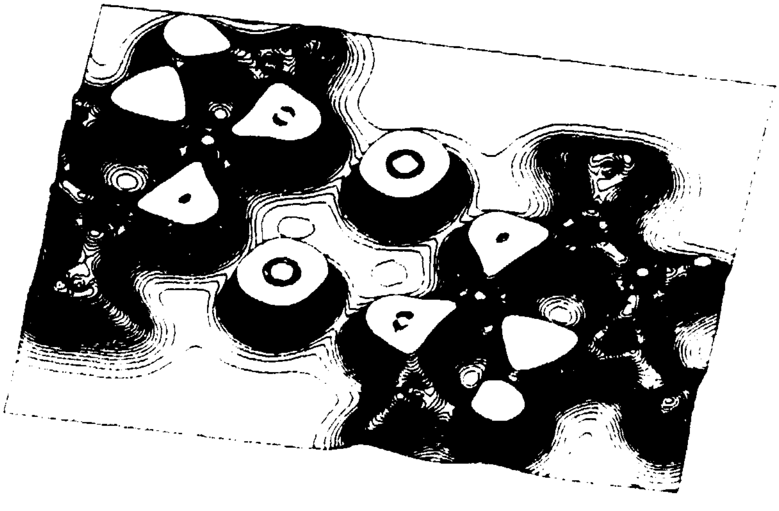
The ESR spectra for the binuclear Mn(II) Mn(II) compounds show a band centered about g=2 in solid state and, in solution, show the hyperfine coupling to the nuclei of Mn (I=5/2).

AN *AB INITIO* STUDY OF THE SILVER-SILVER INTERACTION IN A DIMER COMPLEX WITH A TRIAZOLE PYRIMIDINE DERIVATIVE.

M.A. Romero Molina. J.M. Salas Peregrín. M.P. Sánchez Sánchez. A. Rahmani. M Quirós Olozábal and J. Molina Molina. *Departamento de Química Inorgánica. Universidad de Granada. 18071 GRANADA (Spain).*

This communication continues our work on the interaction of metal ions with triazolo pyrimidine derivatives. Several silver complexes of 5.7-dimethyl-[1.2.4] triazolo[1.5-a]pyrimidine (DMTP) have been synthesized. their formula being $[Ag_2(DMTP)_2(NO_3)_2]$. $[Ag_2(DMTP)_2(SO_4)]\cdot 4H_2O$. $[Ag(SO_4)(H_2O)_2](DMTPH)$. $Ag(DMTP)_2(ClO_4)\cdot H_2O$ and $Ag_2(DMTP)_3(ClO_4)_2\cdot 2H_2O$. The crystal structure of the nitrate compound has been determined by X-ray diffraction.

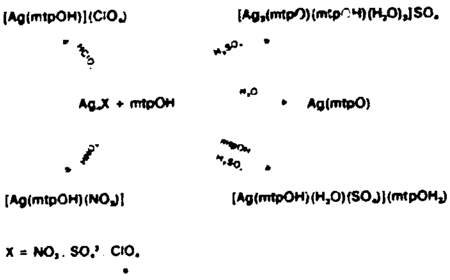
Likewise. this compound has been studied theoretically. its electronic structure having being calculated by *ab initio* methods. The figure below displays a relief map of the electronic charge in the molecular plane of the complex. In this figure. a critical bond point (a saddle point of the electron density function) appears in the middle of the silver atoms on the dimer. suggesting thus that there is indeed a bond between them



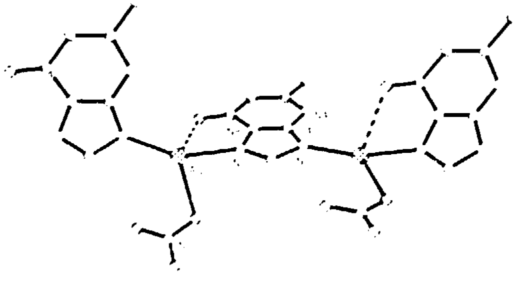
LAICM1178P **18, Tue. 14**

5-METHYL-7-HYDROXY-1,2,4-TRIAZOLO[1,5-a]PYRIMIDINE: A VERSATILE LIGAND. REACTIVITY TOWARDS Ag(I). J. Rodríguez Navarro, M.A. Romero Molina, J.M. Salas Peregrin, M. Quirós Olozábal, M.N. Moreno Carretero y F. Hueso Ureña. *Departamento de Química Inorgánica. Universidad de Granada. 18071 GRANADA (Spain).*

5-Methyl-7-hydroxy-1,2,4-triazolo[1,5-a]pyrimidine (mtpOH) is a purine mimetic compound with a wide versatility to bind metal ions. Its reactivity towards Ag(I) is different depending on the reaction media and the used silver salt, yielding the compounds that are indicated in the following scheme:



The structural characterization of these compounds is being performed by monocrystal X-ray diffraction. A view of the polymeric chain of [Ag(mtpOH)(NO$_3$)] is shown in the below figure. IR data suggest that ClO$_4^-$ and SO$_4^{2-}$ ions are not directly bound to the metal atom in [Ag(mtpOH)](ClO$_4$) and [Ag$_2$(mtpO)(mtpOH)(H$_2$O)$_2$](SO$_4$), while sulphate would be bidentately coordinated in [Ag(mtpOH)(H$_2$O)SO$_4$](mtpOH$_2$).



LAICM1189P **19, Tue. 14**

COPPER (I) AND GOLD (I) COMPLEXES WITH DIBASIC NITROGEN AND PHOSPHORUS LIGANDS

B. Turpin, A.M. Larsonneur, P. Ferté, G. Bernardinelli* and P. Castan

Laboratoire de Chimie Inorganique, Université Paul Sabatier, 118 route de Narbonne, Toulouse, France. * Laboratoire de Cristallographie X, 24 quai Ernest Ansermet, Genève, Switzerland.

Numerous stoechiometries and structures are known for L_nMX complexes (M = Cu, Au) where L is a monodentate nitrogen or phosphorus base, and X a coordinating anion[1, 2]:

L_4Cu^+	L_3CuX	L_2CuX	$L_{1.5}CuX$	$LCuX$
L_4Au^+		L_2AuX		

Because of the variety of potential bonding modes (via nitrogen or phosphorus), it seemed interesting to determine the kind of compounds and the stereochemistry of complexes formed by the bidentate hybrid ligand $Ph_2PCH_2NPh_2$. in this case, possible types of linkage include unidentate bonding through one donnor site, chelation to one metal atom or bridging between two different metal centers.

By addition of $Ph_2PCH_2NPh_2$ to Cu(I) (or Au(I)) and Cu(II) compounds, the ligand acting as complexing and reducing agent, we have synthetized new complexes whith a general formula :

ML_2X M = Au, Cu X = Cl, I, NO_3, ClO_4

The low values of molar conductances in acetone indicate their non electrolytic nature. The complexes have been characterized by IR, ^{31}P, ^{13}C and ^1H NMR spectroscopies however broad signals which appear in solution reveal the existence of exchange reactions. The X-ray structures of CuL_2Cl, CuL_2NO_3 and AuL_2Cl have been determinated. For CuL_2Cl, the coordination geometry about the copper atom is essentially trigonal planar, the ligand being bonded only through the phosphorus atom.

1. S.J. Lippard et al., Inorg. Chem., 1976, 15, 1155.
2. A.H. White et al., J. Chem. Soc. Dalton Trans., 1987, 1089.

LAICM1190P **20, Tue. 14**

NEW σ-BONDED TCNQ NICKEL COMPLEXES WITH POLYDENTATE NITROGEN LIGANDS

M.T. Azcondo, L. Ballester, M.C. Barral, A. Gutiérrez, R. Jiménez, M.F. Perpiñán, A. Sánchez.

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, SPAIN

In the recent years a number of attempts have been made to obtain the so-called *molecular metals* using metal complexes and TCNQ (7,7,8,8-tetracyanoquinodimethane). We have recently proved that polydentate nitrogen molecules are useful ligands in order to prevent the formation of the very stable $[Ni(TCNQ)_2]$ in the reactions of nickel(II) complexes with $TCNQ^-$.

In these reactions, listed below, charge-transfer complexes with different metal to TCNQ ratios have been obtained. On the basis of spectroscopical and magnetic data we can describe the metal environment in $[Ni(N_4)(TCNQ)_2]$ as hexacoordinate with two axial monodentate TCNQ as it has been found by us in the reaction of 1,8-dihydroxyethyl-1,3,6,8,10,13-hexa-azacyclotetradecane nickel(II).

N_2

$[Ni(en)_3]X_2 \xrightarrow{TCNQ^-} [Ni(en)_3(TCNQ)_2]$

$[Ni(en)_3]X_2 \xrightarrow{TCNQ^0 + TCNQ^-} [Ni(en)_2(TCNQ)_2]\cdot 2H_2O$

$[Ni(tn)_2(H_2O)]X_2 \xrightarrow{TCNQ^-} [Ni(tn)_2(TCNQ)_2]\cdot H_2O$

$[Ni(C_6H_{14}N_2)_2]X_2 \xrightarrow{TCNQ^-} [Ni(C_6H_{14}N_2)_2(TCNQ)X]$

N_3

$[Ni(dien)_2]X_2 \xrightarrow{TCNQ^-} [Ni(dien)(TCNQ)_2]$

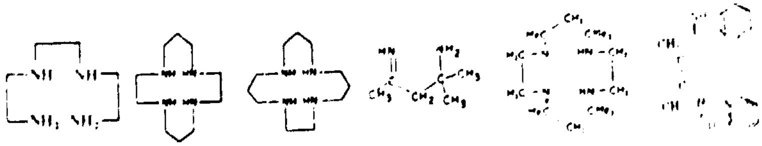
N_4

$[Ni(N_4)]X_2 \xrightarrow{TCNQ^0 + TCNQ^-} [Ni(N_4)(TCNQ)_3]$

$[Ni(N_4)]X_2 \rightarrow [Ni(N_4)(TCNQ)_2]$

$[Ni(N_4)]X_2 \rightarrow [Ni(N_4)(TCNQ)X]$

$[Ni(N_4)]X_2 \xrightarrow{TCNQ^-} [Ni(N_4)(TCNQ)]$



LAICM1192P **21, Tue. 14**

CRYSTAL STRUCTURE OF 5-MERCAPTO-1-METHYL-1,2,3,4-TETRAZOLE METHYLMERCURY(II)

J. Bravo, R. Carballo, B. Cordero and J.S. Casas*.

Departamento de Química Pura y Aplicada. Universidad de Vigo. Aptdo. 874. Vigo (Spain).

**Departamento de Química Inorgánica. Universidad de Santiago de Compostela. (Spain).*

The crystalline solid obtained by reacting an aqueous solution of methylmercury hidroxide with an ethanolic solution of 5-mercapto-1-methyl-1,2,3,4-tetrazole[1] was studied by X-ray diffraction at -50 °C.

Crystal data of $C_3H_6N_4SHg$: M = 330.76, monoclinic, space group $P2_1/m$, a= 10.579(3) Å, b= 6.603(3) Å, c= 10.724(3) Å, β= 98.97(1)°, V= 739.9 Å^3, Z= 4, Dx= 2.969 g cm^{-3}, μ= 209.943 cm^{-1}, F(000)= 592, R= 0.054, Rw = 0.064 for 830 observed reflections with $I \geq 3\sigma(I_o)$.

The assymetric unit is constituted by two planar molecules. The methyimercury is coordinated to the S thiolic atom of the ligand (d_{Hg-S} = 2.38 Å) and it forms also a secondary intermolecular interaction with a nitrogen atom of the next molecule in the same assymetric unit (d_{Hg-N} = 2.76 Å) giving a T coordination. The C-Hg-S angle has values of 173° and 178°.

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[1] B. Cordero, J. Bravo and J.S. Casas. IV Encontro Luso-galaico de Química. Porto, november, 1990.

LAICM1193P **22, Tue. 14**

A STRUCTURAL STUDY OF SOME NEW MANGANESE(III) AND (IV) COMPLEXES

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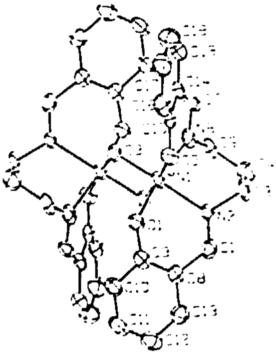
C.A. McAuliffe, R.G. Pritchard.
Chemistry Department. UMIST. Manchester M60 1QD. UNITED KINGDOM.

There is a great interest on the synthesis of manganese(III) or (IV) complexes, in an attempt to mimic the water photolysis action of the photosystem II (PS II) of the green plants. We have succeeded in generating molecular oxygen by visible irradiation of an aqueous solution of the complex [Mn(salpn)](ClO_4).nH_2O[1] in the presence of *p*-benzoquinone. Recently we have prepared new manganese(III) complexes with symmetrical and non-symmetrical tetradentate Schiff bases of the type N_2O_2[2].



Structure of the cation [Mn(salpn)(O)]$_2^{2+}$

This communication reports the X-ray structure of some manganese(III) and (IV) complexes. Some of these complexes are monomers and others are binuclear (see figure). We have also find that some of the unsymmetrical ligand complexes rearrange to symmetrical ligand complexes[2].

[1] F.M. Ashmawy, C.A. McAuliffe, R.V. Parish, J. Tames; J. Chem. Soc.Dalton Trans., 1391 (1985)

[2] A. García Deibe, A. Sousa, M.R. Bermejo, P.T. Ndifon, P. McGlynn, C.A. McAuliffe, R.G. Pritchard; J. Chem. Soc. Dalton Trans. in press (1993).

LAICM1194P **23, Tue. 14**

OXYGEN EVOLUTION STUDIES OF Mn(III) SCHIFF BASE COMPLEXES

M.R. Bermejo, A. García Deibe, E. Gómez Fornéas, M. Rey, J. Sanmartín, A. Sousa and C.A. McAuliffe.*
Departamento de Química Inorgánica. Facultade de Química. Universidade de Santiago de Compostela. E-15706. Galicia
* Chemistry Department. UMIST. Manchester M60 1QD. U.K.

Manganese plays an essential and specific role in the oxygen evolution centre (OEC) of photosystem II (PS II) and there is currently a great deal of interest in mimicing the photolysis process.

A number of new manganese(III) complexes of the type $[MnL]ClO_4.nH_2O$ (L= the dianion of N_2O_2 symmetrical and unsymmetrical schiff bases) have been synthesized and characterized by elemental analysis, magnétic susceptibility measurements, IR and fast atom bombardment (FAB) spectrometry.

We propose here a new authomatic device to do photolysis experiments "in continuo" using these new manganese(III) complexes. All the compounds have been shown to liberate dioxygen and reduce p-benzoquinone to hydroquinone from aqueous solution when irradiated with visible light. The photoactivity of the compounds is dependent on the ligand.

We have also isolated the post photolysis manganese complexes and have found there to be not change in manganese oxidation state, although ligand rearrangements do sometimes occur.

Thus these manganese(III) complexes not only promote dioxygen evolution, and concurrent p-benzoquinone reduction, but can, in some cases, also produce ligand rearrangement.

COPPER(II) COMPLEX WITH A BINUCLEATING LIGAND DERIVED FROM ISOPHTALDEHYDE AND DI(2-PYRIDYL)METHYLAMINE

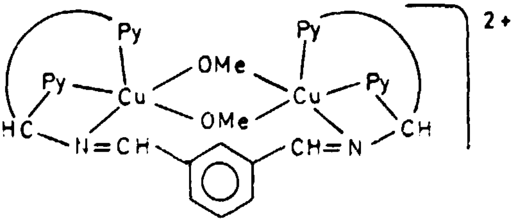
A.M. García[1], J. Manzur[1], M.T. Garland[1], R. Baggio[2], E. Spodine[3]

[1] Facultad de Ciencias Físicas y Matemáticas, U. de Chile. Casilla 2777, Santiago, Chile.
[2] Comisión de Energía Atómica, Buenos Aires, Argentina
[3] Facultad de Ciencias Químicas y Farmacéuticas, U. de Chile, Casilla 233, Santiago, Chile.

Binuclear copper(I) complexes, where the coordinated polydentate ligands undergo copper mediated hydroxylation reactions with dioxygen have been extensively studied by Karlin and Sorrell. Since the ligand remains coordinated after the reaction, the transformed ligand is part of the oxidized copper(II) complex product.

A Schiff base ligand derived from isophtaldehyde and di-(2-pyridyl)methylamine was prepared in order to obtain the copper(I) complex. This species was reacted with molecular oxygen in order to obtain the hydroxylated copper(II) complex.

The structure of the reaction product was determined by x-ray diffraction. Hydroxylation of the arene ring was not observed. The isolated product is a bibridged methoxo binuclear copper(II) complex (1). Each metal center is pentacoordinated, with a distorted square-pyramidal geometry. The basal plane of the copper(II) atoms is described by the two nitrogen atoms of the pyridine rings, and by the two oxygen atoms provided by the bridging methoxo groups. The apical position corresponds to the imine nitrogen atom.



(1)

Financial Support: FONDECYT 1931001

LAICM1198P **25, Tue. 14**

KINETIC DETERMINATION OF THE Fe-H_2 BOND DISSOCIATION ENERGY IN FeH(H_2)(dmpe)$_2^+$.

[a]M.A.Máñez,[a]M.J.Fernández-Trujillo,[b]G.J.Leigh,[a]M.García Basallote

[a]Departamento de Quimica Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, España.

[b]AFRC IPSR Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, U.K.

Transition metal dihydrogen complexes have been extensively studied in the last years, but most work deals with the synthesis, characterization and reactivity of these complexes and little is known about the solution behaviour of these species. In this communication we present a preliminary report of the kinetic of reaction between FeH(H_2)(dmpe)$_2^+$,**1**, and L in thf (L= N_2, PhCN).

$^{31}P\{^1H\}$ NMR spectra of solutions of **1** in thf under N_2 show the formation of FeH(N_2)(dmpe)$_2^+$,**2**, from **1** without formation of detectable amounts of any other species. At 25°C, both the formation of **2** and the disappearance of **1** are first order processes with a rate constant of $1.02 \cdot 10^{-3}$ s^{-1}. The kinetics of reaction of **1** with PhCN in thf under argon is similar, with a value of $1.08 \cdot 10^{-3}$ s^{-1}. These results are consistent with Fe-H_2 bond dissociation being the rate-determining step in substitution reactions of **1**.

A detailed spectrophotometric study of the reaction with PhCN reveals that the process is first order in **1** and independent of the concentration of incoming ligand. Relevant kinetic parameters are k(25°C)=$0.73 \cdot 10^{-3}$ s^{-1},$\Delta H^{\#}$=19.8±0.2 Kcalmol^{-1}and $\Delta S^{\#}$=-6.6±0.7 e.u. Provided that the usual assumptions are made, the value of $\Delta H^{\#}$ can be used as an estimation of the Fe-H_2 bond dissociation energy that is for this complex higher than the calculated value of 12.0 Kcalmol^{-1} [1].

[1] F.Maseras,M.Duran,A.LLedós,J.Bertrán,J.Am.Chem.Soc. 1991,113,2879-2884.

LAICM1199P **26, Tue. 14**

KINETICS OF SUBSTITUTION REACTIONS OF trans-$[Mo(N_2)_2(PPh_2Me)_4]$ WITH THE TRIPOD LIGANDS NP_3 AND PP_3.

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Departamento de Quimica Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11500 Puerto Real, España.

In a recent paper[1], we showed that trans-$[Mo(N_2)_2(PPh_2Me)_4]$,**1**, reacts with PP_3 to give $Mo(PP_3)_2$. On the other hand, we have not yet been able to isolate any complex from the reaction mixture of **1** and the related phosphine NP_3. A kinetic study of both reactions has been carried out to obtain data that could explain the different behaviour of both phosphines.

The kinetics of both processes is similar and very complicated, as revealed by the existence of four steps in the Abs. vs. t. profiles. There are three fast steps completed in the first 1000 s at 25°C and then there is a slower process that leads to the formation of the final products. The kinetic curves can be analyzed using non-linear least-squares methods to obtain the values of the four rate constants. 31P{^{1}H} NMR spectra taken at regular intervals during the reaction have been used to determine the order of ocurrence of the four steps and to propose structures for the reaction intermediates.

The proposed mechanism consists in the initial dissociation of PPh_2Me to form the intermediate previously detected[2] in the decomposition of **1**. This intermediate can then react through two parallel pathways:decomposition to form Mo and reaction with the tripod phosphine. The values obtained for the second rate constants indicate that decomposition is the major pathway in the case of NP_3, what could explain the difficulties found to isolate Mo-NP_3 complexes.

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[1] M.García Basallote,P.Valerga,M.C.Puerta,A.Romero,A.Vegas y M.Martinez-Ripoll,J.Organomet.Chem.1991,420,371.

[2] M.A.Máñez,M.C.Puerta,P.Valerga,M.García Basallote,J.Chem.Soc.,Dalton Trans.,1992,1491.

LAICM1205P **27, Tue. 14**

CYCLOMETALLATED Pd(II) and Pt(II) COMPLEXES OF 2-PHENYLIMIDAZOLINE

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&Lab. Difracción de R.X. Fac. Ciencias Químicas, UCM, 28040-Madrid

In this work we described the syntheses of some platinum and palladium cyclometallated complexes with imidazole derivatives as ligands. These kind of complexes could be interesting because recently it has been found that complexes with planar ligands seem show a special antitumor activity

Cyclometallation of 5-members aryl substituted heterocycles, such as pyrazoles and imidazoles, require to protect the -NH- group to avoid others reactions. The reactions with 2-phenylimidazoline (imd) lead to the formation of cyclometallated complexes with a planar arrangement of the ligands maintaining the -NH- group unaltered.

The compounds prepared have a general formula $[M(\mu\text{-}X)(N,C\text{-imd})]_2$ (M= Pd,Pt; X=AcO, Cl). These complexes have been characterizated by ^{1}H,^{13}C-NMR and IR spectroscopies and elemental analyses. The complex $[Pd(\mu\text{-}AcO)(N,C\text{-imd})]_2$ shows a dimeric folded structure with acetate bridge as it is indicated in the figure. Pd-Pd intramolecular distance is 2.832(1)A and the dihedral angle between the coordination planes of the palladium atoms is 26.1(3)°. Each palladium atom is in a slightly distorted square-planar coordination enviroment.

It was studied the conformational changes of DNA induced to the interaction with these complexes (by Tm, DC and electrophoresis) and "*in vitro*" studies were realized against tumoral cells.

Acknowledgment This work was supported by grand No. FAR 90-0516.

LAICM1206P **28, Tue. 14**

PLATINUM (II) AND (IV) SPERMINE COMPLEXES.

P. Amo. Ochoa*, C. Alonso&, J.R.Masaguer*, C. Navarro-Ranninger*.
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&Dpto Bioquímica. Facultad de Ciencias. U.A.M. 28049-Madrid España.

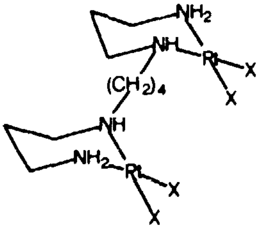
Carboplatin and iproplatin are second generation antitumor drugs, which are more soluble than cis-DDP. They show specific reactivity against particulars types of tumors. It is likely that the Pt(IV) complexes, reducible to Pt(II) in physiological conditions, which have amino or imino ligands with potentially biological activity as well as more than one electrofile centre (poli-Pt), present advantages over the Pt(II) complexes.

In the present work, we have prepared various bis platinum (II, IV) spermine compounds.

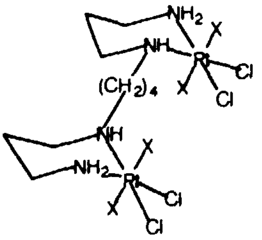
$$K_2PtCl_4 + \text{spermine} \rightarrow Pt_2\text{spermine}Cl_4(1) \xrightarrow{H_2O_2,\ HCl} Pt_2\text{spermine}Cl_4X_4(4.5)$$

$$K_2PtCl_4 + DMSO \rightarrow cis\text{-}Pt(DMSO)_2Cl_2 \xrightarrow{Ag_2oxalate} Pt_2\text{spermine(oxalate)}_2(2.3)$$

The compounds were characterized by microanalyses, IR, ^1H, ^{13}C and ^{195}Pt NMR spectroscopies.



X= Cl(1), Malonate(2), ciclobutanedicarboxilate(3)



x=OH(4), Cl(5)

^{195}Pt NMR Platinum spermine compounds.

Compounds	1	2	3	4	5
δ(ppm)	-2253	-1973	-1958	-872	-86

We have studied the interaction of these complexes with DNA.

Acknowledgment: The work was supported by Bristol-Myers.S.A.E

LAICM1207P **29, Tue. 14**

IN VITRO CYTOSTATIC ACTIVITY OF PLATINUM AND PALLADIUM COMPLEXES WITH BENZOYLBENZYLIDENEAMINES.

I. López-Solera,[a] J.M. Pérez,[b] A. Alvarez-Valdés,[a] C. Navarro-Ranninger,[a] C Alonso,[b] J.R. Masaguer.[a]

[a]*Departamento de Química.* [b]*Departamento de Biología Molecular. Universidad Autónoma. Cantoblanco 28049-Madrid. Spain.*

We have studied the DNA reactivity *in vitro* proliferative activity of several cyclometallated complexes of platinum(II) and paladium(II) derived from benzoylbenzylideneamines. All these compounds were screened *in vitro* against two human tumour cell lines, MDA-MB 468 (breast carcinoma) and HL-60 (leukemic). Selected ID_{50} values (in μg/ml) are gathered below

Ligand	Compound	MDA-MB 468	HL-60
4-Cl-C_6H_4-N=C-(COC_6H_5)-C_6H_4	$[LPtOAc]_2$	1.20	0.94
	$[LPtCl]_2$	1.74	1.50
	$[LPdOAc]_2$	5.82	5.50
	$[LPdCl]_2$	8.20	7.80
4-OMe-C_6H_4-N=C-(COC_6H_5)-C_6H_4	$[LPtOAc]_2$	2.10	1.25
	$[LPtCl]_2$	5.22	4.10
C_6H_5-(CH_2)-N=C-(COC_6H_5)-C_6H_4	$[LPtOAc]_2$	4.35	3.82
	$[LPtCl]_2$	5.12	4.63
	$[LPdOAc]_2$	6.10	5.23
	cis-DDP	0.80	0.62

The ID_{50} values, smaller than 10 μg/ml, shown by these complexes against both types of cell lines suggest that they may be regarded as having potential antitumour properties. In general, our date indicate that the antiproliferative activity of all of these complexes is higher against leukemic cells (HL-60) than against mammary human cancer cells (MDA-MB 468). Moreover, it was detected that the acetate-bridged compounds have a higher antiproliferative activity than the chloro-bridged ones. In addition, it was observed that the platinum compounds are also more active than those with palladium. Interestingly, the antiproliferative activity when the ligand is *N*-(4-chlorophenyl)-α-benzoylbenzylideneamine is similar to that of the *cis*-DDP

Acknowledgement. We thank the CICYT (Grant FAR 516/90) for financial support

ELECTROCHEMICAL INTERACTION: COPPER-HISTIDINE COMPLEXES AND THE TETRATHIOMOLYBDATE ION.

T. Hernández-Pérez * [1], C. Juárez-Gordiano [2], A. Quiroz-Gutiérrez [3] and I. González [4].

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The thiomolybdate ions ($MoS_x O_{4-x}$, $x = 1\text{-}4$) have been found as both active sities of some metalloenzimes and intermediaries of the Copper-Molybdenum antagonism in biochemistry [1]. In these systems, thiomolibdate ions are involved in electrochemical processes which are not still well know. In this communication, the electrochemical interaction between $Cu(His)_n$ complexes and tetrathiomolybdate ion (TTM) is studied by means cyclic, adsorptive and inverse voltammetry in aqueous and non-aqueous systems. In the former, on an Hanging Mercury Drop Electrode (HMDE) two oxidation peaks at -0.85 and -0.25 V/SCE were observed for the $Cu(His)_2$ complex. In latter, on a platinum electrode two oxidation peaks at - 0.82 and 0.15 V versus potential of the Fic^+/Foc couple were observed for the $Cu(His)_n$ complex. These two one-electron transfers are similar to the Cu behavior in metalloenzimes. TTM shown an irreversible and pseudo-reversible reduction in non aqueous and aqueous solutions (in presence of adsorbed histidine) respectively. The reduced species of TTM shown an interaction with the $Cu(I)\text{-}(His)_n$ species (adsorbed on the electrode) and it yielded a compound with electrochemical activity. This may be the compound Mo(V)-Cu(I)-S previously reported by Laurie et. al [2]. Results show electrochemical methods as a good alternative to simulate the redox processes of both the $Cu(His)_n$ complexes and TTM such as occur in biological systems and they permit to study the bioinorganic reactions between Cu and Mo.

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DI(THIOLATO)AURATE(I) COMPLEXES

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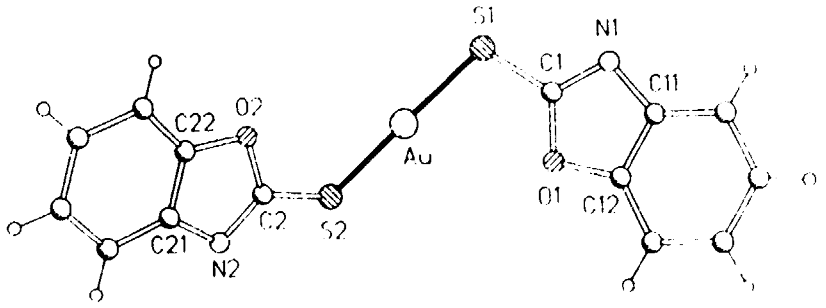
Neutral complexes of the types $[Au(SR)]_n$ and $[Au(SR)PR'_3]$ have been described [1]. Anionic $[Au(SR)_2]^-$ complexes are very scarce although they have been invoked as intermediates in the exchange of thiol groups in biological processes. Some thiolatogold complexes are effective drugs in the treatment of rheumatoid arthritis [2] and the synthesis of new such species is thus of great interest.

We have prepared several $[Au(SR)_2]^-$ complexes by reacting $[Au(acac)_2]^-$ (Hacac = acetylacetone) with the corresponding thiol.

$$[Au(acac)_2]^- + 2RSH \rightarrow [Au(SR)_2]^- + 2acacH$$

where RSH = H_2S, 2-mercaptobenzoxazole, 2-mercaptopyrimidine, 2-mercaptobenzimidazole, 2-thiouracil, thiomalic acid and b-D-Thioglucose tetraacetate.

The crystal structure of $[Au(benzoxazole\text{-}2\text{-}thiolato)_2]^-$ has been established.



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LAICM1218P **32, Tue. 14**

CYANAMIDE COMPLEXES OF PALLADIUM AND PLATINUM

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We have previously shown that cyanamide ($N{\equiv}CNH_2$) undergoes dehydrogenation by the electron-rich metal sites $\{M(dppe)_2\}$ (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) to give the cyanoimido-complexes *trans*-$[M(NCN)_2(dppe)_2]$ [1], whereas it simply adds to the less electron-rich $\{Re(CNMe)(dppe)_2\}^+$ centre [2]. This work has now been extended to Pd and Pt metal centres, as well as to some cyanamide derivatives. Hence, *e.g.*, the cyanamide, dimethylcyanamide or cyanoguanidine complexes $[Pt(CF_3)(PPh_3)_2L][BF_4]$ [L = $NCNH_2$, $NCNMe_2$ or $NCNC(NH_2)_2$] have been prepared from the reactions of such substrates with $[Pt(CF_3)(PPh_3)_2L'][BF_4]$ (L'=NCMe or acetone), whereas $[PdCl_2(NCNR_2)_2]$ (R = H or Me) have been obtained from $[PdCl_2(NCPh)_2]$ or $PdCl_2$. These and related reactions are discussed, and the spectroscopic data of the products are also presented.

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Acknowledgements

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LAICM1217P **33, Tue. 14**

Syntheses of Iron (III) and Copper (I or II) Complexes Using Camphor derivatives as Ligands.

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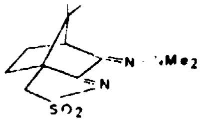
Within the interest of coordination compounds in asymmetric organic synthesis, we have started the preparation of chiral complexes of palladium using camphor(+) derivatives as ligands[1] We now which to report the extension of this study to other camphor(+) derivatives and different metal sites

The following complexes have been obtained through addition of these species to iron (III) and copper (II) chlorides or *via* acetonitrile substitution on $[Cu(NCMe)_4]ClO_4$

$[FeCl_3L_2]$, $[FeCl_3L']$, $[FeCl_3L'']$, $[CuCl_2L'']$, $[CuCl_2L''']$ and $[CuCl(NCMe)L]$, where L, L', L'' and L''' are indicated below

L



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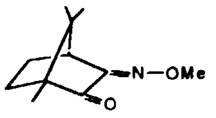

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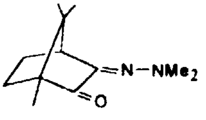

L'''

They have been characterized by elemental microanalysis, I R and N M R spectroscopy

The electrochemical behaviour of these compounds has also been investigated by cyclic voltammetry in aprotic medium

Acknowledgements

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LAICM1245P **34, Tue. 14**

STUDIES ON THE CHELATING BEHAVIOUR OF BISTHIOSEMICARBAZONES IN ZINC COMPLEXES

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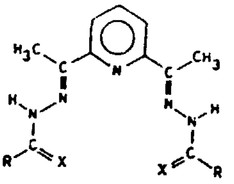
As part of a study to provide structural and spectroscopic models for zinc-sulfur centres in metalloproteins, and following our interest in the chemical and pharmacological properties of thiosemicarbazones (1), we report the preparation, the spectroscopic and the structural characterization of zinc complexes derived from the reaction of zinc chloride, acetate or perchlorate with two more flexible ligands :



R = NH_2 X = S H_2L

R = $-C(CH_3)-N=NHC(S)NH_2$ X - O H_2L'

The main purpose is to investigate the versatility of the ligands in the coordination, their tendency to yield seven or six-coordinate stereochemistry, the ability to behave as neutral or deprotonated ligands and the flexibility in assuming different conformations. The complex $[ZnL]_2 \cdot 2$ DMF, obtained from zinc acetate and H_2L, in the crystalline form exists as a dimeric species .The most interesting feature of the structure pertains to the ligand behaviour of the pyridine ring unusually bridging two zinc atoms, which have a distorted octahedral coordination.

The $[Zn(H_2L')(OH_2)_2]^{2+}$ cation , obtained from zinc perchlorate and H_2L' , exhibits a monomeric nature and an unusual seven-coordinate stereochemistry.

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LAICM1127P **35, Tue. 14**

COMPLEXES OF THE ANTIHYPERTENSIVE AGENT LISINOPRIL.

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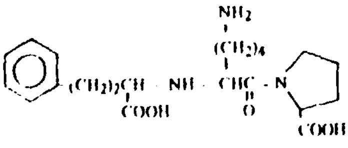
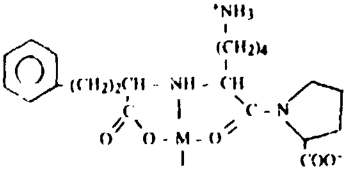
Lisinopril (I) is an antihypertensive agent and acts by inhibiting the zinc metalloenzyme ACE which is responsible for the production of the vasoconstrictor angiotensin II from angiotensin I. Since Lisinopril can also complex with other biologically important metal ions a knowledge of its complexing ability is of importance in order to (a) understand side effects which may result from metal ion sequestration, (b) design alternative drugs with improved selectivity for Zn^{2+} (the host ion) over other metals.

We have therefore investigated complex formation in solution between Lisinopril and the metal ions Cu^{2+}, Ni^{2+} and Zn^{2+}. The pK_a values of Lisinopril, determined potentiometrically at 25°C and at ionic strength 0.2M KCl are 1.4 ± 0.1 (central COOH), 3.00 ± 0.01 (prolyl COOH group), 7.10 ± 0.01 (secondary ^+NH), 10.78 ± 0.01 ($^+NH_3$, lysyl side chain). All the metal ions form complexes MAH (A is fully deprotonated Lisinopril) and the following constants (logs) have been determined for the equilibrium, $M + HA \rightleftharpoons MAH$; CuAH = 6.52 (1), NiAH = 4.36 (1), ZnAH = 3.57 (1). Since the most likely coordination site for the metal involves the secondary amino group and the adjacent carboxylate these values may be compared with those of analogous sarcosine, $MeNHCH_2COOH$,complexes for which log K_{MA} values are 8.83 - Cu(II), 5.95 - Ni(II) and 4.31 - Zn(II). Since the secondary nitrogen in sarcosine is more basic than that in Lisinopril (Δ pK_a = 2.81) the stability constants of the Lisinopril complexes are higher than expected and indicate that the carbonyl oxygen as shown in (II) (and possibly the prolyl carboxylate) may also be involved in coordination.



(I)



(II) MAH

We thank the Xunta de Galicia for financial support for EBG, on leave from the Departmento de Quimica Inorganica, Universidad de Santiago de Compostela.

LAICM1242P **36, Tue. 14**

THE HYPOGLYCEMIC EFFECT OF COPPER (II) COMPLEXES

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The hypoglycemic effect of copper (II) complexes such as Cu(oAc)$_2$ (Imidazole)$_4$, Cu(OAc)$_2$ (2-methyl Imidazole)$_2$, Cu$_2$(OAc)$_4$(N-methyl Imidazole)$_4$·6H$_2$O and Cu(OAc)$_2$(1,2-dimethyl Imidazole)$_2$ was tested on normal and diabetic rats.

Copper compounds were administered to fasted rats by I.M. and I.P. injection, blood samples were taken from the tail tip at various intervals following injection, for the measurement of blood glucose using the glucose oxidase method.

Injection of various doses of Cu(oAc)$_2$ (Imidazole)$_4$, ranging from 10-60 mg/kg body weight, to overnight fasted rats have reduced blood glucose levels in a dose dependent manner which reached its maximum hypoglycemic effect after 3 hours. This effect was completely reversible after 24 hours. Higher doses of the same compound (100 mg/kg) caused a hypoglycemic shock which was irreversible and even lethal. The hypolgycemic changes were more profound after intraperitoneal injection of the copper II complexes.

Similar changes in blood glucose levels were achieved using Cu(OAc)$_2$ (2-methyl Imidazole)$_2$. The same pattern of change but less effective was observed with Cu$_2$(OAc)$_4$(N-methyl Imidazole)$_4$·6H$_2$O and Cu(OAc)$_2$(1,2-dimethyl Imidazole)$_2$. This indicates that the hypoglycemic activity varies with the type of imidazole ligand in complexes. Inorganic forms of copper like copper chloride, copper acetate as well as the parent ligand imidazole have no significant effect on blood glucose levels.

Injection of copper acetate imidazole to streptozotocin induced diabetic rats caused a reduction in glucose values observed during glucose tolerance test.

LAICM1237P **37, Tue. 14**

MONONUCLEAR COPPER (II) COMPLEXES CATALYZED OXIDATION OF TMPD AND O-PHENYLENEDIAMINE AND OXYGEN INSERTION IN THE O-PHENYLENEDIAMINE/Ph_3P/COPPER (II) CATALYST SYSTEM.

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The catalytic activities of bis(acetato) bis (imidazole) copper (II) and bis(valproato) bis(imidazole) copper (II) complexes for the oxidation of TMPD (N,N,N',N'-tetramethyl-P-phenylenediamine) in air were followed spectrophotometrically by monitoring the increase in the $TMPD^{+}$ absorbance in methanol at 565nm as a function of time [1]. For both complexes, the method of initial rates showed a first-order dependence on the catalyst and TMPD concentrations.

These complexes were found to be an effective catalysts for the oxidative cyclization of O-phenylenediamine (OPD) to 2,3-diaminophenazine (DAP). The catalytic activities were followed spectrophotometrically by monitoring the increase in the DAP absorbance in methanol at 428nm as a function of time. When copper (II) complexes were added to a methanolic solution containing OPD and Ph_3P in a mole ratio of 1:4 under the atmospheric air, DAP were not obtained but instead $Ph_3P = 0$ was produced. The production of $Ph_3P = 0$ was monitored by following the increase in the P = 0 IR frequency at 1195 cm^{-1}. The relevance of these copper (II) complexes to the biological functions of copper proteins and enzymes are discussed [2].

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NEW CHIRAL COPPER COORDINATION COMPOUNDS OF QUINIC ACID.

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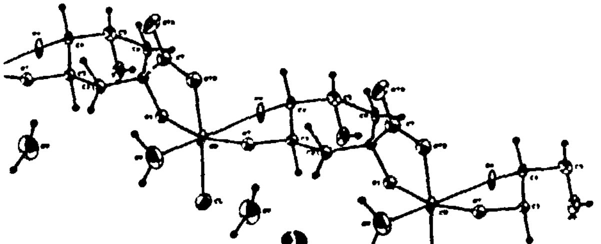
We have been working on the synthesis of metal complexes derived from quinic acid 1[1]. Owing to the polyfunctionality of 1 diverse structures were obtained: polymeric in $[Cu(quin)Cl(H_2O)]_n \cdot H_2O_n$ 2; and $[Cu(quin)(H_2O)]_n$-$(NO_3 \cdot 2H_2O)_n$ 3; and a dimer in $[Cu(Quin)Cl_2] \cdot H_2O$ 4. Herein we present their X-ray diffraction studies. In 2 the copper is a distorted octahedron. Each quinic acid is bonded to two copper atoms forming two five-membered chelates in a helix structure. In 3 the copper is hexacoordinated and is bonded to 3 molecules of quinic acid each one in a different mode. Each quinic acid is bonded to 3 different copper atoms. The polymer forms lineal helicoidal chains. Each chain is linked to another two, giving a net structure. Two linked chains appear as a ladder. Compound 4 is a dimeric square pyramidal complex. Each quinic acid is bonded to 2 copper atoms and each copper is bonded to 2 quinic acid molecules. Both copper atoms are linked together by two oxygen bridges. The structure is heptacyclic and has a C_2 axis. The two axial copper are found in an original *cis* arrangement.
In 2, 3 and 4 the copper is a center of chirality. Only one stereoisomer from 30 is obtained for 2 (OC-6-25-Δ) and 3 (OC-6-53C). Compound 4 (SPY-5-13C) constitutes an example of a chiral copper atom in a square pyramid.



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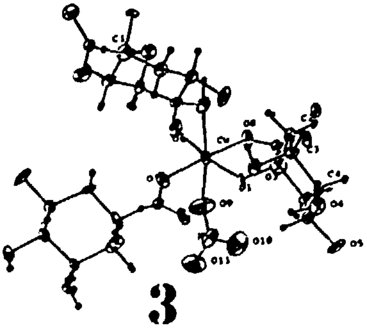

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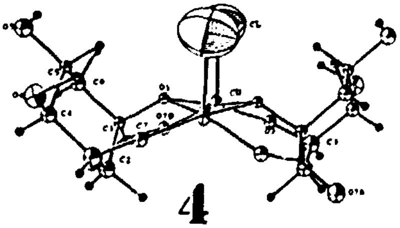

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LAICM1228P **39, Tue. 14**

SYNTHESIS AND NMR STUDY OF NEW PENTACYCLIC PHOSPHORANES

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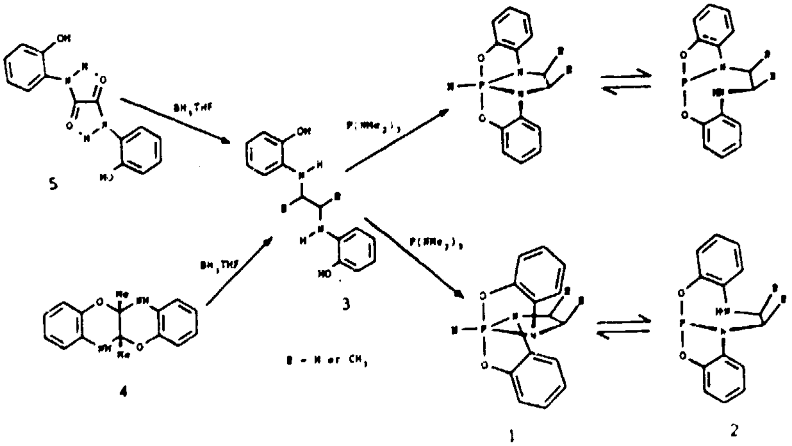
We report the synthesis of new stable, pentacoordinated phosphorus compounds. An aliphatic analogue was reported in the literature,[1] the authors established an structure of trigonal bipyramid geometry (TBP) with one oxygen and one nitrogen in apical positions. The NMR study (^{1}H, ^{13}C, ^{31}P, 2 Dimensions and variable temperature) has shown that the aromatic compounds have a TBP geometry, but with both oxygen atoms in axial, the assignment of this structure will be discuss. A tautomeric behaviour [P(III)- P(V)] was found when compound 1 was dissolved in toluene. The syntheses was done following the scheme:



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STRUCTURE AND REACTIVITY OF Pd(II) AND Pt(II) ALKYL ESTER AMINO ACID COMPOUNDS

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The synthesis of new complexes of Pd(II) and Pt(II) analogues to cisplatin with the dual purpose of obtaining less cytotoxic drugs and understanding the mechanisms of action has become a very interesting field in the last few years.[1].

In a previous paper [2] we reported the structure and behaviour of several amino acid Pd(II) and Pt(II) compounds. In order to avoid hydrogen bonding to the carboxylic group in the amino acid we now report the synthesis of new Pd(II) and Pt(II) complexes with alkyl esters (methyl, ethyl and isopropyl) of methionine and histidine. The reactivity of the two types of compound with nucleobases is compared.

The crystal structure of the Pd(II)- methionine methylester showed only one molecular form in solid state. The new thioether S chiral center bound to the Pd(II) prefers only one of the two possible isomers while the two isomers appeared to be in equilibrium in solution. The ^{1}H and ^{13}C NMR spectra show one broad or two separate signals corresponding to the isomers.

The reactions between the complexes and purine or pyrimidine bases such as guanine and cytosine, nucleotides like 5'GMP, and 5'CMP, were assayed. The corresponding ternary complexes were studied spectroscopically. The substitution of only one Cl^- by the corresponding nucleobase was found in most cases.

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ON THE REACTIVITY OF $\{[Pd_2(\mu\text{-dppm})(\mu\text{-}SC_6F_5)](\mu\text{-}SC_6F_5)\}_4\cdot 2Et_2O$.

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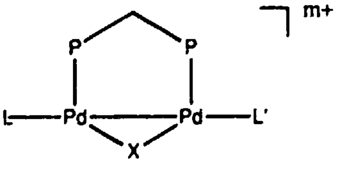
Reaction between $Pd_2(dba)_3\cdot CHCl_3$ (dba = dibenzylideneacetone) and $Pd(dppm)(SC_6F_5)_2$ (dppm = bis(diphenylphosphino)methane) affords[1] the highly symmetrical octonuclear $\{[Pd_2(\mu\text{-dppm})(\mu\text{-}SC_6F_5)](\mu\text{-}SC_6F_5)\}_4$, which offers a variety of potential reaction patterns (cleavage and/or displacement of both types of thiolato bridge, insertion in or oxidative addition to the metal-metal bond).

These possibilities have been explored and the resulting binuclear metal-metal bonded, neutral or cationic compounds (with the frame shown in fig.1) have been structurally characterized by ir and multinuclear nmr spectroscopies and, in some cases, by X-ray diffraction studies.



$X=SC_6F_5$, $L=SC_6F_5$, $L'=PPh_3$, $m=0$;
$X=SC_6F_5$, $L=L'=PPh_3$, $m=1$;
$X=CO$, $L=L'=SC_6F_5$, $m=0$.

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LAICM1221P **42, Tue. 14**

SYNTHESIS OF THE 20-ELECTRON-DINITROSYL COMPLEX trans-[Re(NO)$_2$(dppe)$_2$][BF$_4$] AND ITS REACTIONS WITH ACIDS

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The activation of nitric oxide by electron-rich metal centers is a matter which has not yet been adequately explored. Therefore, we have initiated the investigation of its coordination chemistry at the {ReCl(dppe)$_2$} (dppe = $Ph_2PCH_2CH_2PPh_2$) site, and prepared [1] the mononitrosyl complexes trans-[ReCl(NO)(dppe)$_2$][BF$_4$]$_n$ (1,n = 1 or 2) and trans-[ReCl(NO)(dppe)$_2$][NO$_3$]$_2$ (2), the formation of the latter involving an unusual facile oxidation of NO to nitrate.

We now report the synthesis of the dinitrosyl complex trans-[Re(NO)$_2$(dppe)$_2$][BF$_4$] (3) (formally a 20-electron species) from the reaction of any of the complexes (1) with K/Na or, preferably, in a more direct way, from the reaction of the dinitrogen compound trans-[ReCl(N$_2$)(dppe)$_2$] with NO in the presence of Tl[BF$_4$].

Complex (3) undergoes partial denitrosylation by protic acid (HA) to afford trans-[ReX(NO)(dppe)$_2$]A (X = F or Cl, for HA = HBF$_4$ or HCl), whereas trans-[Re(OH)(NO)(dppe)$_2$][HSO$_4$] is formed from the reaction with H_2SO_4 followed by hydrolysis.

The spectroscopic properties of these complexes are presented and possible mechanisms of those reactions are discussed in terms of the electronic properties of the activated nitrosyl ligands.

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Acknowledgements

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LAICM1220P 43, Tue. 14

SYNTHESIS AND CHARACTERIZATION OF THE *cis* ISOMERS OF THE NITRILE COMPLEXES [ReCl(NCR)(dppe)$_2$]

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In pursuit of our interest in the coordination chemistry of small molecules, particularly unsaturated species, at dinitrogen-binding metal sites [1], we have succeeded in the synthesis of the complexes *cis*-[ReCl(NCR)(dppe)$_2$] (R = alkyl and aryl), by treatment of a toluene solution of the parent compound *trans*-[ReCl(N$_2$)(dppe)$_2$] with the appropriate nitrile, in sunlight, the reaction involving not only N$_2$ replacement by NCR but also the *trans*-to-*cis* isomerization of the metal centre (eq.).

$$\textit{trans-}\left[\mathrm{ReCl(N_2)(dppe)_2}\right] \; + \; \mathrm{NCR} \xrightarrow[h\nu]{\text{toluene}} \textit{cis-}\left[\mathrm{ReCl(NCR)(dppe)_2}\right]$$

These complexes provide the second example of the *cis* isomers [2] of Re compounds of the general type [ReL$_2$L'$_4$] (where the two L ligands can be either identical or different from each other, and L' is commonly a phosphine or ½diphosphine).

The spectroscopic data of the complexes will be discussed, in particular in terms of the non-equivalence of their four phosphorous nuclei as indicated by their ^{31}P-{^{1}H} NMR spectra which were analysed as ABCD-type spin systems

ACKNOWLEDGEMENTS

This work has partially been supported by JNICT

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PINCH PORPHYRINS :A NEW CLASS OF MODEL COMPOUNDS FOR HEME-ENZYMES.

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In the last ten years it has been an increase in the knowledge about hemeproteins other than oxygen carriers. Model compounds for cytochrome P-450 and in low extent peroxidases had been synthetized (1). Nowadays, it is clearly stablished that proximal and distal accesories do control the catalytic activity and influence directly the oxidation and spin state of the iron. With regard to peroxidases, the iron(III)-deuteroporphyrin complex has proved to be a good initial model to reproduce peroxidase chemistry (2) and spectroscopic properties. theorical calculations were carried out on the iron(III)-Deuteropor phyrin-PID complex,where PID is the 1,9,Bis(pyridil)-2,5,8,triazanonane. This complex has a remarkably similar spectroscopic properties when compared with peroxidases from natural sources. Data from structures obtained by X-ray of several porphyrins, as well as, complexes of PID were used as the initial input for MM calculations. We observed very small differences in bond angles, dihedral angles and bond distancies after optimization. Thus, we suggest this structure represents an acceptable model for the title compound. Comparison of such proposed structure with the one of the Bispyridine complex clearly indicates a deviation from the line perpendicular to the plane of the porphyrin ring. Therefore, the PID ligand pinches the porphyrin in a similar way as a protein pinches a heme in type b cytochromes, but not as strongly to cause a complete spin change, consecuently an intermidiate spin state is generated similar to the one found in peroxidases. Thus, by carefully adjusting the proximal and distal environment of this new kind of porphyrins it will be possible to reproduce the spectroscopic an catalytic properties of peroxidases. Supported by a grant from CONACYT-MEXICO.

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LAICM1258P **45, Tue. 14**

A NEW MIXED-VALENCE $Fe^{III}Fe^{II}$ COMPLEX AS A MODEL FOR THE PINK FORM OF PURPLE ACID PHOSPHATASES.

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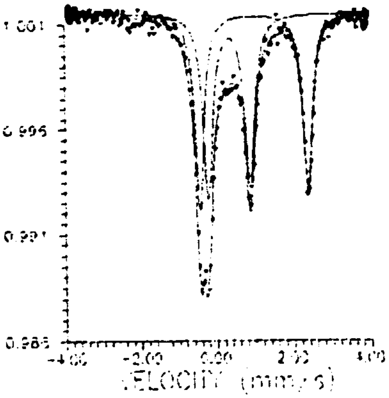
Purple acid phosphathases from bovine spleen (PAPs) constitute a novel class of metalloenzymes involved in the hydrolysis of phosphoric monoesters[1]. The centre of PAPs consists of a dinuclear iron moiety which exists in a catalytically active pink $Fe^{III}Fe^{II}$ form and an inactive purple Fe_2^{III} form. Despite the lack of informations concerning the coordination sphere of the iron centers, the presence of at least one tyrosine as terminal ligand has been confirmed by RR-spectroscopy[1]. We are currently investigating new binuclear iron complexes as models for PAPs[2]. Herein we report the synthesis and some properties of $[Fe^{III}Fe^{II}(BBPMP)(OAc)_2]$.1 where H_3BBPMP is 2,6-bis[(2-hydroxybenzyl)(2-methylpyridyl)-amino-methyl]-4-methylphenol. The visible chromophore at 516nm (ε= 8700 $M^{-1}cm^{-1}$) and the ^{57}Fe Mössbauer spectrum of 1 with two doublets at δ_1=0.44 ; ΔE_{Q1}=1.08 and δ_2= 1.07 ; ΔE_{Q2}=2.81 (mm/s) are comparable to those observed in the pink form of PAPs. However, the $E_{1/2}$=-0.17V vs. NHE for the $Fe_2^{III}/Fe^{II}Fe^{III}$ couple detected for 1 is cathodic shifted by ≈0.4V with respect to the redox potential of PAPs. Therefore, additional appropriate modifications on the H_3BBPMP ligand are necessary to obtain more adequate models for these metalloenzymes.



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LAICM1259P **46, Tue. 14**

SYNTHESIS, STRUCTURE, MAGNETIC AND SPECTROELECTROCHEMICAL PROPERTIES OF A NEW IRON(III) COMPLEX AS A MODEL FOR IRON TRANSFERRINS

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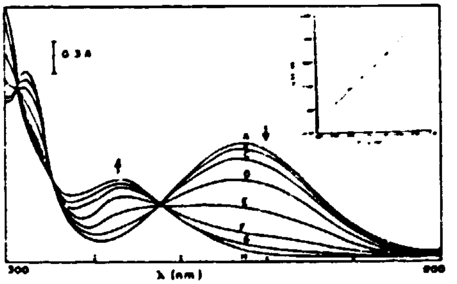
The transferrins are recognized as a important subclass of Fe(III)-tyrosinate proteins that reversibly bind 2 mol of Fe(III) [1]. Despite the recent X-ray structure determination of human lactoferrin and its high K = 10^{20}, the mecanism of release for iron remains open to speculation. In this work we report the synthesis, physicochemical and structural properties of $[Fe^{III}(BBPEN)]I.EtOH$ 1 (H_2BBPEN = N,N'- bis (2-hydroxybenzyl)- N,N'- bis (2-methylpyridyl) ethylenediamine)[2]. Crystal data for 1: triclinic, P$\bar{1}$, a=15.799(4), b=9.720(3), c=9.642(3) Å, α =98.24(1), β =90.68(1), γ =107.11(1)°, Z =2 and R_w =0.026. The high-spin Fe(III) complex (μ_{eff} =5.45 B.M. at 284.5 K) shows a quasi-reversible redox couple at -0.82 V vs Fc$^+$/Fc, which is assigned to the one- electron Fe(III)/Fe(II) process. From spectroelectrochemical reduction (Fig. 1) it was observed a spectral change from 570 nm (Fe(III)) to 434 nm (Fe(III)). The values $E_{1/2}$= -0.84 V vs. Fc$^+$/Fc and n= 1.0 ± 0.1 electrons were obtained from the Nernst plot (inset Fig. 1) and are in very good agreement with CV and coulometric results. Finally, these results are discussed in connection with physicochemical properties of other mononuclear Fe(III) derivatives (mono-, di-, tri-, and tetraphenolate complexes) and those of transferrins.



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SYNTHESIS AND CRYSTAL STRUCTURE AND MAGNETISM OF THE NEW COMPLEX $Et_3NH[Fe(TBEN)]$.1.

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The coordination of tyrosine to iron centers in proteins such as transferrins and purple acid phosphatases is a structural feature recently found for these metalloenzymes [1]. Herein we report the synthesis and crystal structure (Fig. 1) of a new Fe(III) complex containing two amine nitrogen and four phenolate oxygen as donor atoms which are coordinated in a facial NO_2 arrangement. Reaction of tetrakis (2-hydroxybenzyl) ethylenediamine (H_4TBEN) [2] with $FeCl_3.xH_2O$ in CH_3OH in the presence of Et_3N affords suitable crystals for X-ray diffraction studies of **1**. *Crystal data*: $P2_1/n$ a=14.053(3), b=10.781(5), c=21.406(5) Å, β=102.84(2)°, V = V=3161(1) $Å^3$, Z=4, R=4.7% . The Fe-O(phen) bonds in the equatorial plane (av. 1.923(3) Å) are significantly shorter than the two others (av. 2.004(4) Å) which are mutually in *trans* positions. This is a reflection of the weak *trans* effect of the shorter Fe-O(phen) bonds which accounts for the longer Fe-N(amine) bonds (av. 2.235(4) Å. Magnetic susceptibility data of 1 in the temperature range of 4.6 to 296 K fit Curie-Weiss law with μ_{eff}=5.48BM and is indicative of a small intermolecular coupling

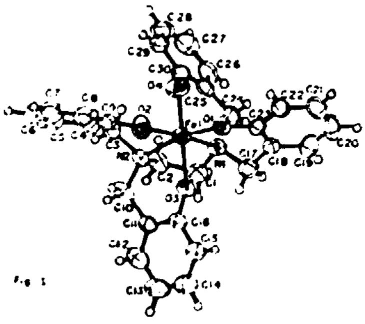

Fig 1

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LAICM1265P **48, Tue. 14**

SYNTHESIS, CRYSTAL STRUCTURE, ELECTROCHEMICAL AND MAGNETIC PROPERTIES, INFRARED SPECTRA OF $Cu_4[PhN_3C_6H_4N_3(H)Ph]_4(\mu_2\text{-}O)_2$ (1), A TETRANUCLEAR COMPLEX OF COPPER(II) WITH 1-PHENYLTRIAZENO-2-PHENYLTRIAZENIDO-BENZENE (2) AS LIGAND.

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Complex (1) is obtained by the reaction of aqueous $[Cu(NH_3)_4]^{2+}$ and 1,2-bis(phenyltriazene)benzene in ether. It cristallizes in the orthorhombic space group Pba2 with the lattice parameters a = 1661.52(1), b = 1914.74(1), c = 1269.20(3) pm, Z = 2. The structure of the tetrameric complex (1) has been refined to $R = 0.066/R_w = 0.093$ based on 5547 reflections, with $I>3\sigma(I)$; $R_{int.} = 0.024$. It shows the site symmetry C_2 and a $(Cu^{2+})_4$ tetrahedron (Cu - Cu: 298.3(4) - 337.1(1) pm). Both μ_2-oxo ligands occupy the C_2 axis and bridge two opposite edges of the $(Cu^{2+})_4$ tetrahedron (Cu O: 190.0(3) and 192.9(4) pm). The ligands (2) bridge two Cu^{2+} ions chelating one metal centre and coordinating monodentately the neighbouring one (Cu - N: 191.0(5) - 204.1(4) pm). Cyclic voltammograms of (1) in acetonitrile indicate two quasi-reversible one-electron-transfer processes corresponding to Cu(III)/Cu(II) at $E_{1/2} = 0.47$ V and Cu(II)/Cu(I) at $E_{1/2} = -0.029$ V versus SCE. The magnetic measurements in the range of 100 to 300 K, show no variation of the magnetic susceptibility with the temperature wich indicates the diamagnetism of (1). A very strong and sharp absorption at 1370 cm^{-1} (absent in ligand (2), is assigned to the asymmetric valence vibration of the $[-N \underline{\cdots} N \underline{\cdots} N-]^-$ skeletons chelating the Cu^{2+} ions.

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LAICM1266P **49, Tue. 14**

TETRAMETHYLUREA ADDUCTS OF BISCYCLOPENTADIENYL COMPLEXES OF Sm(II) AND Yb(II))

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During the last years lanthanide (II) compounds have been extensively used as reducing agents for organic synthesis. For this purpose halides and cyclopentadienyl of lanthanides have been investigated[1], but studies concerning the organometallic chemistry of lanthanides (II) have been done mainly with pentamethylcyclopentadienyl ligands[2], due to the solubility of these species in organic solvents.

As we have been working on the synthesis and characterization of the highly soluble tetramethylurea adducts of the tricyclopentadienyl lanthanide complexes $Cp_3Ln.TMU$ (Ln=La, Ce, Nd, Sm, Eu, Yb), we tried to use TMU as an auxiliary ligand in order to confer a higher solubility to the cyclopentadienyl lanthanide (II) complexes. In this contribution we report our attempts to synthesize soluble cyclopentadienyl adducts of Sm(II) and Yb(II) by reduction of the corresponding lanthanide(III) compounds. $Cp_2Yb.3TMU$ has been synthesized by addition of the stoichiometric amount of TMU to $Cp_2Yb.THF$, obtained by reduction of $Cp_2ClYb.THF$ with sodium naphtalenide. The compound has been characterized by metal analysis, IR, ^1H NMR and UV-visible spectroscopies. However, the same procedure applied to $Cp_2ClSm.THF$ yielded an insoluble compound that couldn't be separated from NaCl. Attempts to obtain soluble "Cp_2Sm" compounds with other ligand donors are being undertaken.

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LAICM1269P **50, Tue. 14**

MONO-,DI- AND TRINUCLEAR IRON COMPLEXES WITH POLYFUNCTIONAL HYDRAZONIC LIGANDS

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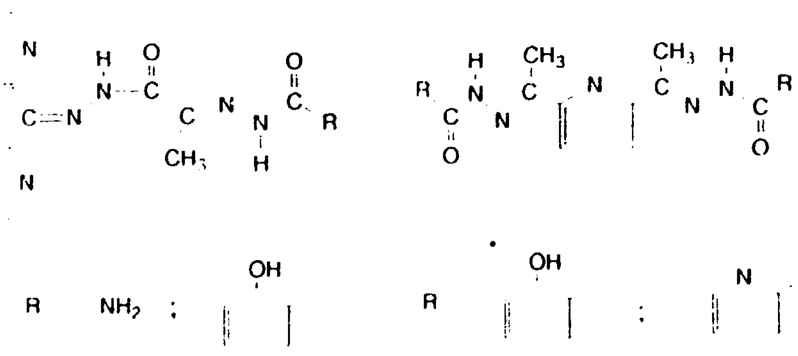
In a continuation of our investigations on the chelating properties of polyfunctional macroacyclic ligands derived from acylhydrazides and in order to contribute to a better understanding of the coordination chemistry of iron, as well as to favour the formation of charge-transfer metal complexes, here we report on the synthesis and characterization of two series of mono-, di- and trinuclear iron(II) complexes with the following hydrazones:



The first series deals with the reaction between the hydrazone and $FeCl_2$, the second one with the reaction of the above iron-chloro complexes with iodine and with cyanometallates. Heterotrinuclear iron complexes have been also obtained.

The complexes have been characterized by spectroscopic techniques and thermal analysis. Information on the iron environment and the nuclearity of the complexes have been provided, in particular, with the ^{57}Fe Mössbauer spectroscopy.

SOLUTION STUDY OF THE MIXTURES OF 4,6-DIMETHYL-2-THIOPYRIMIDINE AND THE Zn(II) AND Cd(II) IONS. CRYSTAL STRUCTURES OF $Zn(LH)_2Cl_2$ AND $Cd(LH)_2Cl_2$.

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The reactivities of 4,6-dimethyl-2-thiopyrimidine(LH) with Zn(II) and Cd(II) ions, respectively, have been studied by potentiometric techniques in aqueous medium at constant ionic strength 0.1M KCl and 25°C. For this, solutions of LH and of the corresponding ligand/metal mixtures, with 2/1 ligand/metal molar ratio and variable ligand concentrations, were titrated with KOH.

The data obtained were computed with the PKAS and BEST programs (1) from which the species existing in the ligand and metal/ligand solutions, were detected and their pkas and stability constants, β, obtained. From them, the distribution species diagram was obtained also, by using the SPE program (1).

On the basis of the last, the $Zn(LH)_2Cl_2$ and $Cd(LH)_2Cl_2$ complexes where synthesized from aqueous solutions whose pH were previously adjusted at the 4.0 valve, and their structures solved by X-ray diffraction methods. The compounds were also spectroscopically characterized by ir and RMN (^{13}C and ^1H) techniques.

The compounds are monomeric and show tetrahedral structures with the two LH molecules S-coordinated. The Zn(II) compounds present a "trans" conformation of the two LH molecules due to the steric hindrances caused by the relatively short S-Zn distances. On the contrary, in $Cd(LH)_2Cl_2$ compound where Cd-S distances are relatively longer the two the LH molecules present "cis" conformation.

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LAICM1277P **1, Thu. 16**

NEW HOMO- AND HETEROPOLYNUCLEAR COMPLEXES WITH NITROSO-OXIMATE BRIDGING LIGANDS MAGNETO-STRUCTURAL STUDY.

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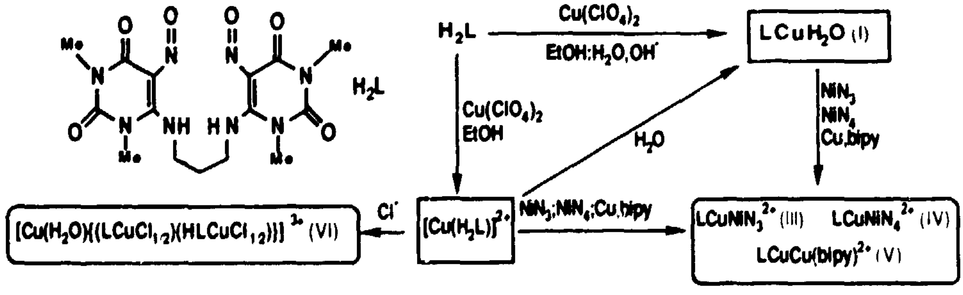
One subjects of interest in homo and heteropolymetallic systems is to design and understand new molecular-based magnets. In particular, new bridging systems which can mediate a strong antiferromagnetic spin coupling between paramagnetic centers have been exploited in the hope of developing ferrimagnetic materials.

α,ω, bis (1,3-dimethyl-5-nitrosouracil-4-yl-amino)propane (H_2L, Fig. 1) is a good candidate to obtain homo- and heteropolinuclear complexes in which the nitroso-oximate groups, wich has been shown to be very eficient to mediante strong antiferromagnetic spin exchange, function as bridges between two metal ions.

By reaction of H_2L with $Cu(ClO_4)_2$ in ethanol/water (ph >7) and absolute ethanol the complexes $LCu(H_2O)$ (I) and $[H_2LCu](ClO_4)_2$ (II), respectively, were obtained. On reacting either I and II with $[NiN_3](ClO_4)_2$, $[NiN_4](ClO_4)_2$ and $Cu(NO_3)_2$/bipy (1:1), the heterodinuclear complexes $LCuNiN_3{}^{2+}$ (III), $LCuNiN_4{}^{2+}$ (IV) and the homodinuclear complex $LCuCubipy^{2+}$(V) were obtained. (N_3= 2,4,4-trimetil-1,5,9-triazaciclodode-1-eno, N_4= d,l-5,5,7,12, 12, 14-hexametil-1, 4, 8, 11-tetraazaciclotetradecane, bipy= bipyridyl). Interestingly, when II is treated with Cl^- the homotrinuclear complex $[Cu(H_2O)((HLCuCl_{1/2})(LCuCl_{1/2}))]^{2+}$ (VI) was isolated.

Structures of I,III, IV, V and VI were determinated by single-crystal X-ray diffraction, whereas that of II was proposed from spectroscopic and magnetic data. It should be noted that all theses polynuclear complexes containing oximate bridges show strong antiferromagnetic exchange coupling, as expected



EPR CHARACTERIZATION OF Ni(I) COMPLEXES WITH PENTADENTATE SCHIFF BASE LIGAND

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Recognition that low valent metal transition metals play important roles as catalysts in the carbon-carbon bond formation reactions of alkyl/aryl halides, has prompted great interest in synthesis and reactivity studies of several Ni(I) complexes. Here we report the spectroscopic characterization of nickel(I) complexes with N_3O_2 pentadentate Schiff base ligands by electronic paramagnetic resonance (EPR).

The Ni(I) complexes were obtained by chemical reduction with $NaBH_4$ of the corresponding nickel(II) complexes - (Ni(saldien)), (Ni(saltrien)) and (Ni(salMetrien)) - in several solvents : acetonitrile (ACN), N,N'-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine (py).

EPR spectra of frozen reduced solutions of the nickel complexes in ACN, DMF and DMSO are similar for all complexes, show axial symmetry ($g_1 \approx$ 2.23–2.25 and $g_2 \approx$ 2.12–2.13) and no hyperfine splittings were detected in both *g* regions. The spectra are typical of nickel(I) complexes with a $(d_{xy})^1$ ground state.

In pyridine, EPR spectra of the Ni(I) complexes are also similar for all the complexes studied, but different from those referred to above in exhibiting rhombic symmetry ($g_1 \approx$ 2.33, $g_2 \approx$ 2.15 and $g_3 \approx$ 2.06); no hyperfine splittings were observed in any of the three g regions.

LAICM1284P **3, Thu. 16**

COORDINATING PROPERTIES OF SYMMETRICALLY DISUBSTITUTED DITHIOXAMIDES SHOWING AXIAL CHIRALITY.

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We have prepared the symmetrically disubstituted dithioxamide derivatives of racemic, S-(+)- and R-(-)- 1-amino-2-propanol of formula $[(CH_3\text{-}CH(OH)\text{-}CH_2\text{-}NH\text{-}C(=S)\text{-})_2]$.
In the starting amino-alcohol, $-CH_2-$ protons appear in the ^{1}H-nmr spectrum ($CDCl_3$ solvent) as an ABX system, but, surprisingly, N,N'-(dl)-2-hydroxypropyl-dithioxamide (dl-DTO) exhibits four groups of ABX spectral lines (fig. 1a). In contrast, both N,N'-S-(+)- and N,N'-R-(-)-2-hydroxypropyl-dithioxamide (R-(-)-DTO and S-(+)-DTO) show the same ^{1}H-nmr spectrum of 16 lines of equal intensity corresponding to the AB part a pair of ABX spectral systems, and whose frequencies are coincident with those of the AB part of two of the four ABX spectral schemes showed by N,N'-bis-dl-2-hydroxypropil-DTO (fig. 1b).

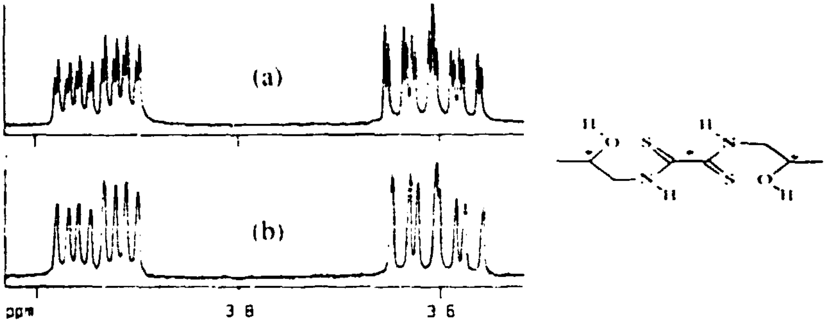

Fig. 1 - Methylene region in the ^{1}H-nmr spectrum of dl- and S-(+) - 2-hydroxypropyl-dithiooxamide.The asterisks in the molecular formula indicate the elements of chirality.

These results are intelligible only if one assumes that the new synthesized N,N' disubstituted dithioxamides possess a chiral torsional barrier around the C(=S)-C(=S) axis. In such a case, a 32 line spectrum of racemic aminoalcohol derivative accounts for the existence of four pair of enantiomers. At the same time, the two identical spectra containing a pair of ABX patterns obtained from the DTO derivatives of optically pure aminoalcohols, account for the existence of R-S-R and R-R-R diastereoisomers in R(-)-DTO, and of their specular images S-R-S and S-S-S in S-(+)-DTO.
The origin of the high torsional barrier around the C(=S)-C(=S) axis is obscure, and the phenomenon itself is surprising. In fact, such a torsional barrier doesn't exist in the many compounds N,N'-R_2-DTO up to date known.
Platinum(II) complexes of racemic-, S-(+)-, R-(-)-2-hydroxypropyl-dithioxamide of formula $[(H\text{-}R_2\text{-}DTO)Pt]$ and $[LR'Pt(H\text{-}R_2\text{-}DTO)]$ (L = Me_2SO, Me_2S, PR_3, CO; R' = Me, Ph) have been prepared and characterized.
In all of them, DTO is contained in the rubeanate form and therefore the C(=S)-C(=S) skeleton is planar. Accordingly, a single ABX pattern appears in the nmr spectrum of the symmetric $[Pt(H\text{-}R_2\text{-}DTO)_2]$ complexes, while in the unsymmetrical compounds $[LR'Pt(H\text{-}R_2\text{-}DTO)]$ the splitting of the ABX scheme is due to the chemical non equivalence of R groups.

LAICM1287P **4, Thu. 16**

CRYSTAL STRUCTURE OF A NEW Co(III) COMPLEX CONTAINING 3-(BIS (2-IMIDAZOLYL)) PROPIONIC ACID.

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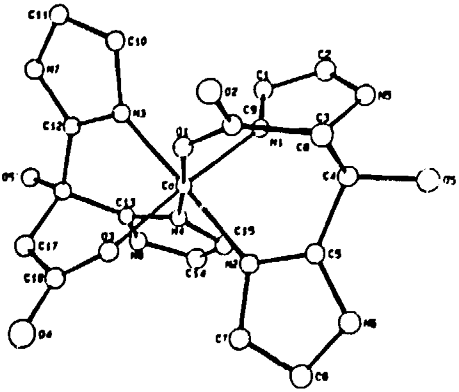
Transition metal complexes containing poly-imidazole ligands are generally used as simple models for some biological systems. The autoxidation of many organic substances can be catalysed by transition metals. We have undertaken a study of the interaction between cobalt and 3-(bis(2-imidazolyl) propionic acid, a system with interesting redox chemistry.

For the synthesis of the compound, aqueous solutions of $Co(NO_3)_2$. $6H_2O$ and 3-(bis(2-imidazolyl) propionic acid were mixed with stirring. Red single crystals were grown by slow evaporation at room temperature after three months, separated by filtration and washed with a water-ethanol mixture. Elemental analyses are consistent with the $(Co(C_9H_9N_4O_2)(C_9H_8N_4O_2OH))NO_3$. $2H_2O$ complexe. Crystals are triclinic, with a=8.124(1), b=17.245(2), c=8.114(1) Å, α=92.35(2), ß=95.64(2), γ=98.54(2)°; V=1117(1) $Å^3$; space group $P\bar{1}$; Z=2. The coordination around the Co atom is distorted octahedral. The ligand is tridentate and binds to the metal atom through the imidazole nitrogen and the carboxylate oxygen atoms. The complexe is diamagnetic. The IR spectrum shows no COOH and NH^+ bands. The d-d bands observed in the reflectance spectrum are consistent with an octahedral environment for Co(III) ion.



LAICM1295P 5, Thu. 16

Reactivity of hydroxo-nickel complexes toward phenols and carboxylic acids.

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Binuclear anionic complexes of the type $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ and $[Ni_2(C_6F_5)_4(\mu\text{-}az)(\mu\text{-}OH)]^{2-}$ (az = azolate ligand) have been reported recently.[1] Their reactivity towards weak protic electrophiles (HX) is consistent with the high-field proton resonances exhibited by the bridging OH groups.[2] These μ-hydroxo-nickel complexes react with ArOH (Ar = Ph, $p\text{-}C_6H_4\text{-}CH_3$, C_6F_5, $p\text{-}C_6H_4\text{-}NO_2$, 2-pyridyl) and carboxylic acids to give μ-aryloxo or μ-carboxylate binuclear complexes. When the hydroxo complex $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ reacts with 2-hydroximethylpyridine, 2-aminophenol, picolinic acid or aminoacids the corresponding mononuclear anionic nickel(II) derivatives are formed.

The new pentafluorophenyl nickel(II) derivatives have been characterized by elemental analyses, conductance measurements and spectroscopic (IR, ^1H and ^{19}F) methods.

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LAICM1297P **6, Thu. 16**

CHEMICAL MODELS OF THE MOLYBDENUM CENTRE IN NITROGENASE

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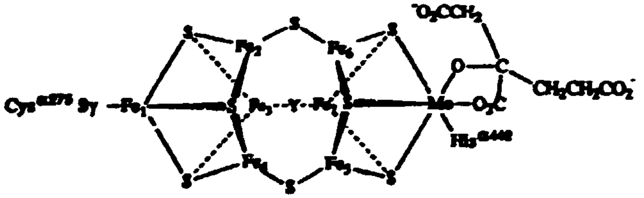
Kim and Rees (1) have recently proposed a structural model, based on 2.7Å X-ray crystallographic data, for the iron-molybdenum-cofactor (FeMoco) of molybdenum nitrogenase from Azotobacter vinelandii (Figure). No synthetic chemical models exist of molybdenum in such an environment. As part of a broader study we



have used the tripodal thiolate ligand 1,4,7-(4-mercaptobenzoyl)-1,4,7-triaza-cyclononane (2) to prepare $MoFe_3S_4$ clusters in which the three irons are bound to the thiolate sulfurs and molybdenum is ligated by cathecol and solvent. The solvent molecule can be replaced by either imidazole or histidine to give molybdenum with a 3 sulfur, 2 oxygen, 1 nitrogen co-ordination sphere.

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LAICM1299P 7, Thu. 16

FIVE-COORDINATE COMPLEXES OF NICKEL(II) BASED ON CYCLIC TRIAMINES AND SALICYLALDIMINES

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The halophenyl hydroxo complexes of the nickel group metals have shown to be good precursors in synthetic work, due to the considerable nucleophilicity of the bridging OH groups (1). The reaction of the hydroxo complexes $[\{NiL(\mu\text{-}OH)\}_2](ClO_4)_2$ (L= 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene or 2,4,4,9-tetramethyl-1,5,9-triazacyclodode-1-ene) (2) with salicylaldimines $ArNCHC_6H_4OH$ (Ar = C_6H_5, p-ClC_6H_4, p-MeC_6H_4, o-ClC_6H_4, o-MeC_6H_4, o-$OMeC_6H_4$ and 2,4,6-$Cl_3C_6H_4$) yields five-coordinate complexes $[NiL(OC_6H_4CHNAr)](ClO_4)$. These paramagnetic complexes have been characterized by elemental analysis, conductance measurements, single-crystal X-ray diffraction and spectroscopic (IR, V-UV and ^{1}H-NMR) methods. The observed resonance signals can be reasonably assigned on the basis of NOE experiments.

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LAICM1303P **8, Thu. 16**

NEW FERROCENE-CONTAINING LIGANDS: CHIRAL, CHELATING AND MACROCYCLIC LIGANDS.

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The incorporation of ferrocene into an organic host structural framework with the aim of obtaining ferrocene-containing derivatives able to act as molecular or ion receptors, the occurrence of ferrocene groups in close proximity to a host binding site, their one-electron reversible redox-active behaviour, and the possibility of using them as precursors for polynuclear metal complexes, make ferrocene-containing molecules of considerable current interest in fields such as biochemistry, organometallic and coordination chemistry.

Several synthetic routes can be used for obtaining ferrocene-containing ligands: reactions of ferrocenecarboxaldehyde (**1**) and 1,1'-ferrocenedicarboxaldehyde (**2**) with primary amines yield Schiff-bases, which can be reduced to their parent amines. On the other hand, reaction of N,N-dimethylaminomethyl-ferrocene methiodide (**3**) with secondary amines yields the corresponding ferrocenyl-functionalized tertiary amines. These reactions have been studied with several amines:

** Chiral aminoacids.- Reaction of **1** with chiral aminoacids ((R)-(-)-2-phenylglicine, L-alanine, L-valine, L-isoleucine and (D)-(-)-2-aminobutyric acid) have been caried out for yielding new chiral compounds.

Diamines.- Reaction of **2 with diamines as ethylenediamine, N-methylethylenediamine, N,N-dimethylethylenediamine and N-naphtylethylenediamine have been studied. Tetradentate ligands have been obtained and characterized.

** Macrocyclic ligands.- 1,4,8,11-tetraazacyclotetradecane and C-meso-5,5,7,12,12,14-hexamethylcyclotetradecane reacted with **3** for yielding macrocyclic ligands with four and three ferrocene moieties respectively. Redox behaviour and metal coordination ability have been studied.

All compunds have been characterized by IR and NMR spectroscopies, and electrochemically.

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LAICM1305P **9, Tue. 16**

INTERACTION OF METAL IONS WITH NEW LIGANDS OBTAINED BY CONDENSATION OF FERROCENECARBOXALDEHYDE WITH 2-AMINOBENZOIC ACID DERIVATIVES

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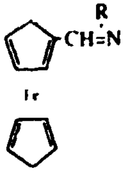
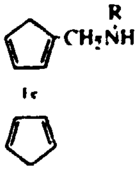
Organometallic ligands containing one or more ferrocenyl groups and their coordination ability towards metal ions have been subjet of great interest in last few years. We have undertaken the incorporation of ferrocenyl group into the skeleton of classical chelating N,O-donor ligands: 2-aminobenzoic acid derivatives react with ferrocenecarboxaldehyde yielding the corresponding Schiff-base species (type A); these imines can be hydrogenated for obtaining their parent amines (type B). All these products have been characterized (IR, NMR, electrochemistry), and, additionally, molecular structure of type B compound with R=CH_3 has been determined.

Type A compounds are stable in the solid state but easily hydrolyze in solution. Hydrolysis processes have been kinetically studied in a methanol-water media, and first-order rate constants were found.The protonation of type B compounds and their complex formation with copper(II) was studied potentiometrically.

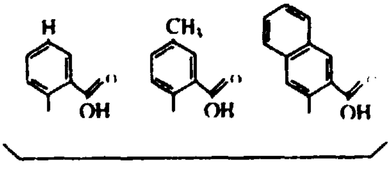
Additionally, reaction of type B compound (R=CH_3) with nickel perchlorate have been studied. Nickel (II) promotes the rupture of the C-N bond and molecular rearrangement to yield a protonated tertiary amine with two ferrocenyl groups: 2-bis(ferrocenylmethyl)ammonium-5-methyl-benzoic acid perchlorate.. Crystal structure of this compound has been determined.



type A



type B



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LAICM1306P **10, Thu. 16**

SYNTHESIS OF IODO URANIUM (IV) COMPLEXES WITH HYDROTRIS(PYRAZOLYL)BORATE LIGANDS

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Most of the chemistry that has been done with U(IV) involves the use of UCl_4 as starting material. This halide has been sucessfully used to synthesize complexes of the type UX_2Cl_2 in THF solution (L=$HBPz_3$, C_5Me_5, C_5H_3-1,3$(SiMe_3)_2$, $C_5H_5Co[P(O)(OEt)_2]_3$, C_4Me_4P)[1]. Some iodide derivatives have also been described but they were obtained by reacting $UR_2(C_5Me_5)$ (R=alkyl) with I_2 or $UCl_2[(C_5H_3$-1,3$SiMe_3)_2]_2$ with BI_3[1]. In this work we report the results obtained when we reacted UI_4 with $KHBPz_3$ in the molar ratio 1:2. When the reaction takes place in CH_2Cl_2 we isolated the orange complex $UI_2(HBPz_3)_2$ (62% yield), soluble in CH_2Cl_2, $CHCl_3$ and slightly soluble in benzene and toluene. Till now, no X-ray structural analysis has been undertaken but the ^1H NMR at 300K is consistent with the equivalence of all the pyrazolyl rings, as observed for $UCl_2(HBPz_3)_2$[2]. The uranium center must be eight coordinated by two iodines and two tridentate $HBPz_3$ ligands. In contrast, if UI_4 reacts with two equivalents of $KHBPz_3$ in THF we isolated and characterized the iodobutoxide derivative $UI[O(CH_2)_4I](HBPz_3)_2$ (65% yield). This green complex is formed due to the ring opening of THF by UI_4. In this work we will discuss the mechanism of ring opening of THF and we also will describe the synthesis of new alkoxide derivatives of the type $UI(OR)(HBPz_3)_2$ (R=Et,Ph) that have been prepared by reacting $UI_2(HBPz_3)_2$ with the respective alkoxides in toluene.

Acknowledgement

M. P. C. Campello acknowledges the award of a *PhD* grant from JNICT.

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LAICM1307P **11, Thu. 16**

RHENIUM COMPLEXES WITH TETRAKIS(PYRAZOL-1-YL)BORATE

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In contrast with $[HBPz_3]^-$ and $[HB(3,5\text{-}Me_2Pz_3)]^-$ the coordination chemistry of $[BPz_4]^-$ is relatively unexplored [1]. We have been using $[BPz_4]^-$ as a stabilizing ligand for Re in different oxidation states. The complexes $[ReO_3(BPz_4)]$ (1), $[ReOCl_2(BPz_4)]$ (2), $[ReCl_2(BPz_4)(PPh_3)]$ (3), $[Re(BPz_4)(CO)_3]$ (4) have been isolated and characterized. Characterization was done by elemental analysis, electronic, IR, ^1H and ^{13}C NMR spectroscopies and for complex (1) the solid state structure has been determined by X-ray crystallography. In solution all the compounds present a static behaviour, as shown by ^1H and ^{13}C NMR spectra. The pattern observed for the protons of the pyrazolyl rings indicates a tridentate coordination for $[BPz_4]^-$ and are consistent with C_{3v} (1,4) and C_s symetries (2,3). For the paramagnetic complex (3) large isotropic shifts were observed as well as a line broadening of the signals. In this work we report the synthesis and characterization of compounds (3) and (4). The electrochemical behaviour of the above compounds (1-4) has been studied by cyclic voltammetry in an aprotic medium , commonly CH_3CN, although for the Re(VII) complex thf and CH_2Cl_2 were also used as solvents. Bu_4NBF_4 or Bu_4NClO_4 were the supporting electrolytes and a Pt wire was employed as the working electrode. In some cases controlled potential electrolysis has been also performed. Further work involving these compounds is in progress in order to study the influence of the $[BPz_4]^-$ ligand in the chemical and redox behaviour of the Re centre and allow its comparisonwith other tripodal anionic ligands previously described.

Acknowedgements

This work was partially supported by JNICT. I.Santos and A.Paulo thank Prof. J.R Ascenso, C.Q.E., IST, for NMR facilities.

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STRUCTURE OF A SECOND CRYSTALLINE FORM OF TRIS[HYDRIDOTRIS(PYRAZOL-1-YL)BORATO]YTTERBIUM(III)

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The molecular structure of the homoleptic complex $Yb(HBPz_3)_3$ was determined by Takats et al[1]. The geometry about the eight-coordinate Yb^{3+} ion was found to be approximately bicapped trigonal prismatic, having one bidentate and two tridentate polypyrazolylborate ligands.
In the course of our research work on the chemistry of polypyrazolylborate complexes of Ln(II) and during the crystallisation process of $Yb(HBPz_3)_2$.DME we have isolated a second crystalline form of $Yb(HBPz_3)_3$. Here we report the crystal structure of this second form. Crystals are orthorhombic,space group $P2_12_12_1$ with unit cell parameters a=13.740(1),b=14.446(1),c=17.286(2)Å ,V=3431(1)Å^3 and Z=4. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to a final R of 0.038 and R_w=0.042 (3695 reflections with $F>3\sigma(F)$). The coordination geometry found is also bicapped trigonal prismatic but a different packing is observed in the new unit cell.

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LAICM1309P **13, Thu. 16**

URANIUM(IV)-LIGAND BOND DISSOCIATION ENTHALPIES

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The thermochemistry of lanthanide and actinide complexes is a field of considerable interest, as reflected by a number of publications over the last decade. The results of reaction-solution calorimetry of reaction 1 enable to calculate the U-$OCMe_2CH_2C(O)Me$ bond dissociation enthalpy.

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(sln) + HOCMe_2CH_2C(=O)Me(sln) \longrightarrow U[HB(3,5\text{-}Me_2Pz)_3]Cl_2[OCMe_2CH_2C(=O)Me](sln) \qquad (1)$$

The equilibrium 2, on the other hand, was studied at various temperatures and led to a van't Hoff plot from which the U-thf bond dissociation enthalpy, $\Delta H_r(2)$, was calculated.

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl_3.thf(sln) \rightleftharpoons U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(sln) + thf(sln) \qquad (2)$$

From the two previous results it was possible to conclude that in the $OCMe_2CH_2COMe$ ligand the second oxigen atom forms a donating bond to the uranium center.

Some preliminary results on other polypyrazolylborate complexes are also presented, compared with literature data and used to discuss the transferability of bond enthalpies.

LAICM1310P **14, Thu. 16**

INTERACTION BETWEEN POLYALCOHOLS AND HETEROPOLYTUNSTATES OF KEGGIN TYPE

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Heteropolytungstates are known to be photosensitive in the presence of organic solvents [1]. These compounds can be very useful as photocatalysts in oxidation of organic compounds [2].

In this work we studied several heteropolytungstic acids of the Keggin type and some of their salts, having P, Si, B and Co as heteroatoms. We also studied several analogous lacunary compounds - $[XW_{11}O_{39}]^{n-}$ - and lacunary substituted - $[XW_{11}MLO_{39}]^{m-}$.

The interaction between these compounds and several polyalcohols, with chains varying from C2 to C6, was studied mainly by i.r. spectroscopy.

The type of interaction observed in each case will be discussed and compared with NMR results.

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[2] W. P. Griffith, *Trans. Met. Chem.*, 1991, **16**, 548

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LAICM1312P **15, Thu. 16**

SPECTROSCOPIC CHARACTERIZATION OF A NICKEL(I) COMPLEX WITH A N_2OS ASYMMETRIC LIGAND

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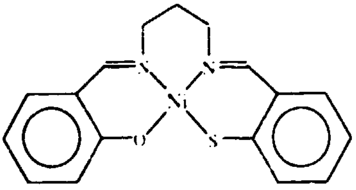
In the last few years several studies with nickel(I) complexes have been performed to rationalize the factors that contribute to stabilize this unusual oxidation state for nickel. We report an EPR study of a nickel(I) complex with a N_2OS coordination sphere, obtained either by chemical or by electrochemical reduction of the parent nickel(II) complex.

(Ni(*t*-salsalpd)) was prepared by template Schiff condensation of the appropriate nickel(II) complexes.[1] The compound was studied by ^1H NMR and UV-Vis and the results indicate a square-planar geometry for the complex. Cyclic voltammograms obtained in $(CH_3)_2SO$/0 1*M* TBAP reveal a reversible reduction process with $E_{1/2} = -1.4V$ vs Ag/AgCl (1*M*, NaCl).



(Ni(t-salsalpd))

The nickel(II) complex was reduced, in $(CH_3)_2SO$, by constant potential electrolysis and by using Na/Hg. EPR spectra of reduced frozen solutions are rhombic, with $g_1 = 2.272$, $g_2 = 2.095$ and $g_3 = 2.063$, typical of a nickel(I) oxidation state with a $(d_{x^2-y^2})^1$ ground state. The electronic spectra of electrochemically reduced solutions show, in addition to the nickel(II) bands, a new band at 720 nm assignable to a d - d transition of the nickel(I) complex.

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Acknowledgments: E.P. and L.G. thank JNICT (Lisboa) for fellowships.

LAICM1313P **16, Thu. 16**

SYNTHESIS AND CHARACTERIZATION OF COPPER(II) COMPLEXES WITH TETRADENTATE N_2OS LIGANDS

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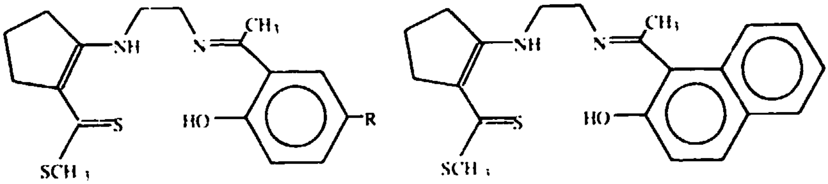
Recognition that in the active site of type I blue copper proteins the metal ion exists in a highly distorted environment with a mixed donor coordination sphere, has spurred great interest in the synthesis of models for these centers that could mimic their unusual spectroscopic behavior. In the present work we describe the synthesis of copper(II) complexes with tetradentate ligands that provide a N_2OS coordination sphere.



H_2cdMeRsalen *H_2cdMenapen*

Schematic drawing of the ligands used in this work

Electronic spectra of the complexes, obtained in Nujol mulls and in N,N-dimethylformamide solutions show one broad band centered at 14.5 kK (ε = 100 - 200 $M^{-1}cm^{-1}$), typical of square-planar copper(II) complexes, followed by several very intense absorption bands at higher energies. Frozen solution EPR spectra in N,N-dimethylformamide indicate a rhombic environment around the copper(II) ion, with $g_z > (g_x, g_y)$ and show hyperfine coupling due to the copper and to two nitrogen nucleus.

Acknowledgment: E.P. thanks JNICT (Lisboa) for a fellowship.

LAICM1314P **17, Thu. 16**

ELECTROCATALYTIC REDUCTION OF METHYL IODIDE IN THE PRESENCE OF NI(I) SCHIFF BASES COMPLEXES

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Complexes of nickel(I) have been shown to act as effective catalysts in the electrochemical reduction of alkyl halides, and this finding has spurred considerable interest in the study of the catalytic process. Here we report the catalytic efficiency towards methyl iodide reduction of several electrochemically generated Ni(I) complexes with pseudo-macrocyclic tetradentate ligands with a N_2O_2 coordination sphere.

Cyclic voltammograms were run for (a) pure solutions of the nickel(II) complexes (NiL), (where L = *salen, salpd, salbd* and *salhd*) 2.0x10^{-3} *M* in DMSO/TBAP 0.1M and (b) for similar solutions to which methyl iodide was added stepwise so that its concentration ranged from 2x10^{2} to 1x10^{1} *M*. In the absence of substrate, cyclic voltammograms of Ni(II) complexes show a single reversible one-electron reduction ($E_{1/2}$ range from −1.40 to −1.65 V, in the order: *salpd, salbd, salen* and *salhd*). Upon addition of methyl iodide, the cyclic voltammograms reveal that reactions of Ni(I) complexes with the electrophile are fast, and the observed substantial increase in cathodic peak current suggests that the chemical process regenerates the electroactive nickel(II) complexes. The results show that the catalytic efficiency depends on the half-wave potential of the redox catalyst: nickel complexes with the most negative half-wave potential show the highest catalytic activity toward CH_3I reduction.

Acknowledgments: This work was partially supported by JNICT, contract No. PBIC/C/CEN/1188/92 (CF). FA thanks JNICT for a fellowship

INTERACTION OF SQUARE-PLANAR N_4 NICKEL (I) COMPLEXES WITH AXIAL P-DONOR LIGANDS

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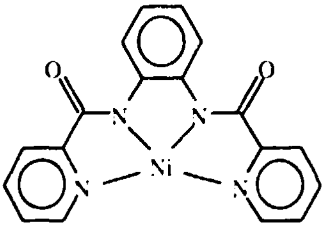
The possibility of Ni(I) macrocyclic complexes to mimic the behavior of the active centers of nickel enzymes has spurred enormous interest in these complexes. Our work with nickel in low oxidation states led us to study, mainly by electron paramagnetic resonance (EPR), the axial interactions of several phosphorous donor ligands with the Ni(I) ion in a N_4 square planar environment.

The Ni(I) complex was generated by reduction of (Ni(bpphen)) in DMF with Na(Hg). The phosphorous aducts were made by addition of the relevant P-donor in large excess to a solution of freshly generated Ni(I) complex. EPR data suggest that all ligands do coordinate to the initial Ni(I) species, except for $P(o\text{-}MePh)_3$, probably because of steric requirements of this bulky phosphine. Frozen solution EPR spectra show, for all Ni(I) species, axial symmetry, and hiperfine splittings in the $g_\perp$ region (a = 0.09 mT) due to coupling of the unpaired electron with the four equivalent nitrogens of the equatorial plane, thus suggesting a $(d_{xy})^1$ ground state for nickel. Axial coordination of P-ligands results in a shift of $g_\parallel$ to lower fields; the strongest π acid cause the largest shift.



(Ni(bpphen))

Acknowledgments: M.V. thanks JNICT for a fellowship.

LAICM1316P **19, Thu. 16**

EPR CHARACTERIZATION OF Ni(III) COMPLEXES WITH N3O2 SCHIFF BASE LIGANDS DERIVED FROM NAPHTHALDEHYDE

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Stabilization of d^7 nickel(III) centres by mixed donors pseudomacrocyclic ligands has been the subject of much interest in recent years . This work presents a study by electron paramagnetic resonance (EPR) of nickel (III) complexes with N_3O_2 Schiff base ligands derived from naphthaldehyde, obtained by iodine oxidation of the corresponding Ni(II) complexes, in the solvents: methanol, acetonitrile (ACN), N,N'-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine (py).

Contrasting with oxidized solutions of (Ni(napdien)) in *py* that are EPR silent, oxidized solutions of this complex in the other solvents exhibit EPR signals. In methanol and ACN the oxidation originates predominantly radicalar species, but in DMF and DMSO the EPR spectra clearly indicate the presence in solution of hexacoordinate Ni(III) species with axial elongation. These spectra do not exhibit hyperfine structure, thus suggesting that the nitrogen atom of the diimine bridge is not coordinated to nickel. Oxidized solutions of (Ni(naptrien)) and (Ni(napMetrien)) exhibit EPR spectra in all the solvents used. They show higher rhombicity than the other complexes and hyperfine structure in the high field region: one triplet in oxygen coordinating solvents, and one non-resolved multiplet with five bands in ACN. These results suggest that the bridge nitrogen atom is bound to nickel and that the complexes should be formulated as (Ni(naptrien)•S)$^+$ and (Ni(napMetrien)•S)$^+$. Oxidized solutions of these complexes in *py* reveal EPR spectra with quite different *g* features and thus imply that significant structural rearrangements induced by pyridine coordination must have taken place.

ACETAZOLAMIDE INTERACTION IN Cu(II), Zn(II) AND Co(II) MODEL COMPLEXES OF THE CARBONIC ANHYDRASE ENZYME.

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Carbonic Anhydrase (C.A.) is the enzyme that catalyzes the biological interconversion between CO_2 and HCO_3^-. The Zn ion at the active site of the enzyme is bound to three imidazole groups and an apical water molecule with an approximately tetrahedral geometry .

Unsubstituted sulfonamides are strong inhibitors of this enzyme, among them, the Acetazolamide(H_2acm) is the most prominent one. Although the ligation of the Zn(II) ion in the enzyme active center has been modeled by triamine ligands [1], few models of H_2acm metal complexes have been reported [2]

We have initiated a systematic investigation of the binding of acetazolamide to Cu(II), Co(II) and Zn(II) with ligands which can be considered as mimics of the C A active site. We have selected the diethylentriamine (dien), dipropylenetriamine(dpt) and Tris[2-(1-methyl-2'-benzimidazoyl)ethyl]nitromethane (trisbim) as model ligands.

In this paper, the interaction of acetazolamide is described in basis on a solution UV-vis study of M(II)-acetazolamide-model ligand systems [M=Cu(II), Co(II) and Zn(II)] From both UV and vis spectra the coordination of acetazolamide is deduced to take place only in a deprotonated form of the sulfonamide

1 - Kimura E and Koike T., *Comments. Inorg. Chem.* 1991, 11, 285

2 - Ferrer S., Jiménez A and Borràs J., *Inorg. Chim. Acta* 1987, 129, 103

LAICM1325P **21, Thu. 16**

CRYSTAL STRUCTURE AND PROPERTIES OF $Cu(Hstz)_2(EtOH)Cl_2$

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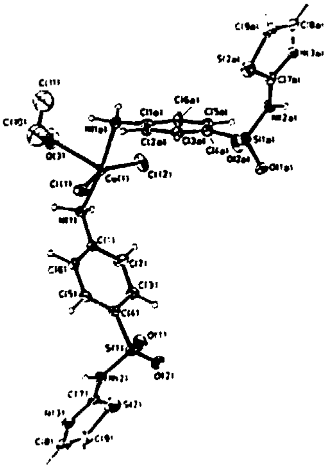
Interest on the sulfanilamide derivatives arises primarily from their antibacterial activity, which is due to the competitive antagonism of PABA(p-amino benzoic acid) and the sulfanilamide. Among them, the sulfathiazole, 4-amino-N-2-thiazolylbencenosulfonamide (Hstz) is one of the most used. Apart from their farmacological interest, the chemical importance of the sulfathiazole is related to their versatile coordination behaviour [1, 2].

Here, we report the synthesis, crystal structure and properties of the $Cu(sulfathiazole)_2(EtOH)Cl_2$ complex.

The Cu(II) ion is five coordinated being the geometry of the compound intermediate between square pyramidal and trigonal bypiramidal (figure).



The comparison of the crystal structure with those of the related compounds reveals interesting aspects such as the different grade of the distorsion from the two five regular geometries

EPR SINGLE CRYSTAL OF $Cu(sulfathiazole)_2(MeOH)Cl_2$.

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Gatteschi D and David L
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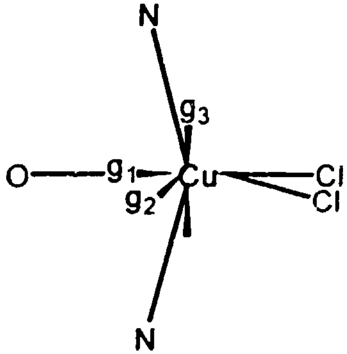
As a part of our work on the coordination behaviour of sulfathiazole ligand (Hstz) we have described the crystal structure of $Cu(Hstz)_2(MeOH)Cl_2$ complex [1] The Cu(II) ion is surrounding by two N amino atoms from the Hstz ligand, two chloride anions and the oxygen atom from the methanol molecule. The geometry of the compound, intermediate between square pyramidal and trigonal bypiramidal, makes the study of the electronic properties of the compound of interest

In the present communication the single EPR spectrum is studied and related with the crystal structure

The compound presents a rhombic EPR spectrum with the following g values: g_1= 2.25, g_2= 2.09 and g_3= 2.03 The corresponding principal directions are shown in figure. g_1 is roughly parallel to the Cu-O direction, while g_3 is within error parallel to the Cu-N bond directions The R value [$R=g_2-g_1/g_3-g_2$] indicates, in agreement with the crystal structure, a strong distorsion from the two five regular geometries (square pyramidal and trygonal bypiramidal) [2]



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1 - Casanova J , Alzuet G , Borrás J , Amigo J M and Debaerdemaeker T , *Zeit fur Kristall*, in press

2 - Hathaway B J and Billing D E , *Coord Chem Rev* , 1970, 5, 143

LAICM1327P **23, Thu. 16**

HALOCUPRATES(II) OF THE TRIAMTERINIUM, A DIPROTONATED PTERIDINE DERIVATIVE. CRYSTAL STRUCTURE OF $(TRIAMTERINIUM)_2CuCL_4$.

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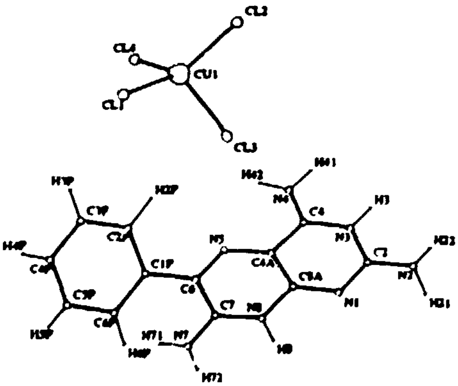
Natural pteridine derivatives such as folic and biopterin are important cofactors in biological redox reactions. Pteridines are fused-ring nitrogen heterocyclic compounds that function as cofactors for enzymes involved in hydroxylation and methyl transfer and as redox mediators. Between the pteridine derivatives we have chosen the triamterene. Triamterene (2,4,7 triamino 6 o-tolylpteridine) is a potassium retaining diuretic drug [1].

The structure of the $[H_2 triam][CuCl_4]$ complex (Figure) consists of one independent H_2triam^{2+} cation and one $CuCl_4^{2-}$ anion. In the anion, there is a significant deviation from both of the two ideal geometries, square planar and tetrahedral, since the Cl-Cu-Cl angles around the metal atom are 143.71(5), 95.91(5), 98.42(5), 93.37(5), 100.10(6) and 133.83°(5).

With respect to the cation nature, the first aspect to be noted is that the protonation takes place in the endociclyc nitrogen N(3) and N(8) atoms.



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LAICM1328P **24, Thu. 16**

COORDINATION BEHAVIOUR OF SULFATHIAZOLE: CRYSTAL STRUCTURE OF $Cu(stz)(py)_3Cl$.

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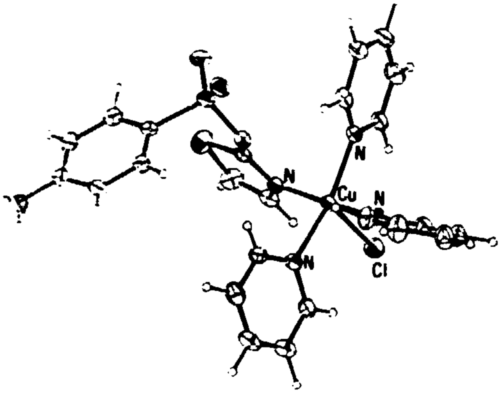
The synthetic and structural studies of sulfathiazole metal complexes are receiving significant attention due to the different complexing behaviour of such ligand and consequently different coordination possibilities with the metal.

In fact, the only crystal structures of sulfathiazole complexes, recently described by us, show a large variety of coordination modes [1,2]. While in the $Zn(stz)_2 H_2O$ complex the sulfathiazole acts as a bidentate ligand interacting through the N_{amino} and $N_{thiazole}$ atoms, in the $Cu(Hstz)_2(MeOH)Cl_2$ compound the sulfathiazole acts as monodentate ligand, being its donor atom the amino nitrogen.



In this study we describe the crystal structure of $Cu(stz)(py)_3Cl$ complex. The sulfathiazole, acting as monodentate ligand, binds the metal ion through the $N_{thiazole}$ atom (figure). The coordination geometry can be better described as square pyramidal(τ=0.19). The electronic properties of the compound are related to those of the other Cu(II) sulfathiazole complexes whose geometry tend rather towards trigonal bypiramidal

LAICM1329P **25, Thu. 16**

METAL COMPLEXES OF SULFACETAMIDE

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Many drugs possess modified pharmacological and toxicological properties when administered in the form of metal complexes. Sulfonamides and their different substituted derivatives are extensively used in medicine for their antibacterial properties. The sulfacetamide (N-[4-(aminofenil)sulfonil]acetamide, Hsacm) is usually used for ophthalmic and topical applications. The drugs "SULFACET-R", "METIMYD OPHTALMIC", etc. contain Hsacm and its sodium salt (1).

We have initiated a study of the complex formation between Hsacm and metal ions. In this way, we have determined the crystal structure of the $Cu(Hsacm)_2(NO_3)_2$ (2), where the copper (II) ion has a tetragonal octahedral coordination of two nitrogen and four oxygen atoms. The two nitrogen atoms are from the sulfacetamide molecules, two oxygen atoms are from monodentate nitrate anions, and the other two from acetamide moiety. The sulfacetamide acts as a bridging ligand between two copper ions through the N_{amino} and the $O_{acetamido}$.

We have obtained several complexes of Hsacm and Co^{2+} and Cu^{2+} ions. We have characterized these complexes and we are testing their antibacterial properties.

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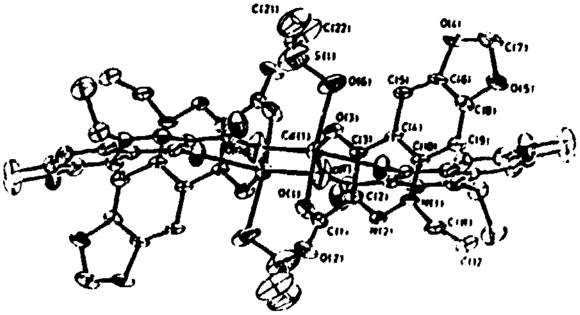
(1) *Physicians' desk reference*, 43th ed 1989, 882,1513,1939

LAICM1330P **26, Thu. 16**

CRYSTAL STRUCTURE OF $[Cd_2(Cx)_4(DMSO)_2].2H_2O$ COMPLEX; HCx=1-ETHYL-1,4-DIHYDRO-4-OXO(1,3)DIOXOLO(4,5g) CINNOLINE-3-CARBOXYLIC ACID.

M.Ruiz[a], R.Ortiz[a], L.Perelló[a], S.Garcia-Granda[b] and M.R.Díaz[b].
[a]Departamento de Química Inorgánica, Universidad de Valencia, SPAIN. [b]Departamento de Química Físic. y Analítica, Universidad de Oviedo, SPAIN.

In the past years we have been investigating the coordination chemistry of cinoxacin (HCx) with transition metal ions in an attempt to examine its mode of binding in the solid state. In all the compounds synthesized, the cinoxacinate ions act as bidentate chelate ligand through one carboxylate oxygen atom and the exocyclic carbonyl oxygen atom(1,2). The complex described here is the first compound in which cinoxacin acts as bridging ligand. An ORTEP drawing of the complex is displayed in the Figure. Crystals of compound contain dimeric $[Cd(Cx)_2(DMSO)]_2$ molecules. Each dimeric unit has crystallographic $\bar{1}$ symmetry, with the inversion center lying on the midpoint of the Cd...Cd interaction. Each dimer contains cadmium atoms bridged by two oxygens from two symmetry-related carboxylate groups [O(1'), O(1'A)] generating planar Cd_2O_2 rings. The metal environment is formed by three O_{carbox}, two O_{ceto} and one O_{DMSO} atoms.



1) Chulvi C., Muñoz M.C., Perelló L., Ortiz R., Arriortua M.I., Vía J., Urtiaga K., Amigó J.M. and Ochando L.E., 1991,42 133, J. of Inorg.Biochem.

LAICM1331P **27, Thu. 16**

COMPLEX FORMATION EQUILIBRIA BETWEEN THE CINOXACIN, AN ANTIMICROBIAL AGENT, AND Co(II), Ni(II) AND Zn(II) IN AQUEOUS SOLUTION.

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Departamento de Química Inorgánica. Universidad de Valencia. SPAIN

The antibacterial activity of 4-quinolone compounds, such as Cinoxacin (HCx = 1-ethyl-1,4-dihydro-4-oxo(1,3)dioxolo(4,5-g)cinnoline-3-carboxylic acid), is apparently due to the inhibition of DNA synthesis. Actually, it seems that chelation cf certain metal ions through the carbonyl and carboxyl groups of these molecules and the binding of the resulting complex to DNA (with some base specificity), may be essential prerequisites for their antibacterial activity. In order to enhance the knowledge of the behaviour of Cinoxacin as complexing agent in biological systems, in the present comunication we study the complex formation between Co(II), Ni(II) and Zn(II) and Cinoxacin in aqueous solution (NaCl 0.1M) at 37°C. The stability constants were refined by the method of rigorous least-squares using the computer program SUPERQUAD (1).

Species	logβ		
HCx	4.450(1)		
$[H_2Cx]^+$	6.46(2)		
	Co^{2+}	Ni^{2+}	Zn^{2+}
$[MHCx]^{2+}$	8.40(3)	----	7.3(1)
$[MHCx_2]^+$	11.95(1)	11.22(3)	----
$[MH_2Cx_2]^{2+}$	----	14.98(9)	15.72(8)
$MHCx_3$	15.71(2)	14.72(5)	15.2(1)
$[MH_2Cx_3]^+$	21.16(5)	19.60(5)	19.57(7)
$[MCx]^+$	4.07(3)	3.248(8)	-----
MCx_2	7.19(1)	7.278(7)	10.62(7)
$[MCx_3]$	-----	10.46(5)	14.42(5)

1) Gans P. Sabatini A. and Vacca A. 1985 1195 J. Chem. Soc. Dalton Trans

LAICM1345P **28, Thu. 16**

1-(2-CARBAMYLETHYL)BENZIMIDAZOLE NICKEL(II) COMPLEXES WITH UNUSUAL MAGNETIC BEHAVIOUR

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In the course of work on NiX_2L_4 complexes, where L is a 1-(2-carbamylethyl)imidazole derivative, to study the effect of different axial ligands (X) on their properties, we have obtained three compounds with L = 1-(2-carbamylethyl)benzimidazole (CBIm), $NiCl_2(CBIm)_4$, $NiBr_2(CBIm)_4$ and $NiBr_2(CBIm)_4.H_2O$ which exhibit anomalous room temperature magnetic moments.
Spectroscopic properties were studied at room temperature and magnetic susceptibilities measurements and its temperature dependence were carried out on the complexes in the solid state.
The molar magnetic susceptibility as function of temperature for the chlorocomplex gives a non-Curie-Weiss plot, decreasing with temperature lowering (300-80 K) with magnetic moments ranging from 2.18 to 1.14 B. M.. This behaviour may indicate the presence of nickel(II) ions in two different spin states but the electronic spectrum does not provide clear evidence of the existence of both singlet and triplet states.
The anhydrous bromocomplex shows a room temperature magnetic moment of 2.11 B. M. and a magnetic susceptibility virtually independent of temperature from 300 to about 150 K. Below this temperature the susceptibility increases. A possible explanation for this behaviour is that a phase change occurs. However, in the absence of X-ray data at different temperatures, it is impossible to confirm it. The presence of water in the other compound with bromide provokes different magnetic properties.
All the compounds [illegible] electrolytes in methanol solution and give electronic spectra indicative of the presence of pseudo-octahedral species but in interaction with the solvent.

Acknowledgements. [illegible] financial support to G. V. A. [illegible]

LAICM1353P **29, Thu. 16**

PREPARATION, CRYSTAL STRUCTURE AND SPECTRAL BEHAVIOUR OF $Cd(S_2PPh_2)_2$.

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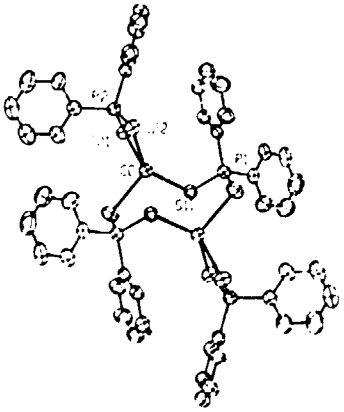
Departamento de Química Inorgánica, Universidad de Santiago de Compostela, España. *Inst. de Fis. e Quim. de Sao Carlos, USP, CEP13560, Sao Carlos, SP Brazil.

Monocrystals of the title compound suitables for X-ray diffraction studies were grown by recrystallation in DMSO of the product obtained reacting an ethanolic solution of ammonium diphenyldithiophosphate (2.6 mmol) with a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (1.3 mmol) in the same solvent. $Cd(S_2PPh_2)_2$ is triclinic, space group $P\bar{1}$, a=9.273(1), b=10.426(1), c=13.845(3) Å , β=103.16(1)°, U=1248.3(7) $Å^3$, Z=2, D_c= 1.625 g cm^{-3}, $\mu(M_oK_\alpha)$= 13.30 mm^{-1}, R= 0.036 y Rw= 0.041 . The structure consists of dimers. The dimeric arrangement contains two chelated and two bridge ligands, reaching the two cadmium atoms a distorted tetrahedral coordination.The two monomers are related to each other by a C_2 symmetry axis. Structural, IR, ^{31}P and ^{113}Cd n.m.r. data of the compound are compared with those for other cadmium (II) dithiophosphinates.



COORDINATION AND REACTIVITY OF N-(2-AMINOETHYL)-2-{[(PYRIDINE-2-YL)METHYL]THIO}ACETAMIDE

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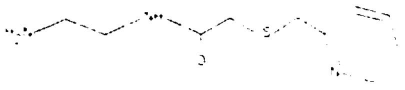
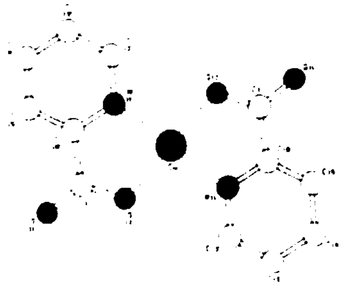
In recent years, the study of metal complexes containing flexible tetradentate ligands has been an area of active interest. Investigations have involved evaluation of factors governing the overall geometry of the complexes, their reactions, and the stereochemistry of the reaction products.



egpy

We have now investigated the preparation of Cu(II) complexes which contain *N-(2-aminoethyl)-2-{[(pyridine-2-yl)methyl]thio}acetamide* (egpy), a linear tetradentate ligand having an NSNN donor atom set. Elemental analysis and spectroscopic techniques were used to characterize the complexes.



In addition, we have found that irradiation with visible light at room temperature induces the reaction of CO_2 with the copper(II) complexes of **egpy**, yielding *copper(II)-bis(pyridine-2-carboxilate)* (see Fig.) which was studied by single-crystal X-ray diffraction techniques to unequivocably establish its structure.

Further studies on these and related reactions are in progress.

This work was financed by the project **PB91-0787** of the DGICYT.

METAL IONS IN DEMOSPONGIAE OF THE NORTH ATLANTIC

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3-Instituto Superior Tecnico. Av. Rovisco Pais 1. 1096 Lisboa Codex Portugal

Determinations of metal content in sponges are scarce[1]. Preliminary assays with Demospongiae of the portuguese coast revelead that these sponges possess a wide variety of metals [2].

Geodia cydonia and a Stellettidae were collected in Atlantic Ocean (37°N.9° W) 500 m deep. In the laboratory they were carefully washed with "synthetic sea water" and freeze dried.Determinations of metal elements were done by EDXRF spectroscopy and by flame and graphite furnace absorption spectroscopy.

Metal concentrations are very similar in both species but lower than in sponges from the intertidal zone of the portuguese coast.Vanadium .which has been found to be present in the active site of haloperoxidases in Algae. Lichen and some Fungi - if present in these sponges- is below the limits of detection.

The physiological role of these metals is being currently investigated since sponges. being the most primitive Metazoa. possess some unusual halometabolites that may be promoted through some metal enzymes.

[1]- A P Vinogradov **1953**. *The elementary chemical composition of marine organisms.*Sears Foundation. New Haven. Conneticut

[2] - F Araújo.M T Lopes. A Cruz. M C Vaz. M Simões Almeida. M Humanes. J J Fraústo da Silva. VI th International Conference on Bioinorganic Chemistry. San Diego. **1993**

SYNTHESIS AND STUDY OF INSULIN MIMICKING VANADIUM COMPLEXES

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Vanadate salts and several oxovanadium(IV) complexes have been found to reduce the concentration of glucose in the blood of laboratory animals (rats), thus mimicking the action of insulin. The use of such compounds in the therapy of diabetes melitus is of interest, but one drawback is that they are poorly absorbed in the gut and the amounts used can be toxic. Since VO^{2+} is similar in some respects, to Cu^{2+} and Fe^{3+}, it is to expected that ligands which are potent iron chelators are also good vanadyl chelators. The purpose of this work is to obtain less toxic and more easily absorbed complexes of VO^{2+} which can mimic the action of insulin. With this objective, several 1-alkyl-3-hidroxy-2-methylpyridin-4-one compounds, *e. g.* (1-H, 1-CH_3, 1-C_2H_5 and long chain alkyls), which are good iron chelators, were synthesised and tested as complexing agents for the vanadyl ion in aqueous solution. It was found that the overall stability constant of the 2:1 complex of VO^{2+} of, *e. g.* 1-methyl derivative (18.9) is higher than that of the Cu^{2+}complex (16.6) and much higher than that of the Ni^{2+} complex (12.1). The overall stability constant of the 3:1 Fe^{3+} complex, determined for the 1-ethyl derivative by other authors, is even higher (36.9). The 3:1 vanadium complex was not yet detected in aqueous solution but, in methanol, EPR spectra provide evidence for the possible formation of three different species, one possibly being a nacked V(IV) complex.

LAICM1371P **33, Thu. 16**

HALOPEROXIDASES FROM THE ALGAE *Ascophyllum nodosum*

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The discovery of haloperoxidases containing vanadium in Fungi, Lichens and Algae is one of the most recent developments of the biological chemistry of this element [1].

The aim of our work is to improve the methods of extraction and purification of this enzyme and to compare the properties of haloperoxidases associated with different algae. *Ascophyllum nodosum* (Fucaceae;Phaeophyta) is the most extensively studied organism from this point of view. The specimens for the present study were collected in the north coast of Portugal (Viana do Castelo) which corresponds, probably, to the meridional limit of the habitat of this species. A particular morphology has been described for this location under the name *A.nodosum* var. *lusitanica.*

Preliminary studies have shown that the extracts of this seaweed have iodo-peroxidase activity as determined by the iodide test [2]. *A. nodosum* specimens collected in northern Atlantic exhibit bromo-peroxidase activity, which as not yet been detected in the portuguese specimens. Purification and characterization of this enzyme is on progress to ascertain whether the haloperoxidase are identical or depend specifically on the variety.

1- R Wever, J W P M Van Schijndel, E G M Vollenbroek, EUROBIC 1, Newcastle upon-Tyne, 1992

2- H Vilter, K-W Glombitza, A Grawe, **Bot. Marina**, 1983, **26**, 331

LAICM1376P **34, Thu. 16**

NON COVALENT INTERACTION IN THE SYSTEM CYCLODEXTRIN-DYE-BIOLOGICALLY ACTIVE NITROGEN BASES.

Díaz D., Yatsimirsky A.K., Escobar-Llanos C.*, Bernad-Bernad M.J.* and Gracia-Mora J.

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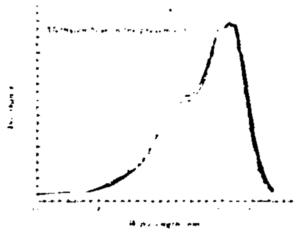
In 1991, T. Morita[1] have established the relationship between structure and anti-HVI activity in the series of 50 cyclodextrine (CD) derivatives including polysulfated and hydrophobically substituted. Later D.B. Weiner et al[2] noted that several polysulfated CD's manifested significant anti-HIV effects practically without side effects. To this moment the mechanism of the action of sulfated CD's is not clearly determined.

It is known that CD's have the ability to form inclusion complexes with different molecules. However, there is no information about the inclusion complexes of dodecasulfated CD, as well as other sulfo CD derivatives.



In this communication we report for the first time the results of systematic study of interactions of dodecasulfated CD with several dyes and biologically active nucleosides and nucleic bases.

The figure shows the typical effects of CD on the absorption spectrum of a dye, the methylen blue (MB). Similar effects were observed when nucleosides were added to the solution of MB. These spectral changes allow us to calculate the association constants for CD and nucleoside interactions with dyes, summarised in the Table below.

Binding constants (mole^{-1}) T=25 °C

		In the presence of	
Bases	Methylen blue	β-CD	β-CD$(SO_4)_{12}$
Adenine	71±3	60±7	86±6
Adenosine	87±4	75±3	89±5
Idoxuridine	41±3	30±4	53±6
Histamine	<1	<1	<1
Thymine	<1	<1	<1
Purine	17±.35	10.5±1	15.44±.35

Evidently sulfated CD forms a more tight complex with cationic MB than neutral β-CD. There is now indication for the inclusion of bases into CD's. So the most probable mechanism of sulfated CD anti-HIV effect is by its interaction with some receptors rather than with components of nucleic acids.

[1] Morita, T.; Kurita, H.; Matsumoto, K.; Otake, T.; Mori, H.; Morimoto M.; Ueba, N.; Kunita, N., *J. Med. Chem.* **34** (1991), 2301

[2] Weiner D.B., Williams W.B., Weisz P.B. and Green M.I. *Pathobiology*, **60**, [4], (1992), 206

LAICM1377P **35, Thu. 16**

Study of the interaction between several copper (II) complexes of the Casiopeina's family with DNA.

Ruiz-Ramirez Lena[1], Gracia-Mora Isabel[1], Moreno-Esparza Rafael[1], Cirigo Claudia[1], Tovar Araceli[1] and Garcia-Carranca Alejandro[2]
1) Universidad Nacional Autonoma de Mexico (UNAM), Facultad de Quimica, Departamento de Quimica Inorganica y Nuclear Ciudad Universitaria 04510 D.F., MEXICO
2) Universidad Nacional Autonoma de Mexico (UNAM), Instituto de Investigaciones Biomedicas, Departamento de Biologia Molecular Ciudad Universitaria 04510 D.F., MEXICO

The development of a new series of antineoplastic drugs so call Casiopeinas has been carried on in our group. The synthesis (1), the *in vivo* antitumor activity in murine models (2) and the cytostatic effect of some of these drugs have been reported.

Also the mutagenic effect evaluated in *Drosophila melanogaster* has shown that the complexes produces somatic mutations, in eyes and wings. The above results implies that there is an interaction between the drugs and the DNA.

In the present work we have performed a serie of experiments with copper complexes from three families of Casiopeinas I, II and III. The interaction with linear and supercoiled DNA has been followed by electrophoresis in agarosa gel. The variables are drugs concentration and incubation temperature and all experiments have been done at a constant time (30 min).

The aim of this work is to obtaing a correlation between the intensity of the interaction drug-DNA with respect to the substituients of the general structural skeleton of the Casiopeinas.

Some of the general conclusions can be summarized as that the Casiopeinas with more hydrophobic sustituents interact easily with the linear DNA and those with less hydrophobic substituents interact easily with the supercoiled DNA.

The equilibrium constant of the more soluble complexes has been determined by spectrochemical or potentiometrical methods.

It is important to mention that the antineoplastic activity shown by these drugs has been compared with cis-platinum (2) and the toxicity is lower.

1. Lena Ruiz A. U.S.A. Patent number 5-107,005 (1992)
2. Ruiz-Ramirez L., Gracia-Mora I., et al Journal of Inorganic Biochemistry ((1991) 43,2,615

LAICM1389P **36, Thu. 16**

SYNTHESIS AND XPS, IR AND LAXS ANALYSIS OF 1:1 Co(II) 1-(D-3-MERCAPTO-2-METHYLPROPIONYL)-L-PROLINE COMPLEX

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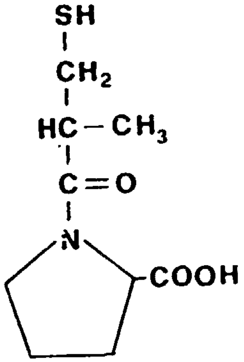
A. Corrias,
Dipartimento di Scienze Chimiche, Via Ospedale 72, I-09124 CAGLIARI, Italy

A series of 1:2 metal complexes with title legand (known as Captopril (CAP) see figure) and Zn(II), Co(II), Cd(II) and Ni(II) has been synthesized and investigated by means of LAXS (Large Angle X - ray Scattering), IR, XPS and NMR spectroscopies [1,2]. Adding perchloric acid to an alkaline solution of the 1:2 cobalt complex a 1:1 dark violet amorphous compound is obtained.



IR spectra show the absence of ν(SH) and ν(OH) bands in 1:1 complex indicating the loss of the two captopril protons after coordination. The separation between ν_a(COO) and ν_s(COO) , Δ = 295 cm^{-1}, is greater than that found for 1:2 complex [2]. The large Δ value appears to indicate a unidentate carboxylate coordination.

XPS and LAXS analysis of this complex suggest that Cobalt is tetracoordinated with a chain structure. CAP is bonded *via* sulphur and *via* amidic oxygen with a Co^{2+} ion and by an oxygen of a carboxylate group to another Co^{2+} ion. A water molecule completes the coordination sphere. A distance of 2.3 Å is found for the first neighbours in the complex.

(1) D. Atzei, D. De Filippo, A. Rossi, A. Lai, G. Saba, R. Bucci, Spectr. Acta, 48A, No 7, 911 (1992)

(2) D. Atzei, A. Corrias, R. Caminiti, C Sadun, R. Bucci, Phosphorus Sulfur, proofs No LM466 (1993)

LAICM1390P **37, Thu. 16**

POLYNUCLEAR COPPER(II) DIMETHYLGLYOXIMATO COMPLEXES

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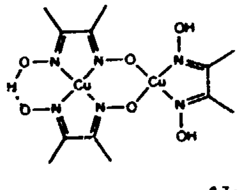
[b]*Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, URA 419 CNRS, 75252 Paris, France.*

[c]*Departamento de Física Aplicada, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain.*

$[Cu(Hdmg)_2]$ (H_2dmg, dimethylglyoxime) and its deprotonated form $[Cu(Hdmg)(dmg)]^-$ can work as bidentate ligands, coordinating metal ions through two oximate oxygen atoms, with the formation of binuclear metal complexes. Further deprotonation to $[Cu(dmg)_2]^=$ yields a bis-bidentate bridging ligand($\mu,\eta^2:\eta^2$) allowing the formation of trinuclear metal complexes. We report here the formation in solution, synthesis, structural characterization and magnetic properties of the following polynuclear copper(II) dimethylglyoximato complexes : $[Cu_2(Hdmg)_2(H_2dmg)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (1) $[Cu_2(dmg)(Hdmg)(H_2dmg)]X \cdot nH_2O$ [X=ClO_4, n=1.5] (2); [CLO_4, 0] (3), [Cl, 1] (4), [SO_4, 2.5] (5) and $[Cu_3(dmg)_2)(H_2dmg)_2](ClO_4)_2 . 2H_2O$ (6). The crystal structure of complexes (1) and (5) has been determined by X-ray diffraction methods. The copper ions are doubly bridged by two oximate groups in *cis* arrangement (Cu-NO-Cu two-atom bridges) in (1), (2) and (6), whereas compounds (3), (4) and (5) reveal one new and unexpected oximato bridge (Cu-O-Cu monoatomic bridge). All the compounds exhibit a very strong antiferromagnetic coupling between the metal centers.



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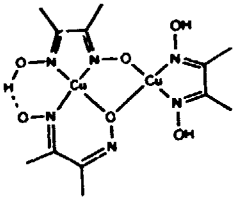

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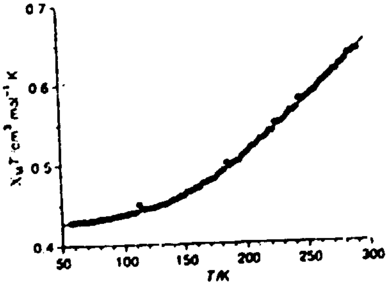

6

LAICM1394P **38, Thu. 16**

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF THE FIRST CHARACTERIZED Mn(II) DINUCLEAR SYSTEM WITH END-ON AZIDO BRIDGES: $[Mn(terpy)(N_3)_2]_2.2H_2O$.

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Departamentos de Química Inorgánica[1] y Mineralogía Petrología[2], Univ. País Vasco/Euskal Herriko Unibertsitatea, Aptdo. 644, 48080 Bilbao.

Polynuclear compounds with *end-on* azido bridging ligands have been structural and magnetically characterized in the last years. In the case of the Cu(II) and Ni(II) compounds ferromagnetic interactions have been observed with such a type of bridging. This kind of nickel complexes can be obtained by following a developed synthetic strategy, which involves tridentate aromatic amine ligands (2,2':6',2''-terpyridine, etc.), and we are now trying to extend that strategy to other first row transition metals.

The Mn(II) title compound has successfully been obtained by following the cited synthetic strategy. It crystallizes in the triclinic system, space group $P\bar{1}$, with a= 8.575(2), b= 10.737(1), c= 10.772(1) Å, α= 70.64(1), β= 69.10(1), γ= 68.20(1) °, Z=2, R= 5.5, R_w= 5.5. The structure consists of $[Mn(terpy)(N_3)_2]_2.2H_2O$ dinuclear units, formed by union of two crystallographically related $[Mn(terpy)(N_3)_2].H_2O$ fragments through one of their azide ligands, in end-on fashion. The Mn(II) ion is hexacoordinated with a slightly distorted octahedral topology (see Figure 1).

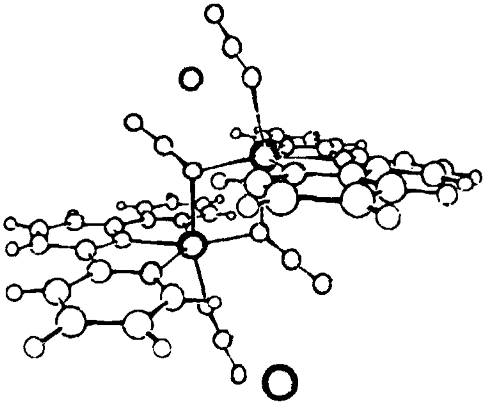

Figure 1.- Perspective view of the $[Mn(terpy)(N_3)_2]_2.2H_2O$ complex.

Preliminary magnetic susceptibility measurements, up to 77 K, clearly indicates ferromagnetic type interactions for the compound.

LAICM1395P

39, Thu. 16

CRYSTAL STRUCTURES AND SPECTROSCOPIC STUDIES OF THE $[Cu(C_7H_7N_3S)X]_2$ (X= Cl, Br) COMPOUNDS.

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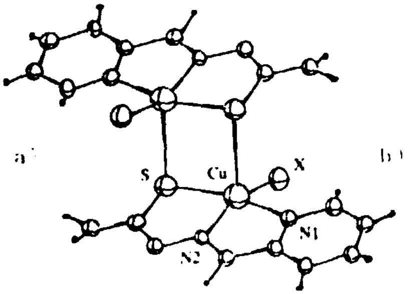
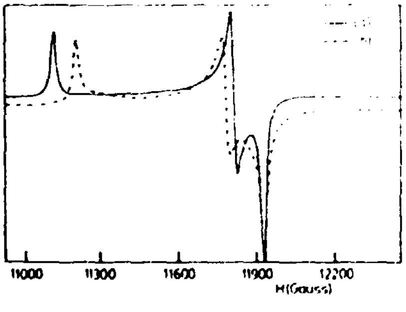
Departamentos de Mineralogia Petrologia[1] y Quimica Inorgánica[2], Univ. Pais Vasco/Euskal Herriko Unibertsitatea, Aptdo. 644, 48080 Bilbao.

The tiosemicarbazones, in particular the carboxaldehyde ones, have antitumor activity in their own right. Early mechanistic studies led to the postulate that the mode of action is by inhibition of ribonucleotide reductase. Cu(II) complexes with these ligands have significantly greater antitumor activity than the free ligand. Biochemical studies showed that the metal complexes enter cells to a greater degree than free ligand, the copper(II) complex being subsequently reduced to the quite stable Cu(I)L. In this work we present two unusual Cu(II)-halide complexes with a carboxaldehyde thiosemicarbazone ligand. They crystallize in the $P\bar{1}$ triclinic space group, the crystal parameters being a= 7.915(3), b= 8.262(5), c= 9.016(3) Å, α= 67.97(4), β= 92.26(4), γ= 71.33(5)°, Z=2, R= 3.8, R_w= 3.9 and a= 7.617(1), b= 8.451(3), c= 8.966(2) Å, α= 68.50(2), β= 95.94(1), γ= 71.73(2)°, Z=2, R= 3.5, R_w= 3.5 for the chloride and bromide compounds, respectvely.

a)



b)



The structures consist of discrete dimeric molecules in which the copper ions are bridged through the sulphur atoms of the thiosemicarbazone ligand (Figure a), being the halide anions as terminal ones. The topologies of the copper(II) ions are elongated square pyramidal. The EPR spectra are characteristics of orthorhombic symmetry for the g tensor (Figure b) with g_1= 2.183, g_2= 2.053, g_3= 2.033 (Cl), and g_1= 2.161, g_2= 2.057, g_3= 2.033 (Br). Preliminary magnetic susceptibility measurements show antiferromagnetic interactions in both complexes.

LAICM1399P **40, Thu. 16**

SYNTHESIS, SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF A NEW COMPLEX OF S-VALINE WITH Cr(III).

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[b] Department of Chemistry, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, U.K.

A fundamental process in the carcinogenicity and toxicity of chromate ions is the intracellular reduction of those species to Cr(III), with the formation of DNA strand breaks and cross-links[1]. A number of complexes of Cr(III) with natural aminoacids have been reported [2]. The structural characterization of a new and unique complex of S-valine and Cr(III), $[Cr(S\text{-}val)_2(S\text{-}Hval)_2].NO_3$ $6.5H_2O$, is now reported. The compound was prepared using a modification of the literature methods and the crystal structure was determined by X-ray diffraction methods.
Circular dichroism and other spectroscopic studies in solution and solid state were used to fully characterize the new compound. The unusual structure of the complex, containing both mono and bidentated coordinated valine is discussed and compared with related results for the complexation of Cr(III) by other aminoacidates.

Acknowledgements: The financial support of Gulbenkian Foundation, INIC (Centro de Quimica do Meio Aquático da Universidade de. Aveiro) and JNICT (STRIDE program) is acknowledged.

References:

[1] - P.H. Connett and K. E. Wetterhahn, *J. Am. Chemical Soc.*, 1985, 107, 4282

[2] - H. Oki, *Bull. Chem. Soc. Japan*, 1977, 50(3), 680 and references therehein.

LAICM1401P **41, Thu. 16**

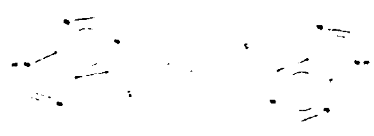
INTERACTION OF 6,6'-ETHYLENEDITHIO-BIS(PURINE) (BPDTB) WITH COPPER(II) SALTS

R. Carballo[1], A. Castiñeiras[2] and C.V. Montero[2]

[1]Departamento de Química Pura y Aplicada, Universidad de Vigo, 36200 Vigo (Spain); [2]Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela (Spain)

Nucleic acids and their derivatives are natural polydentate ligands. Their interaction with several metal species has attracted considerable interest in the study of the active centres of metallobiomolecules. Some particular constituents of the nucleic acids, such as purines, are used as bases in the study of model compounds. Also, the thio-analogues of these bases and their derivatives are among the most active anti-metabolites, some having anti-tumor activity.

Based on the above and as part of a more comprehensive study of systems consisting of metal ions with NSSN-type ligands, some of the results obtained for the interaction of *6,6'-ethylenedithio-bis(purine)* (bpdtb) with copper(II) are reported.



bpdtb

The complexes synthetised, which have the general formula Cu(bpdtb)$X_2 \cdot nH_2O$ (X = Cl, Br, ClO_4 or NO_3 and n = 2-5), were characterized by elemental analysis, IR and electronic spectroscopy, and magnetic susceptibility. The magnetic moments calculated from preliminary magnetic susceptibility data at room temperature suggest the occurrence of anti-ferromagnetic interactions, which may be explained by the presence of polynuclear species.

This work was financed by the project **PB91-0787** of the DGICYT.

LAICM1417P

42. Thu. 16

SYNTHETIC, STRUCTURAL AND SPECTROSCOPIC STUDIES ON THE DONATING PROPERTIES OF SULFUR-RICH MOLECULES: X-RAY STRUCTURES OF $[Cu_2Br_2(ptc)_4]$ AND $[Cu_2Br_2ptc]_n \cdot n/2$ THF (ptc= 1,3-dithiane-2-thione).

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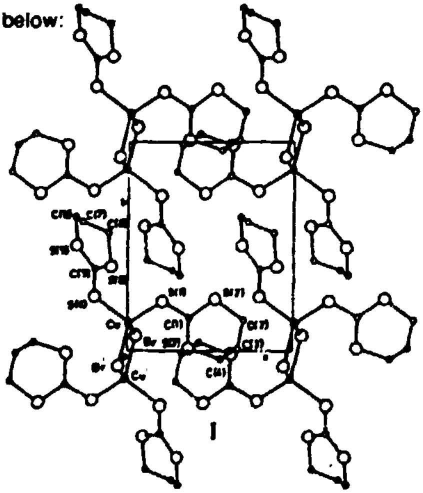
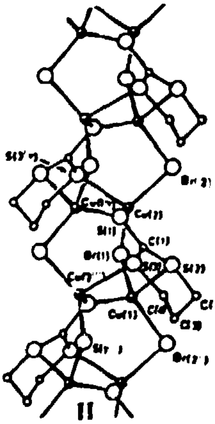
Sulfur donors are soft bases and form stable complexes with soft acids. Consequently they may generate a favourable thermodynamic situation for the spontaneous reduction of Cu(II) to Cu(I), Cu(I) being a soft acid while Cu(II) is a borderline hard acid. Moreover these ligands can coordinate with various combinations of terminal and bridging sulfur atoms, and the halogens, when involved in the coordination, can also act as terminal or bridging ligands, giving rise to a variety of mononuclear or polynuclear complexes. We are investigating the coordinative properties of sulfur-rich ligands towards copper halogenides and in this communication we report the characterization of the dimer $[Cu_2Br_2(ptc)_4]$ (I) and of the polymer $[Cu_2Br_2ptc]_n \cdot n/2$ THF (II), obtained by reacting ptc with $CuBr_2$ in CH_3CN and THF respectively. These compounds are diamagnetic and air stable. In I, 1,3-dithiane-2-thione acts as terminal ligand through the thione-sulfur, while the bromide atoms are bridging. The structure of II consists of two polymeric chains -Cu-Br-Cu-Br-, held together by the bridging ligand, which is here tridentate. The Cu atoms have in both compounds a distorted tetrahedral coordination. X-ray crystal structures of I and II are reported below:



I



II

LAICM1418P **43, Thu. 16**

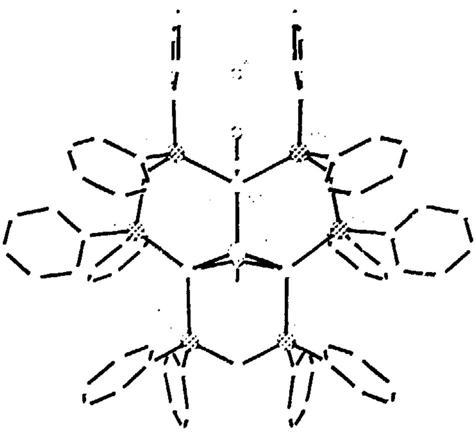
THE SYNTHESIS AND MOLECULAR STRUCTURE OF μ_2-[TRIS(DIPHENYLPHOSPHINE)METHANE]-μ_3-3-METHYL-8-ETHYLXANTHINE,N,O]-μ_3-CHLORO-TRIANGLE-TRICOPPER(I) COMPLEX.

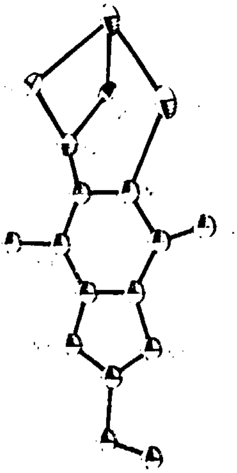
R. Cuesta, J. Ruiz, J.M. Moreno and E. Colacio.

Department of Inorganic Chemistry, University of Granada, 18071-Granada, Spain.

As continuation of our studies on metal-phosphine-purine complexes with potential biological activity, we report on the $[Cu_3(dppm)_3(L)(Cl)]\cdot H_2O$ complex obtained from the interaction of μ-tris(diphenylphosphine)methane-tris[chlorocopper(I)] with the 3-methyl-8-ethylxanthine in dichloromethane.

The crystal structure was solved by conventional Patterson and Fourier methods. The compound crystallizes in the monoclinic system, space group $P2_1/m$. The main feature of this Cu_3 cluster consists in the bridging coordination mode of the purine ligand. Thus, the purine bridges the three copper(I) ions through the N(1) and O(2) atoms, this latter acting in a very unusual bridging coordination mode. This mode is consequence of the crystal position of the purine, which lies on a symmetry plane. Moreover, the net charge is balanced by a chlorine ion, which is coordinated to the three copper(I) ions, at the apical position, in a μ_3-bridging fashion.





LAICM1419P **44, Tnu. 16**

EXCHANGE INTERACTION IN OXIME-BRIDGED $Cu^{II}M^{II}$ COMPLEXES

R. Ruiz,[a] **J. Faus,**[a] **F. Lloret,**[a] **M. Julve,**[a] **C. Bois,**[b] **and M. C. Muñoz**[c]
[a] *Departament de Química Inorganica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot (València), Spain*
[b] *Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, URA 419 CNRS, 75252 Paris, France*
[c] *Departamento de Física Aplicada, Universidad Politécnica de València, Camino de Vera s/n, 46071 València, Spain*

In this communication, we present the structural and magnetic characterization of a series of dinuclear complexes of formula $Cu^{II}(pdmg)M^{II}(L)(ClO_4)_2 \cdot nH_2O$ complexes (H_2pdmg = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime ligand and M=Cu, Ni and Mn). The structure of the copper derivative is shown in Figure 1 (with L=bpy).

In a first step, we show how the antiferromagnetic coupling in the dinuclear copper(II) complexes could be modulated by modifying the relative orientation of the magnetic orbitals, which can be done by changing the terminal ligands L (i.e. from bpy to terpy). In a second step, we investigate the evolution of the exchange parameter *J* as changing the number of unpaired electrons and associated magnetic exchange pathways from one complex to another in the series $Cu^{II}M^{II}$ with M = Cu, Ni and Mn (with L = bpy, cyclam and phen, respectively).

Finally, the most interesting result is that concerning the magnetic behaviour (Figure 2) of the $[Cu^{II}Mn^{II}]$ compound (with L = bpy), which reveals a low-lying nonet state resulting probably from the ferromagnetic interaction between two quintet pair states within a bis-heterobinuclear $[Cu^{II}Mn^{II}]_2$ entity.

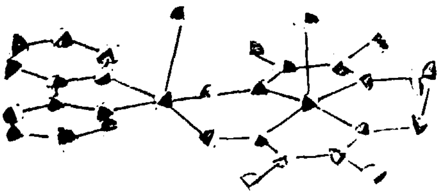


Figure 1

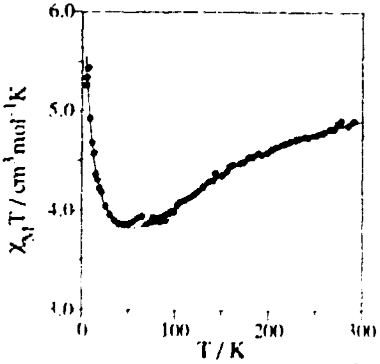


Figure 2

LAICM1437P **45, Thu. 16**

COSY and NOESY CHARACTERIZATION OF Ni(II) AZURIN FROM *Pseudomonas aeruginosa.*

J.M. Moratal, H.R. Jiménez, A. Donaire, J. Salgado and J. Castells .

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Azurins are blue copper proteins that participate in the denitrification respiratory chains of several bacteria. The crystal structure of Cu(II)-azurin from *Pseudomonas aeruginosa* (*Pae*), has recently been determined to 1.93 Å resolution[1]. The copper ion is strongly bound to the Sγ of Cys-112 and to the Nδ of both His-46 and His-117, and weakly ligated by the Sδ of Met-121 and the carbonyl oxygen of Gly-45, resulting in a distorted trigonal-bipyramidal geometry. It has been recently reported that the hydrophobic patch, around the copper-ligand His-117, would be involved in the electron transfer reactions and the residue His-117 has been suggested as a specific pathway for the transit of electrons.

Paramagnetic metal ions, such as Nickel(II), have been successfully used as spectroscopic probes replacing the copper ion in many blue copper proteins. It has been suggested that the copper substitution would have minimal effects on the metal site geometry because of the rigidity of this part of the structure, associated with the abundance of hydrogen bonds. The study of the Ni(II)-azurin, by 1D and 2D ^{1}H NMR spectroscopy, has allowed us a more detailed analysis of the effects of the conformational change on the ligand arrangement.[2]

Here we report the results of the application of 2D ^{1}H NMR spectroscopy as a powerful tool in the assignment of the isotropically shifted proton resonances of Ni(II)-azurin, aiming at a better understanding of the structural features in the metal-binding site of this protein in solution. The 400 MHz COSY and NOESY spectrum of the Ni(II)-azurin in D_2O and H_2O solvent were performed with a large number of transitions, gh protein concentration and different temperatures. Via the NOESY and COSY spectra, the protons of the His-46, His-117, Met-121 and Gly-45 coordinated residues, and other non bounded aminoacids have been assigned.

A more complete assignment, which is actually in progress, will open new possibilities of connecting the observed changes in the spectrum with structural modifications affecting specific residues in the protein.

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$[(PtMe_3)_3\{\mu\text{-}I,\mu\text{-}S(CH_2)_2NHEt_2\}_2]I$. THE FIRST PLATINUM THIOLATE COMPLEX WITH A DEFECTIVE CUBANE STRUCTURE

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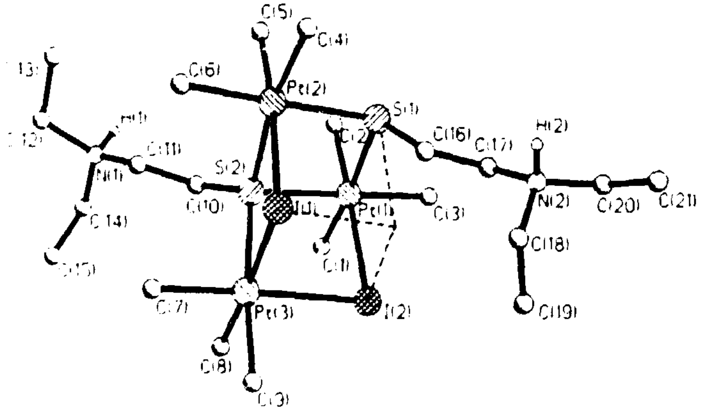
Our systematic study on metal complexes of aminoalkanethiol ligands has led us to a totally unprecedented structure among group 10 metal complexes with any type of thiolate ligands.

The complex was prepared by stirring $HS(CH_2)_2NEt_2$ (0.87 mmol) with $[PtMe_3I]_4$ (0.205 mmol) in CH_3CN under a nitrogen atmosphere at room temperature for 5 days.

The crystal structure determination indicates that the complex consists of trinuclear cluster cation, I^- anion and CH_3CN. The principal structural features of the cation are summarized as follows: (i) It contains a defective cubane-like $Pt_3S_2I_2$ cage, composed of Pt_3-trigonal and a distorted S_2I_2-tetrahedron. (ii) The only symmetry element of the cage is the plane defined by Pt(3), S(1) and S(2) atoms. (iii) Each platinum is in the center of an octahedron, where the three Me groups of $PtMe_3$ give rise to the *facial* isomer. Each octahedron shares two adjacent edges with the other two. (iv) One S and the two I are doubly bridging meanwhile the other S is triply bridging.



Mean values of Pt-S, Pt-I, Pt-S-Pt, Pt-I-Pt, S-Pt-S and I-Pt-S are respectively 2.48 Å, 2.82 Å, 101.3°, 88.7°, 82° and 83°. The position of the missing atom for a cubane structure is indicated.

LAICM1454P **47, Thu. 16**

DINUCLEAR COMPLEXES OF Cu(II) WITH 2-ANILINOPYRIDINE AND 7-AZAINDOLE AS BRIDGE LIGANDS

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2-Anilinopyridine (N-phenyl 2-pyridinamine, PhNHpy) and 7-azaindole (1H-pyrrolo[2,3-b]pyridine) may behave as bridge ligands in their anionic form. The complexes:

a) $[(bipy)Cu(L)_2Cu(bipy)](SO_4)$ HL = 7-azaindole

b) $[(bipy)Cu(L)_2Cu(bipy)]X_2$ X = Cl^-, Br^-, I^-, SCN^-, ClO_4^-

c) $[(bipy)Cu(L')_2Cu(bipy)](PF_6)$ HL' = 2-anilinopiridine

have been prepared by substitution of OH groups in the respective di-μ-hydroxo complexes.

Compound (a) is obtained by refluxing (5 h) in methanol, the di-μ-hydroxo dimer and 7-azaindole, in 1:5 metal:ligand proportion. By refluxing (6 h) in methanol, the original dimer with 7-azaindole in anionic form (HL and Na in ethanol), in the same metal:ligand proportion, the complexes (b) are obtained. Complex (c) is prepared in analogous conditions, with reflux in acetone (10 h) and a metal:ligand proportion of 1:2.

The neutral ligand, HL', is not effective in the substitution of OH group. The anionic form, L'^- ($PhNpy^-$), is a strong reductor; by any excess higher of 1:2, Cu(II) is reduced to Cu(I) and the compound CuL' is formed.

The complexes have been characterized by elemental analysis and infrared and ultraviolet-visible spectroscopies. The absence of ν (N-H) band, at 3.300 cm^{-1}, in the 2-anilinopiridine complex infrared spectra confirms the anionic form of the ligand.

The results of conductance measurements in solution, when possible by solubility conditions, are similar to those of the initial dimers.

LAICM1455P **48, Thu. 16**

MAGNETIC PROPERTIES OF BIACETYLDIHYDRAZONE COMPLEXES

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In this paper the magnetic properties of a series of compounds are presented. The nitrates and bis(dithiooxalate)nickelates(II) have been previously prepared and characterized (1,2). A mononuclear octaedral configuration is proposed for all cationic complexes, excepting $[Cu(BdH)_2][Ni(dto)_2]$, which is probably a dithiooxalate bridged dimer. The cyano complexes have been obtained by reaction, in aqueous solution, between $[M(BdH)_3](NO_3)_2$ and $K_2[Ni(CN)_4]$ or $K_2[Zn(CN)_4]$. In all cases a dimer with cyano bridged groups is formed, as the IR spectra show.

The magnetic results (between room temperature and helium liquid) are summarized in the following table:

Compound	μ_{ef}(MB)	θ(K)	
$[Fe(BdH_3)](NO_3)_3$	1,85	- 6.37	low spin
$[Co(BdH)_3](NO_3)_2.H_2O$	3,65(285K): 2,58(7,5K)		anomalous
$[Ni(BdH)_3](NO_3)_2$	2,97	0,80	
$[Cu(BdH)_3](NO_3)_2.H_2O$	2,03	- 5.59	
$[Zn(BdH)_3](NO_3)_2$	diamagnetic		
$[Fe(BdH)_3]_2[Ni(dto)_2]_3.H_2O$	1,89	- 7,84	low spin
$[Co(BdH)_3][Ni(dto)_2].H_2O$	3,71(285K); 2,30(10K)		anomalous
$[Ni(BdH)_3][Ni(dto)_2].H_2O$	2,92	1.48	
$[Cu(BdH)_2][Ni(dto)_2]$	1,83	3.93	
$[Zn(BdH)_3][Ni(dto)_2].H_2O$	diamagnetic		
$(BdH)_2Co(CN)_2Ni(CN)_2.H_2O$	3.13	- 2,10	
$(BdH)_2Ni(CN)_2Ni(CN)_2$	2,88	- 2,70	
$(BdH)Cu(CN)_2Ni(CN)_2.H_2O$	1,88	- 1,25	
$(BdH)_2Zn(CN)_2Ni(CN)_2.H_2O$	diamagnetic		
$(BdH)Zn(CN)_2Ni(CN)_2.H_2O$	diamagnetic		
$(BdH)_2Ni(CN)_2Zn(CN)_2.H_2O$ (pink)	2,61	- 0,38	
$(BdH)_2Ni(CN)_2Zn(CN)_2.H_2O$ (yellow)	diamagnetic		
$(BdH)Cu(CN)_2Zn(CN)_2.H_2O$	1,65	5.38	

For Co(II) complexes, the EPR data are discussed, in forms of high and low spin states participation

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LAICM1456P **49, Thu. 16**

REACTIVITY AND ELECTROCHEMICAL STUDIES OF DIRUTHENIUM(II,III) COMPOUNDS

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Dimer compounds of ruthenium(II,III) of the type $Ru_2Cl(\mu-L)_4$ (L= anionic three-atom-bridging ligand) are usually obtained from $Ru_2Cl(\mu-O_2CCH_3)_4$. We have observed previously that when the carboxylate ligand has a nitrogen atom in α, respect to the COO group, the reaction not leads to a substitution process. In this communication, we study the influence of O or S atoms in α, respect to the COO group. We study also the influence of the change in the nature of the bridging ligand. The reaction of $Ru_2Cl(\mu-O_2CCH_3)_4$ with carboxylic acids (2-thiophene- and 2-furane-carboxylic acid), in water/methanol, or p-tertbutylbenzamide, in molten ligand, leads to $Ru_2Cl(\mu-L)_4$, which contain multiple bond ruthenium-ruthenium. Elemental analysis, spectroscopic data and magnetic measurements show that, in all cases, the total substitution of the acetate ligand, in the starting material, has produced. The compounds are polymer with the chlorine ligand bonding different diruthenium(II,III) units.

The polymer structure of these compounds is broken with $AgBF_4$, giving $[Ru_2(\mu-L)_4(thf)_2]BF_4$. The reaction of these thf adducts with ligands, such as $OPPh_3$ or PCy_3, leads to new compounds of the type $[Ru_2(\mu-L)_4(L')_2]BF_4$. The electrochemical behaviour and the influence of the solvent in their electrochemical properties, of the compounds isolated, are also studied.

LAICM1458P **50, Thu. 16**

QUINALDINATE COMPLEXES OF RUTHENIUM(II). CRYSTAL STRUCTURE OF TRANS-Ru(QUIN)$_2$(DPPM)$_2$

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The compounds Ru(quin)$_2$(dppm)$_2$ and Ru(quin)$_2$(PPh$_3$)$_2$ [quin = 2-quinaldinate anion, dppm = bis(diphenylphosphino)methane] have been prepared by the reaction of RuCl$_3$·3H$_2$O and Hquin, in basic alcoholic medium, in the presence of phosphine. Thus, with dppm only the *trans* isomers has been obtained whereas with PPh$_3$ the *cis* and *trans* isomers have been isolated. The compounds have been characterized by elemental analysis, IR, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. These data indicate, in all cases, the presence of two quinaldinate and two phosphine ligands. The structure of trans-Ru(quin)$_2$(dppm)$_2$·2MeOH has been determined by X-ray crystallography and show unequivocally that this compound has two bidentate N,O-quinaldinate and two monodentate dppm ligands in a trans-N, trans-O, trans-P arrangement. An ORTEP view is shown in the figure.

LAICM1462P **127, Thu. 16**

CHARACTERIZATION OF *Pseudomonas fluorescens* NITRITE REDUCTASE (CYTOCHROME cd_1)

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Pseudomonas fluorescens denitrificans ATCC 17822, a denitrifier bacteria, is quite abundant in soils and utilitizes ethanol (one of the most probable carbon sources in conjunction with acetate) for denitrification in situ. This organism has the metabolic capability of carrying out complete denitrification from nitrate to dinitrogen.

The understanding of the respiratory chain requires the definition of the electron carrier proteins involved. Special attention was given to the enzyme that reduces nitrite to NO, an important pathway in the dissimilatory nitrate utilization.

Nitrite reductase was purified from bacterial crude extracts by chromatographic methods and characterized by visible and EPR spectroscopies. Hemes c and d_1 in equimolar amounts were detected. The enzyme was studied in different states: native (oxidized), reduced (ascorbate plus phenazine methosulfate and dithionite) and reacted with nitrite and NO. Nitrite was shown to have inhibitor effect on the growth of *Pseudomonas fluorescens* denitrificans. Results are compared with nitrite reductases (cytochrome cd_1) extensively studied, isolated from *Pseudomonas aeruginosa* and *Thiobacillus denitrificans* [1,2]. Detailed activity measurements were made in order to infer about the influence of nitrite and nitrate concentrations, as well as pH.

A cytochrome c_{551} was also purified and a preliminar spectrocopic characterization is presented.

We would like to thank Mr. M.-Y.Liu for bacterial cell growth and JNICT and STRIDE for finantial support.

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LAICM1489P **128, Thu. 16**

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF THE TETRAMERIC COMPLEX: $[Cu_4(mpppz)_4(NO_3)_3](NO_3)$ mpppz = 2-(6-metil)pyridyl-2-pyridyl-(3,5-pyrazole)

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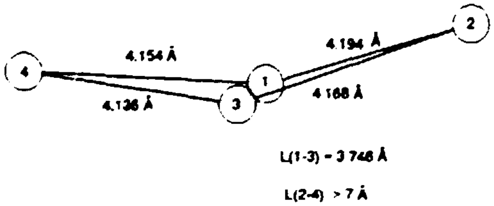
Research on the coordination chemistry of pyrazole-derived ligands has progressed very rapidly over the last few years. One of the major research areas of interest is the metallocycles of the type $M(pz)_2M'$ where pz is a pyrazole or pyrazole-derived ligand[1].

We have shown in some recent publications that novel metal complexes containing the synthesized pyrazole ligands bpypz ($C_{13}H_{10}N_4$), mpppz($C_{14}H_{12}N_4$) and mmpppz ($C_{15}H_{14}N_4$) can be prepared[2]. For example the reaction between bpypz and $Cu(NO_3)_2 \cdot 6H_2O$ yielded the tetrameric complex $[Cu_4(bpypz)_4(H_2O)_2][NO_3]_4 \cdot H_2O$ [1] whose solid state structure has been determined by X-ray crystallography[2].

Furthering our investigations we have reacted Cu(II), Ni(II) and Co(II) nitrate salts with the ligand mpppz. It was found that the reaction between $Cu(NO_3)_2 \cdot 6H_2O$ and mpppz afforded $[Cu_4(mpppz)_4(NO_3)_2\mu\text{-}(NO_3)][NO_3]$ [2] whose x-ray crystal structure shows that the four copper atoms are each bridged by two pyrazole ligands. Two of the copper atoms contain terminal nitrate groups while the other two copper atoms are bridged by one nitrate group.

Figure shows a representation of the bond distances between the four copper atoms in [2].



It is interesting to note that [1] and [2] exhibit different magnetic properties. The magnetic measurements of [2] show a maximum in the susceptibility temperature curve at 25 K while [1] exhibited a maximum at 210 K. This difference can be interpreted by supposing different antiferromagnetic interactions between the four copper atoms in [1] and [2] wich has arisen from the presence of the different pyrazole ligands. The reaction of the mpppz ligand with the Co(II) and Ni(II) salts gave complexes which showed Curie-Weiss behaviour in their temperature interval studies. This change in the magnetic properties can be explained on a structural bases i. e. the Co(II) and Ni(II) nitrate salts reacted with the mpppz ligand affording dinuclear complexes of the formula $[M_2(mpppz)_2](NO_3)_2$ where M = Co, Ni

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2 *ORGANOMETALLIC CHEMISTRY AND CATALYSIS*

THE NEW ROUND WORLD OF FULLERENE CHEMISTRY AND MATERIALS SCIENCE

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The Fullerenes were discovered in 1985 during experiments which simulated the chemistry occurring in the shells of Red Giant Carbon Stars. The Family has now come down to Earth bringing us a new *"Periodic Table"* of novel cluster pseudoelements. Each fullerene exhibits its own intrinsic *pseudo-valency* and pattern of reactivity and the molecules promise to be precursors of exciting new 21st Century Materials. The Sussex Program is now probing Fullerene Chemistry, Physics, Materials Science and Astrophysics: Our **Chemistry** studies have produced some of the first fully characterised analogues: $C_{60}Hal_n$ (n=6,8,24), $C_{60}(Cp)_2Fe$ etc. **Physical** investigations of the solid state properties are being carried by the group of Kosmas Prassides. **Nanoparticle** and **Nanofiber** studies indicate that there is an intimate relationship between carbon chains, fullerenes and graphite particles with fascinating implications for carbon fibers. Studies of onion-like nested giant fullerenes and nanofibers are revealing unexpected structures so changing the textbook picture of graphite. **Supersonic Jet Cluster Beam** studies show that sub-C_{60} fullerenes: C_{24}, C_{28}, C_{32} etc.. form during laser vaporization so confirming earlier Sussex work which predicted that fullerene-28 should form stable derivatives.

FROM IONIC SALTS TO EARLY TRANSITION METAL AND ACTINIDE COMPLEXES: THE ENERGETICS OF METAL-OXYGEN BONDS IN LITHIUM, SODIUM, ZIRCONIUM, AND URANIUM COMPOUNDS

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There was a considerable growth of reliable information on the energetics of metal-carbon and metal-hydrogen bonds in the last decade. The recognition that these data are relevant to the understanding of organometallic reaction mechanisms fostered the development of several experimental techniques and attracted the interest of theoretical chemists. Despite all the efforts, our knowledge of the energetics of M-C and M-H bonds is still incipient. Establishing general (and accurate) prediction methods, such as those available for organic compounds, is still not possible. This will require not only further thermochemical studies of reactions involving the cleavage or the formation of metal-carbon and metal-hydrogen bonds, but also additional information on the energetics of bonds between metals and other ligands.

In the course of our studies on the systematics of transition metal-ligand bond dissociation enthalpies we have decided to probe the energetics of bonds between oxygen groups and several electropositive elements. These data are not abundant, despite the importance of some of the substances examined (e.g. lithium alkoxides) in chemical syntheses. By studying the thermochemistry of several families of compounds, our main goal was to search for reliable estimation methods, that could eventually be used for other series of organometallic compounds. These attempts were successful. In addition, they have revealed interesting similarities between the bonding energetics of transition metals, actinides, and main period elements with oxygen moieties.

LAICM2321S **B, Mon. 13**

ACTIVATION OF TERMINAL ALKYNES : NEW ACCESS TO ALKENYL- AND POLYENYL-CARBENE METAL COMPLEXES.

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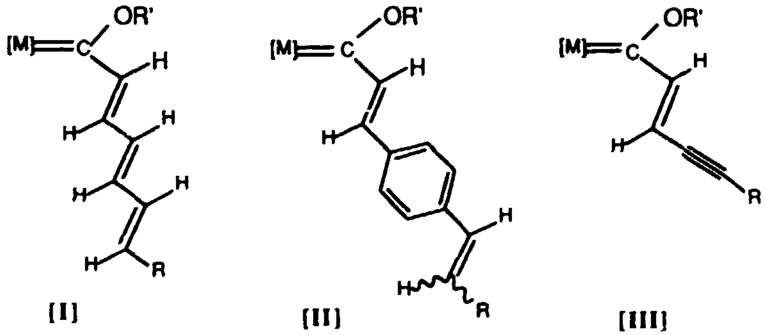
Fischer-type alkenylcarbene complexes are useful reagents for both organic and organometallic synthesis. Arene ruthenium(II) complexes $RuCl_2(PR_3)(\eta^6\text{-arene})$ readily promote the dehydration of prop-2-yn-1-ols $HC{\equiv}C\text{-}C(H)(Z)OH$ to give new (alkoxy)alkenylcarbene and polyenylcarbene ruthenium complexes **I-III**. This strategy can be successfully applied to the one step synthesis of a variety of (alkoxy)α,β-unsaturated chromium and tungsten complexes **I-III**, by photolysis of $M(CO)_6$ in the presence of prop-2-yn-1-ol derivatives and primary alcohols. These group 6 carbene complexes undergo several interesting reactions such as intramolecular cyclopropanations leading to bicylic alkenylcyclopropanes.



[I] [II] [III]

[M] = $[(\eta^6\text{-Arene})RuCl(PR_3)]^+$; $Cr(CO)_5$; $W((CO)_5$

R' = Me ; $CH_2CH_2CH{=}CH_2$; $CH_2CH_2C{\equiv}CMe$; ...

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METALLOMESOGENS: HOW THEY ARE FISHED FOR, AND COOKING RECIPES.

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Liquid crystals (mesogens) are materials which spontaneously produce ordered arrangements in a fluid phase, a kind of molecular self-organisation. The fluid phase can be induced by adding a solvent (lyotropic liquid crystals) or by melting the material (thermotropic liquid crystals). Until 1980, most of the mesogenic materials reported were organic compounds, but during the last decade a new class of mesogens incorporating transition metals has burst into this field.[1]

Although still dominated by the initial approach of imitating the organic structural types, more and more examples of metallomesogens departing from this rule are being described. Some successful approaches in the introduction of added properties such as optical activity or paramagnetism are being developed. Also a certain control in the tuning of thermal properties and stability is being attained.

Contact with this field demands from an organometallic chemist a certain change in perspective, perhaps a quite radical one: Stability is the aim, not reactivity; physical properties are the target rather than chemical properties; coordination geometry surrenders to molecular shape; old-fashioned familiar molecules are the star in the play, better than novelties (this is comforting when one is in his forties). Yet, chemistry is the matter, if not what matters.

The lecture will illustrate how inorganic compounds, particularly organometallic molecules, have a place in the liquid crystal field, but hopefully it will show also that making liquid crystals is a way of making chemistry.

1.- P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, and E. Sola, *Coord. Chem. Rev.*, **117** *(1992)* 215-274.

URANIUM COMPLEXES WITH OXYGEN, SULFUR, NITROGEN AND PHOSPHOROUS LIGANDS. INFLUENCE OF ELECTRONIC FACTORS ON STRUCTURE AND STABILITY

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Alkoxide, hydroxide and μ-oxo complexes of uranium(IV) have been synthesized by

a) reaction of alcohols, ketones and water with hydride or borohydride derivatives,

b) coupling reaction of ketones with UCl_4 in the presence of sodium amalgam,

c) reduction of CO_2 by $(C_5H_4SiMe_3)_3U$ or $(C_5H_4SiMe_3)_3UH$,

d) deoxygenation of CO by $(C_5H_5)_3UR$ complexes and

e) condensation reactions of alkoxide and hydroxide compounds.

A special attention was paid to the tristertiobutylmethoxide ligand, $(CMe_3)_3CO$, which has the same size than the ubiquitous cyclopentadienyl group, while rendering the metal centre more electrophilic.

Thiolate complexes were made by treatment of uranium borohydride or hydride compounds with thiols. Reaction of UCl_4 with NaSR reagents afforded the homoleptic thiolate complexes $[(THF)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(THF)_3]$. The first crystallographically characterized uranium tetrathiolate complex, $U(SPr^i)_4[OP(NMe_2)_3]_2$, and the first uranium - sulfur cluster, $U_3(S)(SBu^t)_{10}$, were obtained from the corresponding $U(SR)_4$ compounds. The distinct structures and reactions of analogous uranium alkoxide and thiolate complexes can be explained by the less electron donating ability of the SR ligand.

The structure and properties of analogous compounds with the isosteric ligands C_5Me_5 and C_4Me_4P have been compared. The tetramethylphospholyl group is less electron donating than C_5Me_5 and, in contrast to the trispentamethylcyclopentadienyl complexes, $(C_4Me_4P)_3UCl$ and its derivatives could be easily synthesized.

Amide compounds, including U(V) derivatives, were prepared from $U(NEt_2)_4$.

NEW FRONTIERS IN BOND ACTIVATION BY ELECTRON-RICH METAL COMPLEXES

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Although bond activation by oxidative addition to electron-rich metal complexes is well known, activation of some of the strongest bonds is relatively unexplored. We have observed facile activation of N–H, O–H. C–F amd Si–Cl bonds by iridium and rhodium complexes and have studied the mechanisms of these reactions, aiming at activation of these bonds towards selective transformations. Our studies regarding water and ammonia activation will be described in some detail, including some interesting bonding features and catalytic aspects.

LAICM2071S **B, Tue. 14**

PLATINUM CATALYZED OXIDATIONS WITH HYDROGEN PEROXIDE: THE BAEYER-VILLIGER OXIDATION OF KETONES

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Platinum metal is a well known industrial catalyst for a variety of important oxidation processes. This high efficiency as oxidation catalyst depends on the low adsorption energy for dissociative chemisorption of O_2 and the lability of adsorbed oxygen atoms on Pt surfaces and contrasts sharply with the solution chemistry of Pt complexes.

Complexes of the Platinum metals have been known for years to activate molecular oxygen heterolytically by forming side-bonded peroxo species, however, these were of little practical use in the oxidation of organic compounds since they are reactive only toward a variety of easily oxidizable substrates or in the formation of stable insertion products. The major difference between these d^8 side-bonded peroxo species and the analogous d^0 complexes lies mainly in the absence of easily accessible molecular pathways available to the former for the release of the oxidized molecules.

This gap has been recently covered with the use of hydrogen peroxide[1], a chemical that is becoming increasingly fashionable and whose production is expected to increase significantly in the next few years, largely because of its nature of environment friendly oxidant. Platinum complexes have proved successful in the use of H_2O_2, t-BuOOH and caroate as primary oxidants in reactions like the epoxidation and ketonization of olefins, the hydroxylation of aromatics and the Baeyer-Villiger oxidation of cyclic ketones. Work carried out on the latter reaction will be considered in detail, particularly with respect to mechanistic investigations and studies on the chemo- regio- and enantioselectivity of the catalytic system.

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LAICM2381S

B, Tue. 14

SOME OF THE CHEMISTRY OF PHOSPHIDO BRIDGED CARBONYL CLUSTERS

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The tetranuclear species $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (1) is a versatile species, that provides an alternative, more selective entry into iridium tetra and octanuclear carbonyl cluster chemistry than $Ir_4(CO)_{12}$ (2). Under mild thermolysis, it undergoes dimerization <u>via</u> H_2 loss, with sequential formation of $Ir_8(CO)_{16}(\mu\text{-}PPh_2)_2$ (3), then $Ir_8(\mu\text{-}CO)_2(CO)_{13}(\eta^1\text{-}Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ (4) (30%), a species exhibiting a "square based pyramid fused to an octahedron" array of metal atoms. By comparison, thermolysis of (2) only leads to decomposition. The bridging phosphido and hydrido groups in (1) induce site selectivity in the CO substitution reactions of (1) with phosphines PR_3 and phosphites $P(OR)_3$, that result in the formation of monosubstituted derivatives <u>via</u> an associative mechanism, at a rate of the order of 10^4 times faster than similar reactions of (2). In the reactions with isocyanides, however, six isomers of the mono and of the bisubstituted products are formed. The phosphido ligand functions also as an anchor in the condensation reaction of $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ (5) with $[Rh(CO)_2Cl]_2$ in the presence of $TlPF_6$, that yields $RhIr_4(CO)_{12}(\mu\text{-}PPh_2)$ (6) (90%). The structure of (6) consists of a trigonal pyramidal arrangement of metal atoms and a $\mu\text{-}PPh_2$ ligand bridging an apical Rh and an Ir atoms, showing therefore, for the first time that this ligand can be labile. Changing the μ-H ligand in (1) for the $\mu_3\text{-}Rh(CO)_2$ fragment results in labilization of the cluster and a different mechanism for the substitution reactions. Compound (6) reacts with PPh_3 to yield $RhIr_4(CO)_{(12-n)}(PPh_3)_n(\mu\text{-}PPh_2)$ ($n = 1\text{-}3$), the first step being too fast for kinetic measurements, under the conditions studied, and the bis and trisubstitution steps proceeding by dissociative mechanisms.

Organo-metallic chemistry of lanthanides and some implications in diolefine polymerization.

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P. Andreussi, Enichem Elastomeri R&D, Assago, Italy.

Organo-metallic chemistry of lanthanides (Ln) is a subject of current investigation even for their involvement in Ziegler-Natta catalysis for a-olefines and diolefines[1]. Ln-based systems for 1,4-Cis poly-diolefines give easy industrial processes and and a final elastomer with better mechanical properties[2]. The catalyst preparation generally involves a reaction between a lanthanide salt and a tris-alkylaluminum; lanthanide-alkyl bonds are likely formed 'in situ' in the first step of the polymerization reaction. We studied the reaction between homoleptic Ln salts and tris-alkylaluminum derivatives at low Al/Ln molar ratio. The aim was the isolation and identification of the alkylated species for a better knowledge of this step of the formation of the catalytic centre. Experimental data show that the alkylation reaction is strongly dependent on the the Ln salt, the direct Ln-ligand/aluminum-alkyl exchange taking place only in a few cases. The nature of the ligand of the starting Ln salt and the tris-alkylaluminum moiety both are determinant for the isolation and characterization of the alkylated complex. As a general remark, we never had evidences of reduction of the Ln atom working in a temperature range comparable with that claimed in the patent litterature for the industrial processes.

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LAICM2264S **B, Tue. 14**

BINUCLEAR ORGANOMETALLIC DERIVATIVES: SYNTHESIS AND REACTIVITY.

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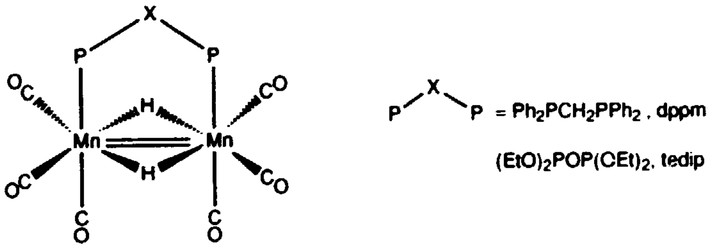
During the last years we have been studiing the chemistry of the unsaturated manganese dihydrides



which exhibit a rich chemistry under mild conditions with a great variety of reagents. We have studied their behaviour against a range of small organic molecules (1-alkynes, nitriles and isonitriles, aldehydes and ketones, etc) or inorganic ones (S_8, Se_8, CO_2, etc). We have also studied their reactivity against main group derivatives containing E-H bonds (E=P, Si, Sn, B), as well as several types of TM organometallic derivatives [e.g. $Fe_2(CO)_9$, $Mo(CO)_6$, $MeAuPPh_3$, group 11 alkynyls].

The lecture will describe some recent results in this area and in other related ones. It will be surveyed e.g. the preparation of anionic derivatives such as $[Mn_2H_3(\mu\text{-tedip})(CO)_6]^-$, $[Mn_2\{\mu\text{-}(EtO)_2P\text{-}O\}\{\mu\text{-}(EtO)_2P\}(CO)_6]^{2-}$, or the unsatured $[Mn_2(\mu\text{-dppm})(CO)_6]^{2-}$ (Mn=Mn), all of which show a high reactivity and are precursors of a wide spectrum of compounds (e.g. hydrides, heteronuclear clusters). Similarly, we will also comment on our studies on related ditungsten complexes, which improves our knowledge of the decarbonylation processes occurring in Cp-carbonyl dimers. New reactivity patterns of binuclear, neutral or cationic, unsaturated compounds (containing multiple M-M bonds) under mild conditions will be given.

REACTIVITY OF PENTADIENYL TRANSITION METAL COMPLEXES TOWARDS NEUTRAL NUCLEOPHILES.

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During the past several years, we have been studying the chemistry of metal complexes containing the acyclic pentadienyl group. Through these studies, it has become evident that pentadienyl is a highly versatile ligand, which possess diverse and novel reactivity. In order to expand our knowledge concerning the behavior of different sort of pentadienyl complexes we selected complexes with good π acceptor ligands $(\eta^5\text{-}C_5H_7)Mn(CO)_3$ and stronger donor ligands $(\eta^5\text{-}C_5H_7)RuCl(PPh_3)_2$, both species analogues to the classical and well known $\eta^5\text{-}C_5H_5Mn(CO)_3$ and $\eta^5\text{-}C_5H_5RuCl(PPh_3)_2$ complexes which have shown a rich chemistry. Then, we performed a thorough investigation of the chemical properties of these compounds in the presence of neutral nucleophiles, such as tertiary, secondary and primary amines and phosphines. The studies on the reactivity of $\eta^5\text{-}C_5H_7Mn(CO)_3$ with secondary amines and diphenylphosphine has been recently described in the literature. Then, we turned to the study of the reactivity of this complex with primary amines, which allowed us to isolate an intermediate species which supports the proposed 1,5-addition mechanism in the syntheses of aminopentenyl compounds. It is clear that the key factor that determines the reactivity patterns in $(\eta^5\text{-}C_5H_7)Mn(CO)_3$ is the presence of NH or PH function.

In the case of the ruthenium complex a different chemistry was observed. The addition of $PHPh_2$ was exclusive on the metal involving PPh_3 displacement, giving the complex $[(\eta^5\text{-}C_5H_7)RuCl(PHPh_2)(PPh_3)]$ without evidence of nucleophilic attack at the metal-coordinated organic ligand. Owing to the smaller size of the $PHPh_2$ ligand, replacement of both PPh_3 ligands was never observed.

LAICM2498S **B, Thu. 16**

NOVEL POLYNUCLEAR METALLOCENES SPECIES TO EXPLORE ELECTRONIC DELOCALIZATION, MAGNETIC AND CONDUCTIVE PROPERTIES.

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It has been developed a rational synthetical strategy of new building block precursors for the preparation of homo and heterometallic one-dimensional organometallic polymers. In this context, we prepared the following binuclear, triple and quadruple decker complexes derived from pentalene

$[(C_8H_7)Fe(C_8H_6)CoCp^*]$ $[(C_8H_7)Fe(C_8H_6)FeCp^*]$

$[Cp^*Fe(C_8H_6)Fe(C_8H_6)FeCp^*]$ $[(C_8H_7)Fe(C_8H_6)Fe(C_8H_6)FeCp^*]$

These new precursor building blocks (olygomers), were characterized and their electrochemical properties determined showing a high electronic delocalization and cooperative interaction between their metallic centers.

The coordination of the $[Cp^*Ru]^+$ fragments to the cromophore 9,9'-bifluorenylidene (BFD) and fluorene afforded the new complexes:

$[Cp^*RuBFD]^+$ $[Cp^*Ru\,BFDRuCp^*]^{2+}$ $[Cp^*Ru\,(C_{13}H_{10})RuCp^*]^{2+}$

1 **2** **3**

Complexes **1** and **2** show electron-transfer phenomena coupled with electrochromic properties (small energy gap, LUMO-HOMO), that represent a strong electronic delocalization confirmed by a theoretical study.

Complex **3** undergoes an specific deprotonation by n-BuLi affording the new lithiated complex $[Cp^*Ru\,(C_{13}H_9Li)RuCp^*]^{2+}$, **4**. This compound presents an unusual quenching of electrophilic attacks on the C_9-Li bond. Molecular structure of **4** show a very short distance C_9-Li of 1.625 Å.

Acknowledgment. This study is supported by FONDECYT-CHILE Grants N°825-92 and N°1930024

LAICM2263S **B, Thu. 16**

RECENT ADVANCES IN THE CHEMISTRY OF PERHALOPHENYL PLATINATE (II) COMPLEXES.

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Anionic perhalophenyl platinum complexes are useful precursors for the synthesis of polynuclear derivatives. Thus, complexes such as $[NBu_4]_2[Pt(C_6F_5)_4]$, $[NBu_4][Pt(C_6F_5)_3(SC_4H_8)]$ and $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ act as Lewis bases and react with several metal (M) complexes, or salts yielding polynuclear derivatives containing Pt→M donor-acceptor metal-metal bonds.

On the other hand, the anionic phosphido complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(C_6F_5)_2]$ (M = Pd, Pt) can be used as starting materials for the synthesis of polynuclear complexes with or without metal-metal bonds and the acetylide derivatives $[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2(C\equiv CR)_2]$ (R = Ph, ^tBu) are adequate precursors for the synthesis of polynuclear complexes without metal-metal bonds.

Several recent results in this field will be presented.

LAICM2027S

B. Thu. 16

MOLECULAR DIHYDROGEN COMPLEXES IN HOMOGENEOUS CATALYSIS

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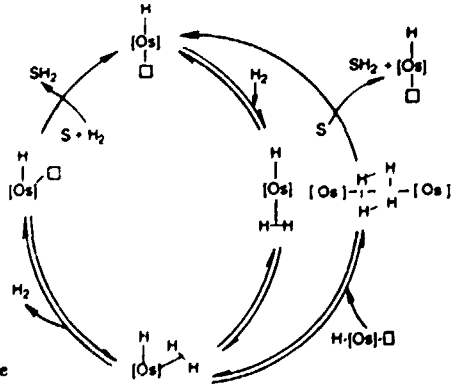
The dihydrogen compounds have distinctive properties of great utility in rationalizing some fundamental steps of the catalytic cycles. Thus, it has been proved that this type of compounds can play a fundamental role in the homolytical and heterolytical hydrogen activation. Furthermore, the η^2-H_2 ligand may behave as a good leaving group, and acts to stabilize unsaturated complexes in solution, without affecting the coordination of substrates to the metal center of the catalysts.

We have found experimental evidences for the participation of a variety of $M(\eta^2$-$H_2)$ complexes in catalytic hydrogention processes. Thus, the complexes $OsHCl(CO)(PR_3)_2$ (PR_3 = PiPr$_3$ (1), PMe-t-Bu$_2$ (2)) catalyze the selective hydrogenation of benzylideneacetone to 4-phenylbutan-2-one. The mechanisms deduced for these reactions (Sheme I) illustrate new roles of the dihydrogen complexes. 1 initially nonactive, is activated as a result of the formation of *trans-(hydride, dihydrogen)*-$OsHCl(\eta^2$-$H_2)(CO)(PiPr_3)_2$, which isomerizes to *cis-(hydride, dihydrogen)*-$OsHCl(\eta^2$-$H_2)(CO)(PiPr_3)_2$. The reaction catalyzed by 2 is proposed to go by the intermediate *trans*-$[OsCl(CO)(PMe$-t-$Bu_2)_2]_2H_4$, which could be formed by rection of 2 with *cis-(hydride, dihydrogen)*-$OsHCl(\eta^2$-$H_2)(CO)(PMe$-t-$Bu_2)_2$. According to theoretical works, this binuclear intermediate could contain a planar 4-gon of cyclically bound hydrogen atoms.

Scheme I



S = benzylideneacetone
SH$_2$ = 4-phenylbutan-2-one

LAICM2184S **B, Thu. 16**

PROTONATION AND DEHYDROGENATION OF COMPLEXES WITH SMALL UNSATURATED-CARBON OR -NITROGEN LIGANDS: A CHEMICAL AND ELECTROCHEMICAL APPROACH

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Complexes with nitriles, isocyanides, or alkyne-derived vinylidene or allene ligands at electron-rich rhenium phosphinic centres, trans-$[ReCl(L)(dppe)_2]$ (L = NCR, CNR, C=CHR or $H_2C=C=CHR$; dppe=$Ph_2PCH_2CH_2PPh_2$), undergo protonation either at the metal, to form the hydride complexes $[ReHCl(L)(dppe)_2]^+$, or at the activated ligand to afford methyleneamide, aminocarbyne, carbyne or η^2-vinyl products, $[ReCl(HL)(dppe)_2]^+$ (HL = NCHR, CNHR, CCH_2R or CH_2CCH_2R, respectively). The mechanisms of some of these fast reactions, as indicated by stopped-flow spectrophotometry, is also presented and discussed, e.g., in terms of site competition for the proton attack.

The electrochemical behaviour of those and related complexes is presented and shown to involve deprotonation or dehydrogenation processes, upon N-H, C-H or Re-H metal bond cleavage induced by electron transfer.

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Acknowledgements

This work has been partially supported by JNICT and INIC.

COMPARATIVE STUDIES ON THE REACTIVITY OF CYCLIC AND ACYCLIC PENTADIENYL CHLORIDE BIS (TRIPHENYL PHOSPHINE) RUTHENIUM COMPLEXES TOWARDS DIPHENYLPHOSPHINE.

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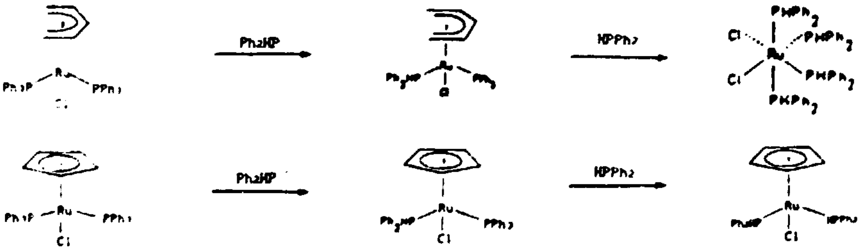
We have investigated the syntheses, physical, chemical and structural properties of various pentadienyl and cyclopentadienyl ruthenium compounds.

Reaction of $[\eta^5\text{-}C_5H_nRuCl(PPh_3)_2]$ (n=5,7) with an equivalent of diphenylphosphine affords the monosubstituted compounds $[\eta^5\text{-}C_5H_nRuCl(PHPh_2)(PPh_3)]$ by replacement of one of the triphenylphosphine ligands in each case, while the disubstituted complex $[(\eta^5\text{-}C_5H_5)RuCl(PHPh_2)_2]$ is only isolated for the cyclic derivative.

A great deal of similarity between some complexes with cyclic and acyclic pentadienyl ligands has been reported and we found that the monosubstituted $[(\eta^5\text{-}C_5H_n)RuCl(PHPh_2)(PPh_3)]$ (n=5,7) is another example of this similarity.



The addition of two equivalents to $[(\eta^5\text{-}C_5H_7)RuCl(PPh_3)_2]$ or just one equivalent to $[(\eta^5\text{-}C_5H_7)RuCl(PHPh_2)(PPh_3)]$ affords the complex *cis*-$RuCl_2(PHPh_2)_4$. Spectroscopic evidence for the formation of a phosphido dimer will be discussed, as well as the comparative stability of these $\eta^5\text{-}C_5H_n$ ligands.

COPPER-CATALYZED CYCLOHEXANE OXIDATION WITH HYDROGEN PEROXIDE AT ROOM TEMPERATURE

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Cyclohexane can be efficiently oxidized to cyclohexanone with some cyclohexanol at room temperature in pyridine/acetic acid, using hydrogen peroxide in the presence of ferric chloride. On the other hand, the reaction is slow (10 h) and the turnover numbers are normally low (<10). We studied the possibility of substituting ferric chloride by cupric chloride and found that the reactions are much faster. This system is more efficient in pyridine without acetic acid, giving only cyclohexanone with 33% efficiency in 30 min of reaction time. The turnover number is low (1.7) but can be increased to 7.3 (20% efficiency) or even to 48 (10% efficiency) by reducing the quantity of copper chloride used as catalyst. Other copper(II) salts are less efficient showing that chlorine is an active ligand. The efficiency of the system is maintained with up to 5 mL of water, which makes it appropriate for accumulating oxidized products. In up to 4 accumulations, the efficiency is maintained at 33% and 7.3 mmol of oxidation products are formed, which corresponds to a final concentration of 0.2 M. Interestingly cyclohexanol is also formed in the accumulation reactions, reaching an one:ol ratio of 4.4. After 4 accumulations the system deactivates producing no further oxidation products. We are presently trying to find out how we can avoid the deactivation of the system, which would allow obtaining a higher concentration of oxidation products.

Acknowledgements: FAPESP and CNPq

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NEW OXIDE-SUPORTED ZIEGLER CATALYSTS

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Oxides are normally poor supports for Ziegler catalysts as their basicity is too low for a strong catalyst-support interaction. We studied the possibility of reducing the oxides before heterogenization in order to improve this interaction. N-type oxides which contain oxygen on their surface are easily reduced by organometallic reagents such as butyllithium. Titanium dioxide, for instance, forms on reduction an intensely blue solid, due to the removal of oxygen from its surface which then efficiently heterogenizes titanium tetrachloride. The catalyst thus obtained is very active for ethylene polymerization. At 50°C and 2 bar of ethylene its activity is 7557 kg polyethylene (mol Ti)$^{-1}$h^{-1}bar^{-1}. The polymer chain grows for 1 h, reaching an average molecular weight, Mv, of 2500 kg mol^{-1}. At 70°C the activity is even higher (13800 kg PE (mol Ti)$^{-1}$h^{-1}bar^{-1}) showing the good stability of the catalyst. The molecular weight can be controlled with molecular hydrogen; in the presence of 0.5 bar, polyethylene with a molecular weight of 411 kg mol^{-1} and a low polydipersity factor of 2.2 is obtained. Other n-type oxides also form active catalysts under these conditions. Titanium tetrachloride on reduced lanthanum oxide, for example, polymerizes ethylene to give 4311 kg PE (mol Ti)$^{-1}$h^{-1}bar^{-1}. These catalysts are also efficient in propylene polymerization. Titanium tetrachloride on reduced titanium oxide produces polypropylene (3018 kg PP (mol Ti)$^{-1}$h^{-1}bar^{-1}) with a high molecular weight of 459 kg mol^{-1} and a good isotacticity index of 93%, confirming the strong catalyst-support interaction. Acknowledgements: FINEP, Stifterverband, CAPES-DAAD and CNPq.

LAICM2015P **54, Mon. 13**

DEGRADATION OF TRIBUTYLTIN CHLORIDE (TBT) IN WATER BY EITHER ACTIVE CHLORINE OR HYDROGEN PEROXIDE

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The interest in the environmental chemistry of organotin compounds has been risen dramatically, and a few articles have already been written reviewing certain areas of these topics (1).

The impact of tributyltin chlorides in the aquatic environment and their natural photodegradation by ultraviolet illumination has been recently reported by us (2). Altthough several studies (2) have proved the positive effect of UV-illumination on environmental degradation of butyltin compounds,however this process has its limitations. The maximun absorption wavelenght of butyltin compounds are within the ultraviolet region. Consequentely, butyltin compounds are degraded very slowly by natural sunlight. Moreover the UV-photodegradation of TBT leads to the formation of partially oxidized products from the organic groups attached to the tin atoms. Accordingly new methods must be developed.

Chlorination and oxidation by hydrogen peroxide are widely used to desinfect wastewater, drinking water and swimming pools. In this sense we discuss here two additional methods for detoxifying butyltin chlorides in waters, by the transformation of TBT to less toxic forms: either by hypochlorite solution or with hydrogen peroxide.

The chemical cleavage of butyltin compounds by the action of ClO^- or H_2O_2 has been studied semiquantitatively by an spectrophotometric analytical method. Gas chromatography-mass spectrometry techniques,GC-MS, was used for the analysis of the liquid phase during the degradation process of butyltin chlorides.

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LAICM2018P **55, Mon. 13**

Alkynyl-Vinylidene Coupling as Versatile Route to Enynyl and Dienynyl Ru(II) Complexes

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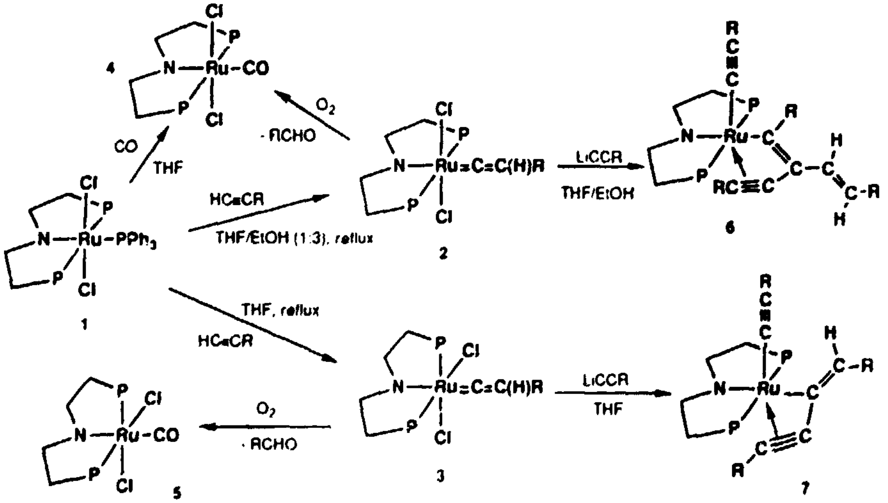
An increasing interest is presently being paid to transition-metal complexes containing highly conjugated organic ligands as they are useful precursors for either further structural elaborations of the organic fragments or may exhibit optical nonlinearity in solution.

In this communication, we report that the reaction of the aminodiphosphine Ru(II) species, *trans,mer*-[(PNP)$RuCl_2(PPh_3)$][1] [PNP = n-$C_3H_7N(CH_2CH_2PPh_2)_2$], with terminal alkynes gives isomeric vinylidenes differing for the *cis/trans* arrangement of the chloride ligands. The two vinylidene derivatives readily react with an excess of LiC≡CR in THF to yield, after addition of ethanol, regio- and stereocontrolled dimerization or trimerization products depending from the vinylidene isomer used. All of the complexes described in the scheme have been characterized by spectroscopic techniques and (for **5**, **6**, and **7**) by complete X-ray diffraction analyses. The mechanism accounting for the selective assembling of the butenynyl and hexadienynyl ligands at ruthenium will be presented and discussed.



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Coordination of Dioxygen at a Dihydrogen-binding site: Crystal structure of $[RuH(\eta^2\text{-}O_2)(dippe)_2][BPh_4]$ (dippe=1,2-bis(diisopropylphosphino)ethane).

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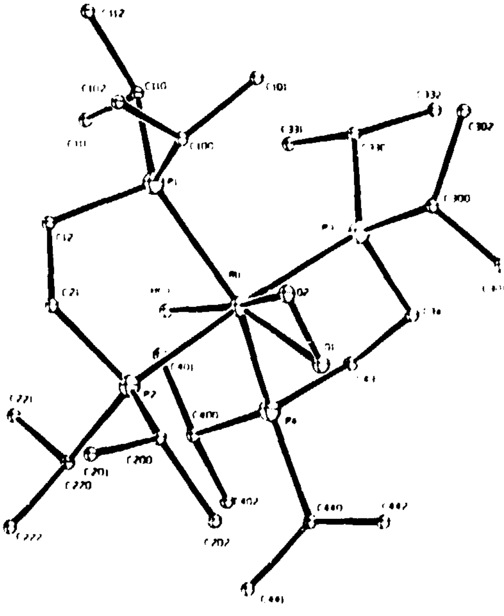
The complex *trans*-$[RuHCl(dippe)_2]$ dissociates the chloride ligand in methanol or ethanol yielding orange solutions containing the five-coordinate, 16 electron cation $[RuH(dippe)_2]^+$, which can be precipitated as tetraphenylborate salt. This complex reacts with hydrogen in acetone or chloroform yielding the labile dihydrogen complex $[RuH(H_2)(dippe)_2][BPh_4]$, which is only stable under a H_2 atmosphere. The nature of the dihydrogen ligand has been established by T_1 and $^1J(H,D)$ measurements, which yielded the values $T_1(min)=10$ ms (acetone-d_6, 300 MHz, 228 K) and $^1J(H,D)=30$ Hz, being both typical for a "non-classical" hydride complex. Both $[RuH(H_2)(dippe)_2][BPh_4]$ and $[RuH(dippe)_2][BPh_4]$ react stoichiometrically with traces of oxygen yielding the hydridodioxygen adduct $[RuH(O_2)(dippe)_2][BPh_4]$, which exhibits fluxional behaviour, as inferred from ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The X-ray crystal structure of $[RuH(O_2)(dippe)_2][BPh_4]$ has been determined, and a view of the cation complex is shown in Fig. 1, displaying distorted octahedral coordination around the ruthenium atom, with one side-on bound dioxygen ligand and one hydride ligand, in mutually *trans* positions.



LAICM2023P

57, Mon. 13

The Synthesis of *trans*-[Mo(N_2)$_2$(dippe)$_2$] (dippe=1,2-bis(diisopropylphosphino)ethane) and its Protonation. Crystal Structures of [MoF(NNH_2)(dippe)$_2$][BF_4] and *trans*-[MoCl_2(dippe)$_2$][BF_4]

By *David L. Hughes*[a], *Manuel Jiménez Tenorio*[b], *M. Carmen Puerta*[b], *and Pedro Valerga*[b]

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The reduction of [MoCl_3(thf)$_3$] with sodium dispersion in thf under dinitrogen in the presence of dippe, allows the isolation of *trans*-[Mo(N_2)$_2$(dippe)$_2$] (ν(NN) at 1900 cm^{-1}) in low yields. This complex has been characterised by the usual analytic and spectral techniques. The tetrahydride [MoH_4(dippe)$_2$] has been obtained from [MoCl_4(thf)$_2$] by reaction with NaBH_4 in the presence of dippe. This compound had been previously prepared by metal-vapour synthesis methods.

The protonation of [Mo(N_2)$_2$(dippe)$_2$] with different amounts of HBF_4·OEt_2 in diethylether has been studied. With two equivalents of HBF_4·OEt_2 the hydrazido(2-) complex [MoF(NNH_2)(dippe)$_2$][BF_4] was obtained, and its X-ray crystal structure determined (Fig. 1). The reaction of [Mo(N_2)$_2$(dippe)$_2$] with an excess of acid (*ca*. 10:1) yielded a red-orange, paramagnetic solid, which upon recrystallisation from CH_2Cl_2/Et_2O showed to be [MoCl_2(dippe)$_2$][BF_4]. The X-ray crystal structure of this complex was also determined, showing a *trans*-arrangement of chloride and phosphine ligands. Further studies on the protonation of the system [Mo(N_2)$_2$(dippe)$_2$] are underway, and the results will be presented.

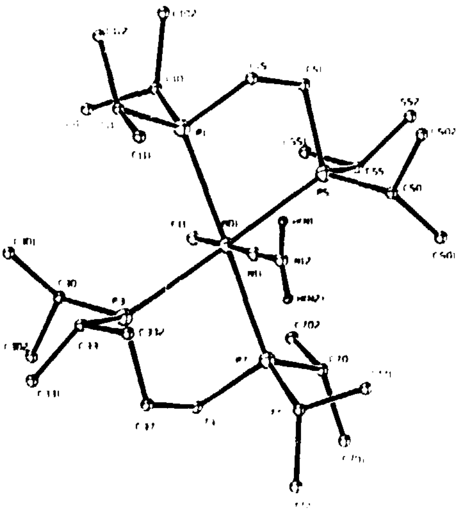

Fig 1

LAICM2024P 58, Mon. 13

Half-Sandwich Halide, Alkyl, Hydride, and other Derivatives of Iron containing the Bulky Diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe)

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The four coordinate iron phosphine complex [$FeCl_2$(dippe)] reacts with LiC_5H_5 or LiC_5Me_5 yielding the corresponding half-sandwich derivatives [Fe(η^5-C_5H_5)Cl(dippe)] or [Fe(η^5-C_5Me_5)Cl(dippe)]. These complexes react with Grignard reagents to give the alkyls [Fe(η^5-C_5H_5)R(dippe)] (R=Me or CH_2SiMe_3) or [Fe(η^5-C_5Me_5)R(dippe)] (R=Me). If ^{i}PrMgCl is used, a β-elimination reaction takes place, and the monohydrides [Fe(η^5-C_5H_5)H(dippe)] or [Fe(η^5-C_5Me_5)H(dippe)] are obtained. We have also prepared these hydrides by reaction with super-hydride (Li[$HBEt_3$]). Both monohydrides are readily protonated by $HBF_4 \cdot OEt_2$ yielding the dihydrides [Fe(η^5-C_5H_5)$(H)_2$(dippe)]$^+$ and [Fe(η^5-C_5Me_5)$(H)_2$(dippe)]$^+$, isolable as their tetraphenylborate salts. No dihydride-dihydrogen equilibrium has been observed for any of these complexes, and therefore, they must be considered as iron(IV) organometallic species.

The vinylidene complexes [Fe(η^5-C_5H_5)(C=CHPh)(dippe)]$^+$ and [Fe(η^5-C_5Me_5)(C=CHPh)(dippe)]$^+$ were obtained by reaction of the corresponding halo-complex with Li(CCPh) and $HBF_4 \cdot OEt_2$, and isolated as tetraphenylborate salts. Deprotonation of these vinylidene complexes with KOBu^t yielded the red acetylides [Fe(η^5-C_5H_5)(CCPh)(dippe)] and [Fe(η^5-C_5Me_5)(CCPh)(dippe)].

All the complexes prepared in this work were characterised by IR, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy, and microanalysis.

LAICM2028P **59, Mon. 13**

MODELS FOR HDS: REACTIONS OF DIBENZOTHIOPHENE AND DIBENZOTHIOPHENE SULFONE WITH LOW VALENT PLATINUM METALS.

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In this work are presented the reactions of low valent platinum metals with the ligands dibenzothiophene and dibenzothiophene sulfone, in an effort to elucidate the mechanism of the hidrodesulfurization process. Our results indicate evidence for insertion of a metal onto the carbon-sulfur bond of the aromatic dibenzothiophene.

LAICM2045P **60, Mon. 13**

SYNTHESIS OF TETRANUCLEAR THIOLATE-BRIDGED Fe_3Au CLUSTERS.

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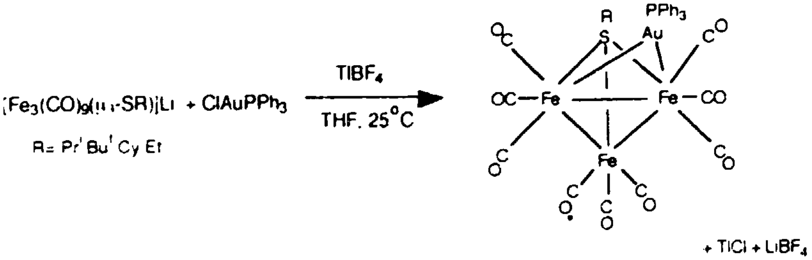
It is known that compounds of formula $[Fe_3(CO)_9(\mu_3\text{-}SR)(\mu\text{-}H)]$ are prepared by reaction of thiols, HSR, and $Fe_3(CO)_9$ [1]. Given the isolobal analogy between the H^+ and the $AuPPh_3^+$ fragments [2], we carried out the synthesis of $[Fe_3(CO)_9(\mu_3\text{-}SR)(\mu\text{-}AuPPh_3)]$ compounds, according to the following scheme.



The new compound have been characterizates by IR, ^1H-, ^{13}C-, ^{19}F-NMR spectroscopies and FAB mass spectrometry.

X-ray data will be provided on $[Fe_3(CO)_9(\mu_3\text{-}SPr^i)(\mu\text{-}AuPPh_3)]$.

References

[1] J A. de Beer and R J Haines Chem Commun. (1970) 288.
[2] J W Lauher and K Wald J Am Chem 103 (1981) 7648.

LAICM2055P **61, Mon. 13**

SUPPORTED AND UNSUPPORTED METAL COMPLEXES OF BENZOYLTHIOUREAS

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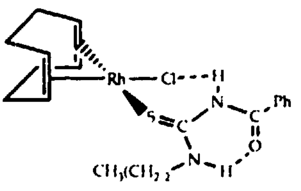
It is well known that substituted thioureas are suitable ligands for different metal species; nevertheless the catalytic properties of the thiourea-metal complexes are practically unexplored, if we exclude the case of the thiourea/PdX_2 (X = Cl, I) complexes, which were found efficient in catalyzing carbonylation of alkynes.[1] Recently, we have prepared thiourea-functionalized silica xerogels by hydrolysis and co-condensation of $Si(OR)_4$ (fourfold cross-linking) with the suitable functionalized siloxane $L\text{-}Si(OR)_3$. Aim of this research program is to produce novel polymeric materials designed to support metal complexes through coordinative linkage.[2]
For this purpose, we have synthesized the benzoyl-thiourea $(EtO)_3Si\text{-}(CH_2)_3NHC(S)NHC(O)Ph$ as a precursor of the new functionalized xerogel XGbztu. The non-siloxanized thiourea $CH_3(CH_2)_2NHC(S)NHC(O)Ph$ (Hbztu) has been used as a model for the surface binding function. It reacts with $[Rh(cod)Cl]_2$ giving the complex [Rh(cod)(Hbztu)Cl] (**1**) and with palladium(II) chloride and acetate affording $[Pd(Hbztu)_2Cl_2]$ (**2**) and $[Pd(bztu)_2]$ (**3**), respectively. The crystal structures of **1** and **2** have been determined by X-ray diffraction methods and are sketched below.



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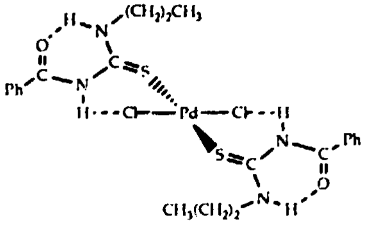

2

The related complexes, tethered to XGbztu, have been tested as hybrid catalyst precursors in hydroformylation and hydrogenation processes with satisfactory results.

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[1] G. P. Chiusoli, M. Costa, S. Reverberi, G. Salerno, *Gazz. Chim. Ital.* **115** (1985) 691.
[2] C. Ferrari, G. Predieri, A. Tiripicchio, M. Costa, *Chem. Mater.* **4** (1992) 243.

LAICM2461P **62, Mon. 13**

LITHIATED FLUORENYL ANION COORDINATED TO TWO $[Cp^*M]^+$ GROUPS, $(Cp^*=C_5Me_5;M:Fe,Ru)$. INUSUAL QUENCHING OF ELECTROPHILIC ADDITIONS AND X-RAY CRYSTAL STRUCTURE OF $[(Cp^*Ru)_2\ \eta^6,\eta^6\text{-}C_{13}H_9Li](OSO_2CF_3)_2$

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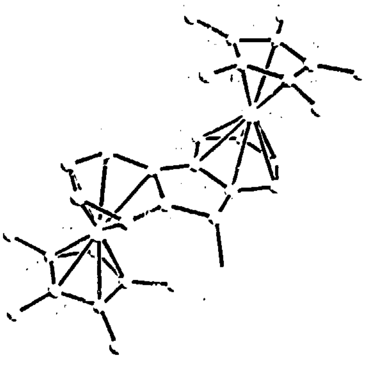
Deprotonation of the binuclear fluorene derivatives $[(Cp^*M)_2\ \eta^6,\eta^6\text{-}C_{13}H_{10}](X)_2$ (**1** M=Fe, X=PF_6^- and **2** M=Ru, X=OTf⁻) by means of one equivalent of n-BuLi, affords the novel dicationic organolithiated complexes $[(Cp^*M)\eta^6,\eta^6\text{-}C_{13}H_9Li](X)_2$ **3** (M=Fe X=PF_6^-) and **4** (M=Ru, X=OTf⁻). These lithiated species in an unprecedent way do not undergo attack on the C_9-Li bond and show a monoelectronic reversible oxidation (*Eox* = + 0.4 V SCE) **without structural change** These results are in contrats with the mononuclear fluorene derivatives $[(Cp^*M)\ \eta^6\text{-}C_{13}H_{10}]X$ (**5** M=Fe **6** M=Ru) where monodeprotonation with n-BuLi affords the classical neutral *exo* - cyclic olefine complexes $[(Cp^*M)\ \eta^5\text{-}C_{13}H_9]$ wich show a rapid electrophilic addition at the C_9 carbon atom and do not display an electrochemical oxidation behaviour

$$[(Cp^*Ru)\ \eta^6\ \eta^6\text{-}C_{13}H_9Li](X)_2 + E^+ \not\longrightarrow$$

$$E^+ = PhCOCl, D_2O, CH_3I$$



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Acknowledgment this work was supported by FONDECYT-CHILE (Grants 825-92 and 0012-92)

LAICM2070P **63, Mon. 13**

METAL VAPOUR SYNTHESIS OF FLUORENE TRANSITION METAL COMPLEXES.

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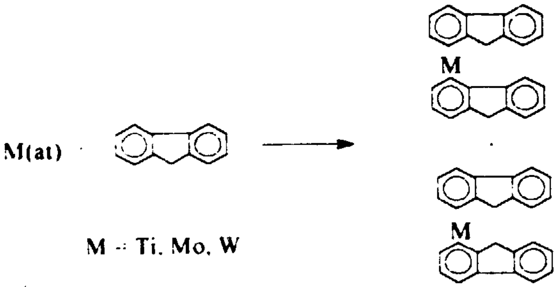
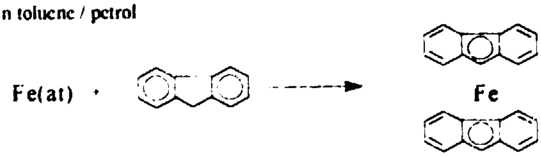
The title complexes were prepared using the Metal Vapour Synthesis technique, by cocondensing metal and fluorene vapours on a glass reactor cooled with liquid nitrogen (-196 °C).

Bis-fluorene complexes were synthesised for Ti, Mo and W. The final product of these reactions was a mixture ≈ 1/1 of two isomers that were recovered by recrystalisation in toluene / petrol or sublimation (Mo)



The bis-fluorenyl iron (0) was prepared by cocondensation of iron and fluorene and also isolated by recrystalisation in toluene / petrol



LAICM2075P **64, Mon. 13**

DIOXOMOLYBDENUM(VI) HALIDES AS OXOTRANSFER CATALYSTS

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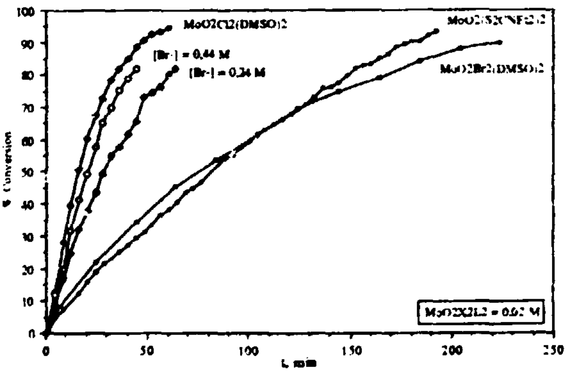
Oxygen atom transfer reaction involving dioxomolybdenum(VI) complexes constitutes a focus of current interest because of its significance in some important biological processes.[1] The first indication that halide complexes might be more efficient as oxygen atom transfer catalysts than those of sulphur was provided by Enemark's group[2], based on qualitative observations on dioxomolybdenum(VI) pyrazolylborate halide complexes.

We have examined the catalytic activity of $MoO_2X_2(DMSO)_2$ (X = F, Cl, Br) in two different oxotransfer reactions: i) oxidation of triphenylphosphine by dimethylsulphoxide, and ii) deoxygenation of azoxybenzene by triphenylphosphine. We have also measured the activity of $MoO_2(S_2CNEt_2)_2$, the prototypical example of dioxomolybdenum(VI) catalyst containing sulfur-donor ligands, having found that in both systems the chloro and bromo-complexes are more effective than the carbamate.



Oxidation of PPh_3 by dmso was carried out at 36 °C in dmso (20% v/v in dmso-d_6) and solutions were analyzed via ^{31}P NMR spectroscopy. Fig. 1 shows the results obtained with chloro, bromo and dithiocarbamate complexes as catalysts as well as the influence of bromide ions in the case of the bromo-complex (which is largely dissociate in dmso). A solution of $MoO_2(S_2CNEt_2)_2$ in dmso was found to be unstable, but our results suggest that $MoO_2(S_2CNEt_2)_2$ increases in activity as it decomposes. No formation of $OPPh_3$ was detected with the fluoro-complex after 24 hours.

Kinetic analysis led to a value of k = 2.57 $(M.s)^{-1}$ for the reaction:

$$\text{"}MoO_2Cl_2\text{"} + PPh_3 \xrightarrow{\text{dmso}} \text{"}MoOCl_2\text{"} + OPPh_3$$

Although this value of k cannot be rigourously compared with the second-order rate constants observed for the reaction of PPh_3 with other dioxomolybdenum(VI) complexes we note it is 1-2 orders of magnitude higher than rate constants observed for dithiocarbamates. From these results it follows that, at least in oxotransfer from dmso and PhN(O)=NPh to PPh_3, Enemark's assumption was correct that many species are expected to be more active than carbamates.

(1) Holm, R.H.; *Chem. Rev.* **1987**, *87*, 1401; *Coord. Chem. Rev.* **1990**, *100*, 183

(2) Roberts, S.A.; Young, C.G.; Kipke, C.A.; Cleland, W.E.; Yamanouchi, K.; Carducci, M.D.; Enemark, J.H.; *Inorg. Chem.* **1990**, *29*, 3650-3656.

LAICM2097P 65, Mon. 13

ORGANOLEAD DERIVATIVES OF COORDINATIVELY SATURATED PLATINUM(II) OLEFIN COMPLEXES

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Angeles Sanchez
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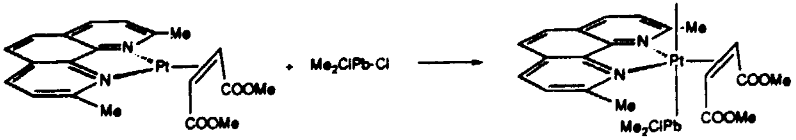
The organometallic compounds of the 14th column metals are useful tools in preparative chemistry [1]. Thus, there is significant ground for the investigations currently concerned with transition complexes bearing organometal 14th column fragments "as ligands". We report here on bimetallic complexes (I) of general formula $[PtCl(PbR_2Cl)(N,N\text{--}chelate)(olefin)]$, having an organolead group in an axial position of a coordinatively saturated platinum(II) TBP olefin complex.The procedure for the syntheses of the type I products involves oxidative to platinum(0) complexes, e.g. according to the following equation:



(I)

A noteworthy feature of the products is the unprecedent stable sequence $Pt(II)\text{-}PbR_2Cl$.

The single crystal structure analysis of $[PtCl(PbPh_2Cl)(2,9\text{-}Me_2\text{-}1,10\text{-}phenanthroline)(C_2H_4)]$ is also discussed.

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LAICM2098P **66, Mon. 13**

RHODIUM AND IRIDIUM COMPLEXES WITH α-DIIMINES.

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Reactions of [ML$_2$Cl]$_2$ (M=Rh, Ir; L$_2$=COD, NBD) with α-diimines RN=C(R')-C(R')=NR, derived from glyoxal(R'=H; R=cyclohexyl; p-dimethylaminophenyl) (GLL) or from biacetyl (R'=CH$_3$; R= phenyl; NH$_2$; OH) (BLL) have been studied.

[Rh(COD)Cl]$_2$ reacts with GLL to give, irrespective of the stoichiometric ratios 1:1 or 1:2, Rh$_2$(COD)$_2$Cl$_2$(GLL) compounds that in solution undergo the following equilibrium, displaced towards the left at low temperatures:

$$[Rh_2(COD)_2Cl_2(\mu\text{-}GLL)] \rightleftarrows [Rh(COD)(GLL)]^+[Rh(COD)Cl_2]^-$$

[Rh(NBD)Cl]$_2$ reacts with GLL to give, irrespective of the stoichiometric ratios 1:1 or 1:2, neutral pentacoordinated Rh(Cl)(NBD)(GLL) compounds that in solution undergo intramolecular rearrengements that are rapid even at -60°C.

[Ir(COD)Cl]$_2$ reacts with GLL to give, depending on the stoichiometric ratios, Ir$_2$(COD)$_2$Cl$_2$(GLL) compounds (Ir:GLL=2:1) or Ir(Cl)(COD)(GLL) (Ir:GLL=1:1). When using BLL ligands only pentacoordinated Ir(Cl)(COD)(BLL) compounds are obtained. Ir(Cl)(COD)(GLL) undergo chloride dissociation while Ir(Cl)(COD)(BLL) undergo intramolecular rearrengements. These processes are slow at -60°C.

When the aforementioned reactions are performed in the presence of SnCl$_2$, trichlorostannato [M(SnCl$_3$)L$_2$(LL)]compounds are obtained in all cases. These compounds are pentacoordinated in the solid state but show dissociation of SnCl$_3$ in solution at room temperature. At low temperatures this equilibrium is displaced towards the pentacoordinated compounds. The tendency to ionic dissociation follows the order: Rh/COD > Rh/NBD > Ir/COD.

Iridium compounds such as Ir(COD)(BLL)(Cl) or [Ir(COD)(BLL)]PF$_6$, catalyse hydrogen transfer from isopropanol to cyclohexanone, and the latter are more active than the former. The influence of the presence of SnCl$_2$ in the reaction mixture of chloro compounds is also studied.

LAICM2100P **67, Mon. 13**

AN NMR STUDY OF THE DISPROPORTIONATION OF ORGANOLEAD DIORGANODITHIOPHOSPHINATES

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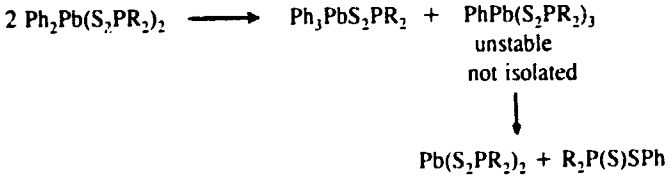
Triphenyl- and diphenyllead(IV) chlorides reacted with diorganodithiophosphinato salts to give the corresponding organolead(IV) derivatives containing dithiophosphorus ligands, i.e. $Ph_3PbS_2PR_2$ and $Ph_2Pb(S_2PR_2)_2$ where R = Me, Et, Ph. The title compounds were characterized by spectroscopic techniques. Diphenyllead(IV) dithiophosphinates undergo disproportionation following the scheme:



$$2\,Ph_2Pb(S_2PR_2)_2 \longrightarrow Ph_3PbS_2PR_2 + \underset{\substack{\text{unstable}\\ \text{not isolated}}}{PhPb(S_2PR_2)_3} \;\longrightarrow\; Pb(S_2PR_2)_2 + R_2P(S)SPh$$

The reaction was studied in detail by ^{31}P and ^{1}H NMR spectroscopy.

AICM2101P **68, Mon. 13**

INORGANIC CHELATE RINGS CONTAINING TIN, PHOSPHORUS, NITROGEN AND OXYGEN/SULFUR. SYNTHESIS AND STRUCTURE

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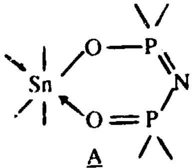
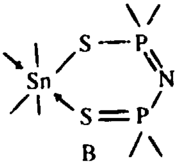
[c] Faculty of Applied Science, Vrije Universiteit Brussel, B-1050 Brussels, Belgium.

A series of di- and triorganotin derivatives containing inorganic (carbon-free) chelate rings A and B have been prepared and characterized by spectroscopic methods.

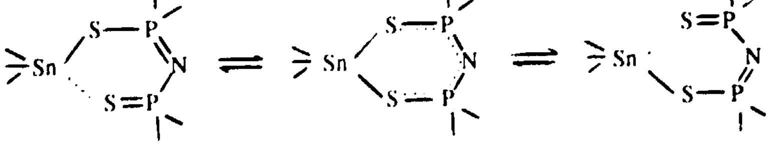


A



B

In diorganotin derivatives $R_2Sn[(OPPh_2)_2N]_2$ and $R_2Sn[(SPPh_2)_2N]_2$ the metal is six-coordinate and the ring is symmetrical with a delocalized π-system. The structures were confirmed by X-ray diffraction. In triorganotin derivatives the spectroscopic data suggest unsymmetrical (anisobidentate) or even monodentate coordination with a rapid exchange in solution:



CO_2 LASER INDUCED PHOTODECOMPOSITION OF TIOPHENE, 2-METHYL-, AND 3-METHYL-TIOPHENE IN THE PRESENCE OF CHROMIUM HEXACARBONYL.

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Continuing with our studies about the photodecomposition of organic and organometallic compounds under an intense IR laser field (1). we have found that sulfur compounds such as : tiophene. 2-methyltiophene and 3-methyltiophene when irradiated in the gaseous statate and in the presence of chromium hexacarbonyl. employing a TEA CO_2 laser tuned to the P-20 line (944.2 cm^{-1}). with energies in the 400 mJoule/pulse range. and focusing with a germanium lense (focal distance = 5.0 cm) resulted in a fast decomposition reaction (dielectric breakdown) giving acetylene. carbon disulfide and hydrogen as the major products. The presence of the chromium hexacarbonyl is necessary for the photodecomposition reaction to happen. acting like a sensitizer (i.e. SF_6) absorbing the IR radiation and through a high vibrational state transfering efficiently the energy to the organic molecule.

(1) Barriola. A. M. y Heredia. M. Rev. de la Soc. Venez. de Catálisis. 1990. Vol. 4(1-2) p.137-148.

SYNTHESIS OF FUNCTIONAL PHOSPHOLYL ANIONS: AN ACCESS TO THE 3-ETHOXYCARBONYL DERIVATIVE.

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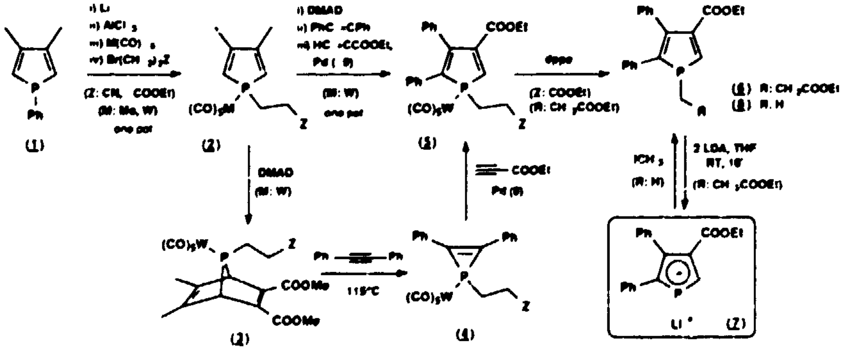
Phospholyl anions[1] have received much attention during the last decades owing to the growing interest focused on the synthesis and properties of phosphametallocenes. The latter can be functionalized by means of electrophilic substitution reactions, but functionalized phospholyl anions themselves have never been reported and hence the aim of the present work.

Up to now, no useful and general method is available for the direct functionalization of phospholes[1a], the only relevant general strategy being the reaction of several electrophiles with 2-lithio-1-phenylphospholes[2] obtained from the corresponding 2-bromophospholes. However, the 2-functionalized phospholyl salts have never been claimed due to the unstability of such functional groups toward the reductive conditions required to cleave the exocyclic P-C bond.

Our approach starts from readily available dimethylphenylphosphole (1) and lie in a [P] + [C2-C3] + [C4-C5] building up strategy for the synthesis of a 3-ethoxycarbonyl-1-(2-ethoxycarbonylethyl)-phosphole pentacarbonyl tungsten complex (5) as key precursor, obtained by one-pot three-steps reaction from the unfunctionalized derivative 2. The transformation 2→5 involves initial 4+2 cycloaddition with DMAD to give a 7-phosphanorbornadiene (3), followed by *in situ* generation of a transient phosphinidene complex [$EtOOC(CH_2)_2P{=}W(CO)_5$] which is trapped with tolane, affording the phosphirene complex 4, and final Pd(0) catalyzed insertion of a terminal alkyne into the strained intracyclic P-C bond[1b] yielding 5.

The target phospholyl anion (7) was obtained from the P,P-bisprotected precursor 5 by decomplexation with "dppe" (6) and smooth non-reductive exocyclic P-C bond cleavage with LDA. Compound 7 shows a remarkable stability and its structure has been proved by P-methylation (8).



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1 a) F. Mathey, Chem.Rev., **88**, 429 (1988); b) *ibid.* **90**, 997 (1990) and references cited therein

2. E. Deschamps and F. Mathey, Bull.Soc.Chem.Fr., **129**, 186-9 (1992)

LAICM2118P **71, Mon. 13**

CYCLOMETALLATION. REACTIONS OF Pd(II) CYCLOMETALLATED COMPLEXES OF *N,N*-DIMETHYL-*ter*-BUTYLMETHYLHYDRAZONE WITH DIPHOSPHINES.

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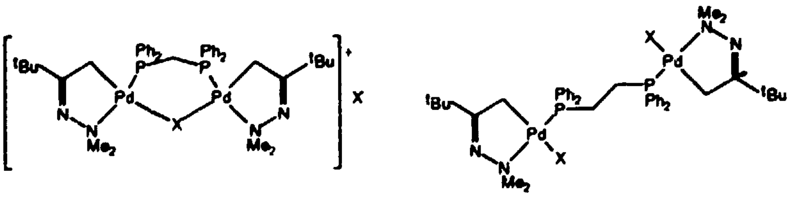
Cyclometallation reactions have been the subject of much attention in recent years. We have been investigating the cyclometallation of ligands which comprise aromatic rings, such as Schiff bases, phenylimidazoles and aromatic diimines. In the present communication we report cyclometallated complexes with non-aromatic ligands and their reactions with diphosphines.

Thus, along with B.L Shaw *et al.* we have synthesized the acetato- and halide-bridged dimer complexes, which were then treated with a variety of tertiary diphosphines in a 1:1 molar ratio to give the corresponding dinuclear species, an example of which is depicted in Fig. 1. The dinuclear species with small "bite" diphosphines, such as 1,1-bis(diphenylphophino)methane, are 1:1 electrolytes; with large "bite" diphosphines neutral species are obtained, as is shown in Fig. 1.



X = Cl, Br

Fig. 1

CYCLOMETALLATED COMPOUNDS OF Pd(II) WITH DIIMINE LIGANDS

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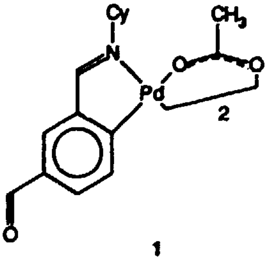
The ligand *N,N*-isophthalylidenebis(cyclohexylamine) may undergo double metallation to produce doubly cyclometallated complexes when the reaction is carried out in dry chloroform. However, when the solvent is glacial acetic acid, double metallation is not produced and instead palladation of only one carbon atom is achieved. This produces an *ortho*-palladated Schiff base with a formyl group in the *para* position to the M-C σ bond, as is depicted in Fig.1.

In the present communication we describe the synthesis and characterization of mono-palladated acetato- and halide-bridged dimer complexes and the study of some of their reactions with neutral or anionic bridge splitting reactants, such as tertiary phosphines, thallium acetylacetonate and thallium cyclopentadienyl.

Treatment of 1,3-$(CyN{=}CH)_2C_6H_4$ with the appropriate amount of palladium(II) acetate in glacial acetic acid under reflux gave the acetato-bridged cyclometallated dimer complex (1). Treatment of (1) with aqueous NaX (X=Cl, Br or I) gave the chloro (2), bromo (3) or iodo-bridged (4) complexes, respectively. Complexes 2, 3 and 4 were reacted further to give mononuclear cyclometallated species.

The complexes were characterized by elemental analysis (C, H and N) and by i.r. and $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy.



1

Fig. 1

LAICM2120P **73, Mon. 13**

PALLADIUM(II) CYCLOMETALLATED COMPOUNDS VIA OXIDATIVE ADDITION REACTIONS

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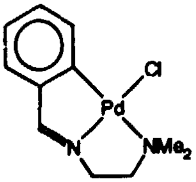
In the past years we have investigated the cyclometallation of various types of ligands among which Schiff bases have been the most widely used in our research. Regardless of the ligand system which was treated with the corresponding metal salt, the formation of the metal-carbon σ bond was achieved by electrophilic or nucleophilic attack of the metal atom on the organic substrate without change of the oxidation state of the metal.

Lately, we have attempted another approach towards cyclometallated complexes, namely that of oxidative addition reactions.

Thus, treatment of an *ortho*-halogenated Schiff base ligand, $o\text{-}ClC_6H_4C(H)=NCH_2CH_2NMe_2$, with $[Pd_2(dba)_3]dba$ gave the cyclometallated complex $[\overline{Pd\{C_6H_4C(H)=NCH_2CH_2N}Me_2\}(Cl)]$ as a yellow air-stable solid (1), depicted in Fig. 1, which was fully characterized.

Reactions of 1 with neutral or anionic ligands, *i.e.*, tertiary phophines or thallium acetylacetonate and thallium cyclopentadienyl, respectively, afforded complexes in which the chlorine atom has been substituted, with, in some cases, opening of the $\overline{PdNCH_2CH_2N}$ ring.



1

Fig. 1

MIXED $Ph_2PCH_2PPh_2$ (dppm) AND $Ph_2PC(=CH_2)PPh_2$ (vdpp) DICARBONYL COMPLEXES OF GROUP VI METALS. HYDRIDE FORMATION AND MICHAEL ADDITIONS TO THE VINYLIDENE DOUBLE BOND

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Complexes of the type $[M(CO)_2(L\text{-}L)_2]$ (M = Cr, Mo, W; L-L = $Ph_2PCH_2PPh_2$(dppm), $Ph_2PC(=CH_2)PPh_2$ (vdpp) or $Ph_2PCH_2CH_2PPh_2$ (dppe)) are known. Hydride derivatives for the complexes of type $[M(H)(CO)_2(L\text{-}L)_2](X)$ (X = BF_4^-, HCl_2^-), have been reported. We have recently prepared mixed phosphine complexes of the type $[M(CO)_3(L\text{-}L)(L')]$ (M = Mo, W; L-L = $Ph_2PCH_2PPh_2$ or $Ph_2PC(=CH_2)PPh_2$, L' = PPh_3, PEt_3 or $PPhEt_2$) and now we describe complexes of type $[M(CO)_2(L\text{-}L)(L'\text{-}L')]$ containing two different diphosphines which are both bidentate and of general formula $[M(CO)_2(dppm\text{-}P, P')(vdpp\text{-}P, P')]$ (M = Cr, Mo, W). An interesting feature of these complexes is the presence of the $C=CH_2$ bond which might undergo Michael type addition similar to those reported earlier. It is now well-established that the $C=CH_2$ double bond in $(Ph_2P)_2C=CH_2$ is activated towards nucleophilic additions by coordination to the electron withdrawing group $M(CO)_4$ whilst the free diphosphine does not react with nucleophiles such as amines or hydrazine. In the complexes reported here the electron withdrawing effect of $M(CO)_2(dppm\text{-}P\text{-}P')$ will be less than that of $M(CO)_4$ or $M(CO)_3PR_3$ and we thought it might not be strong enough to activate the $C=CH_2$ double bond towards the addition of the more weaker nucleophiles.

The compounds in the present communication have been fully characterized by elemental analysis (C, H, N) and by i.r. and $^{31}P\text{-}\{^1H\}$, $^1H\text{-}\{^{31}P\}$ and ^1H n.m.r. spectroscopy.

LAICM2122P

75, Mon. 13

REARRANGEMENT OF A CYCLOMETALLATED Pd(II) COMPOUND IN SOLUTION

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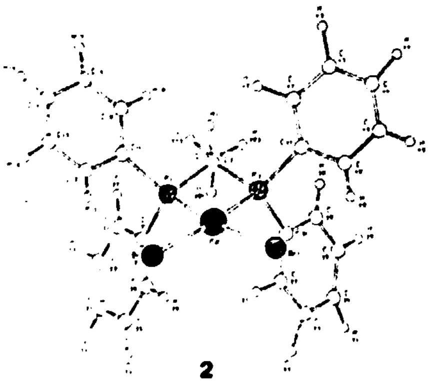
We have recently found that dinuclear Pd(II) cyclometallated complexes with bridging diphosphine ligands may exist in two isomeric forms in solution, *i.e*, a ionic and a non-ionic structure.

At the present time we are studying the behavior of such systems and the reasons for the proposed equilibria.

When one such compound (1), a dinuclear Pd(II) cyclometallated phenylimidazole complex with two bridging ligands, a diphosphine and a bromine atom, which was fully characterized by elemental analysis (C, H and N) and by i.r. and ^{31}P-{^{1}H} and ^{1}H n.m.r. spectroscopy, was set aside for crystallization in chloroform solution, a suitable pale yellow transparent crystal was grown and its crystal structure determined. Surprisingly this results in a Pd(II) coordination complex (2) (Fig. 1).

The central atom is bonded to the two phosphorus atoms of a 1,1-bis(diphenylphosphino)ethane ligand and to two mutually *cis* bromine atoms in a nearly square-planar environment.



2

Fig. 1

LAICM2123P **76, Mon. 13**

CYCLOMETALLATION. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE DINUCLEAR CYCLOMETALLATED COMPOUND $[\{\overline{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N}Cy](Cl)\}_2\{\mu\text{-}Ph_2PC(=CH_2)PPh_2\}]$

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N.A. Bailey and H. Adams. Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, U.K.

The reaction of the Schiff base ligand $2,3,4\text{-}(MeO)_3C_6H_2C(H)=NCy$ with palladium(II) acetate in glacial acetic acid yields the acetato-bridged cyclometallated dimer complex. When this is treated with aqueous sodium chloride the acetato-bridging ligands are exchanged for chloride-bridging ligands in a metathesis reaction. Reaction of the chloride-bridged dimer with 1,1-bis(diphenylphosphino)ethene in a 1:1 molar ratio affords the title compound from which suitable crystals have been grown. The corresponding crystal structure is depicted in Fig.1.

The bimetallic molecule comprises two chloro(diphenylphosphine)palladium(II) fragments, to each of which is chelated a (N-cyclohexyl-1-carbimine-2,3,4-trimethoxyphenyl) ligand; the fragments are linked by a $C=CH_2$ bridge between the phosphorus atoms.

Each palladium atom adopts a square-planar geometry with the donor atoms of the chelating ligand occupying mutually *cis* sites with a somewhat reduced bond angle (79.1° and 80.6°). The sum of angles on palladium is *ca.* 360°. The molecule exhibits approximate C_2 symmetry about the central $C=CH_2$ fragment.

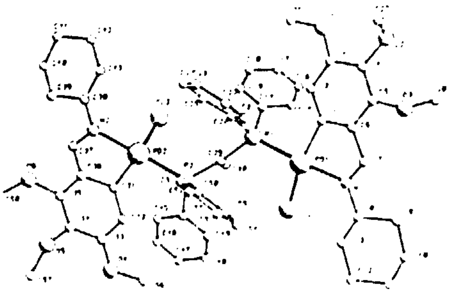

Fig. 1

LAICM2131P 77, Mon. 13

WATER-SOLUBLE ORGANOMETALLIC COMPLEXES OF TUNGSTEN AND RUTHENIUM. SYNTHESIS, CHARACTERIZATION AND PRELIMINARY STUDIES IN THE HYDROGENATION OF OLEFINS IN A BIPHASIC SYSTEM.

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ABSTRACT:

To compare the catalytic activity on olefin hydrogenation, for early transition metal water-soluble complexes, with those of the well-known late transition metals; the synthesis and characterization of two novel complexes of tungsten (group 6) and ruthenium (group 8) were undertaken using ligand substitution reactions.

The novel organometallic complexes of tungsten, $[W(CO)_3(MeCN)(TPPMS)_3]\cdot nH_2O$ (I) and ruthenium $[HRuCl(CO)(TPPMS)_3]\cdot nH_2O$ (II), where n = 2, and TPPMS is the sodium salt of the m-sulphophenyl-diphenylphosphine $[Ph_2P(m\text{-}C_6H_4SO_3Na)\cdot 3H_2O]$, were prepared by ligand exchange in a water/toluene medium, under reflux conditions. Compounds I and II were characterized by IR, NMR (^1H, ^{31}P, ^{13}C), elemental analyses, mass spectrometry and XPS. The stability of both complexes in an aqueous solution were studied using UV-vis spectroscopy. In water both complexes tend to lose one of the coordinating ligand which is replaced by an hydroxyl group from the water. This hydroxyl intermediate complex is supposed to play a key role in the catalytic hydrogenation of olefin substrates in a water/organic medium.[1] The tungsten complex tends to keep its coordination sphere intact after a catalytic run according to ir studies before and after the catalytic reaction.

Preliminary studies on the catalytic hydrogenation of olefin compounds showed the better ability of the late transition metal ruthenium complex to hydrogenate styrene and 1-cyclohexene to ethylbenzene and cyclohexane, in a biphasic water/organic medium, compared to the early tungsten complex

REACTIONS OF $[Os_3(CO)_{10}(MeCN)_2]$ WITH ORTO SUBSTITUTED DERIVATIVES OF PYRROLE

Hernández L*., Arce A**., De Sanctis Y**., Deeming A***.

Abstract

The reactions products of differents pyrrole orto-substituted derivatives toward the Os_3 triangle are reported,also is showed that the chemical reaction mode varies in accordance to ligand type Furthermore when the ligand is an imine group,a nonacarbonilic derivative was obtained,where the coordination mode to the Osmium triangle will depend on the reaction media.So,in polar solvents a C_3-H bond activation will occur, while in non polar solvents the in position 1 metallation will occur.When the substituent is an alkyl group such as a methyl group,a decacarbolinic derivatives like reaction products were isolated. Furthermore,when these last decacarbonilic derivatives were mantained at room temperature during long time in solution, a nonacarbonilic derivative is isolated. The ^{1}H.N.M.R.,I.R. and XR difraction spectral data of the obtained complexes are presented also.

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NEW CARBONYL HYDRIDE CLUSTER DERIVATIVES OF DIPYRIDYLALKANE LIGANDS

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De Sanctis Y.
Centro de Química, IVIC, Apartado postal 21827, Caracas, Venezuela.

Abstract

Treatment of $Os_3(CO)_{10}(CH_3CN)_2$ (I) with 2,2'-Bipyridylmethane (**II**), 2-Pyridyl-4'-(6'-methyl)pyridylmethane (**III**), 2-Pyridyl-2-quinolylmethane (**IV**) and 2-Pyridyl-2-quinolylethane (**V**) in aliphatic hydrocarbons, yields the new carbonyl hydride cluster derivatives. The reaction of the 2,2'-Bipyridylmethane with cluster (**I**) gives two new complexes, (**II-A**) and (**II-B**) isomers. These complexes show IR bands in the carbonylic region characteristic of decacarbonyl hydride systems. The (**II-A**) isomer is obtained via ortho hydrogen metallation at the pyridynic nitrogen on the Os-Os bond. On the (**II-B**) isomer an oxidative addition of the C-H ortho bond to the CH_2 bridge of one of the pyridynic groups on one of the osmium atomso ccurs; whilst the other heterocycle is coordinated to the same metallic center throuhg the lone pair of electron on the nitrogen, thus forming a six membered ring . In the reaction of ligands (**III**), (**IV**) and (**V**) with $Os_3(CO)_{10}(CH_3CN)_2$ only the isomer derived from the metallation at the α-position at the nitrogen was isolated. The thermolysis of the decacarbonyls complexes in n-octane solution brings about the nonacarbonyl hydride derivatives, where the ligand acts as a five electrons donor. These compounds were characterized by IR and ^1H RMN spectroscopy.

LAICM2148P **80, Mon. 13**

HOMOGENEOUS CATALYTIC HYDROGENATION OF KETONES BY RHODIUM COMPLEXES

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Hydrogenation of the C=O group is an important method of organic synthesis. In contrast to numerous studies of homogeneous catalytic hydrogenation of the C=C double bond, there are less frequent reports of hydrogenation of the C=O group in aldehydes and in ketones. In general hydrogenation of carbonylic functions requires more strenuous conditions than those applied to C=C double bond hydrogenation.

The most effective catalysts in the homogeneous hydrogenation of ketones to secondary alcohols are the complex compounds of transition metals, particularly those of the Pt group.

We have found that the complexes $[Rh(PhPy_2P{=}O)(COD)]BF_4$ and $[Rh(Py_3P{=}O)(COD)]BF_4$ are very efficient catalytic precursors in the homogeneous hydrogenation of ketones under mild conditions. Both complexes catalyze the reduction of ketones, in basic medium, very efficiently whether using molecular hydrogen as a source of hydrogen or if the process takes place by hydrogen transfer from 2-propanol.

Use of the above complexes allows us to make a comparative study of the behaviour of the bis-chelate and tris-chelate complexes in the process under study.

LAICM2149P **81, Mon. 13**

DINUCLEAR ORTHOPALLADATED DERIVATIVES WITH MIXED BRIDGES: UNUSUAL *cis*-STRUCTURE.

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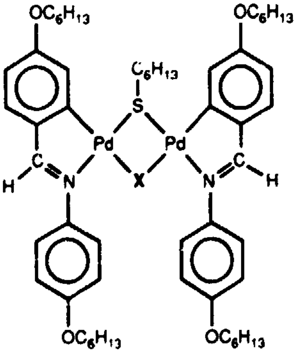
The chemistry of orthometallated Pd(II) dimeric systems with different bridging ligands $[Pd_2(C,N)_2(\mu\text{-}X)_2]$ is dominated by the *trans* isomer; the *cis* isomer either is not formed, or is the very minor component in the mixture. For a number of years we have been investigating the systems derived from imines or azines, and their liquid crystalline behavior. Taking advantage of the great tendency of thiolates to bridge two Pd(II) atoms, we have prepared complexes with mixed bridges thiolate-chloride and thiolate-carboxylate (see figure).



1 $X = CH_3\text{-}CO_2^-$

2 $X = Cl^-$

3 $X = (R)\ CH_3\text{-}\overset{*}{C}HCl\text{-}CO_2^-$

In every case only the *cis* isomer was obtained, as shown by ^1H NMR. The mesogenic behaviour of the complexes has been studied. This *cis* structure has proved useful to produce cholesteric mesophases, previously unknown for metallomesogens.

LAICM2150P **82, Mon. 13**

CARBONYL MOLYBDENUM(0) AND -(II) COMPLEXES WITH PHENYLBIS(2-PYRIDYL)PHOSPHINE

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The first carbonyl molybdenum(0) and (II) complexes with phenylbis(2-pyridyl)phosphine ($PPhpy_2$) have been synthesized. $PPhpy_2$ reacts with $Mo(CO)_5(NCMe)$ to give $Mo(CO)_5(PPhpy_2\text{-}P)$, (**1**). With $Mo(CO)_4(NBD)$ it gives $Mo(CO)_4(PPhpy_2\text{-}P)_2$, (**2**), when ratio 2:1 is used, or $Mo(CO)_4(py_2PhP\text{-}N,N')$, (**3**) for 1:1 ratio. Decarbonylation of any of these pyridylphosphine complexes leads to an oligomer of formula $[Mo(CO)_3(\mu\text{-}PPhpy_2)]_n$, (**4**), which is also obtained after heating $Mo(CO)_6$ in solution with equimolar amounts of $PPhpy_2$. The oligomer undergoes oxidative addition by iodine or allylbromide to give $MoI_2(CO)_3(py_2PhP\text{-}N,N')$, (**5**), or $MoBr(\eta^3\text{-}CH_2CHCH_2)(CO)_2(py_2PhP\text{-}N,N')$, (**6**), respectively. These complexes are also obtained by addition of equimolar amounts of $PPhpy_2$ to solutions of $MoI_2(CO)_3(NCMe)_2$, or $MoBr(\eta^3\text{-}CH_2CHCH_2)(CO)_2(NCMe)_2$, respectively.

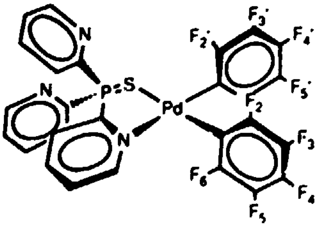
The results nicely agree with the HSAB principle, as soft molybdenum(0) centers show preference for *P*-coordination, whereas hard molybdenum(II) centers stabilize *N,N'*-chelating coordination of the pyridyl moieties.

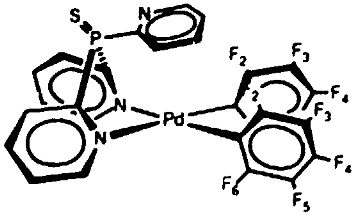
LAICM2151P 83, Mon. 13

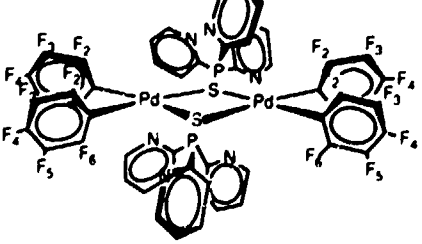
DYNAMIC BEHAVIOUR IN PALLADIUM COMPLEXES WITH PHENYLBIS(2-PYRIDYL)PHOSPHINESULPHIDE AND TRIS(2-PYRIDYL)PHOSPHINESULPHIDE.

Juan A. Casares, and **Pablo Espinet.** *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid. E-47005 Valladolid (Spain).*

The pentafluorophenyl group has been extensively used in organometallic chemistry because of the kinetic and thermodynamic stability of their complexes. Whenever dynamic processes in solution are present, the C_6F_5 group can be used as an easily observable "reporter ligand" for the study of the dynamic behaviour. We describe here the behaviour of $[Pd(C_6F_5)_2(Phpy_2P{=}S)]$ (1) and $[Pd(C_6F_5)_2(py_3P{=}S)]$ (2). ^{19}F COSY and ^{31}P NMR studies allow to identify the three (N,S)-, (N,N)-, and (μ-S)-bonded coordination isomers (figures), whose equilibrium ratios depend markedly on the temperature and the solvent. The bimolecular exchange between (N,S)- and (μ-S)-isomers is very fast, whereas the exchange between (N,S)- and (N,N)-isomers is comparatively slow. In addition, complex (2) shows exchange of coordinate and uncoordinate pyridines.







LAICM2152P **84, Mon. 13**

SYNTHESIS AND CRYSTAL STRUCTURE OF DICHLORODIPHENYLBIS(PYRAZOLE)TIN(IV)

F.J. García Barros[a], E.E. Castellano[b], J. Zukerman-Schpector[c], A. Sánchez González[d], J.S. Casas[d] and J. Sordo[d]

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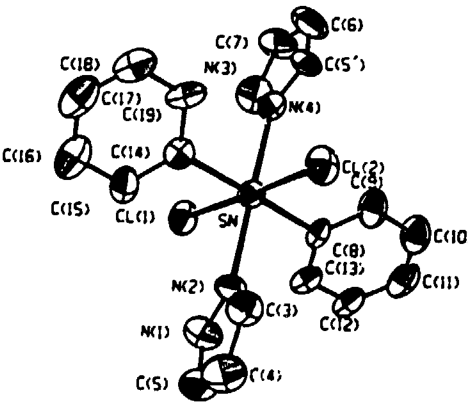
Following our studies of the coordination chemistry of the azole ligands with diorganotin(IV) dihalides[1] we have synthesized the title compound by reacting dichlorodiphenyltin(IV) with pyrazole (HPz) in dichloromethane.

The structure of dichlorodiphenylbis(pyrazole)tin(IV) was determined by X-ray diffraction. The crystal consists of discrete [$SnPh_2Cl_2(HPz)_2$] units with the metal coordinated to two Cl atoms [Sn-Cl(1) = 2.526(2), Sn-Cl(2) = 2.536(2) Å], two phenyl groups [Sn-C(8) = 2.146(7), Sn-C(14) = 2.140(8) Å] and two pyrazole rings [Sn-N(2) = 2.315(6), Sn-N(4) = 2.341(6) Å] in an octaedral all-trans configuration. The phenyl and pyrazole rings are essentially planar and, as in other pyrazole complexes of diorganotin(IV) dihalides[1] the N-H group and Cl atoms are implied in hydrogen bonds.

Crystal data: $C_{18}H_{18}Cl_2N_4Sn$
M = 479.97, Monoclinic, $P2_1/n$
a = 9.283(2) Å
b = 13.846(3) Å
c = 15.824(4) Å
β = 105°
U = 1955.6(6) $Å^3$
Z = 4, D_c = 1.63 $g{\cdot}cm^{-3}$
R = 0.044, R_w = 0.042



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[1] A. Sánchez González, J.S. Casas, J. Sordo and G. Valle, *J. Organomet. Chem.*, 1992, 435, 29 and references therein.

LAICM2153P **85, Mon. 13**

SYNTHESIS AND CRYSTAL STRUCTURE OF TRICHLOROPHENYLBIS(PYRAZOLE)TIN(IV)

F.J. García Barros[a], E.E. Castellano[b], J. Zukerman-Schpector[c], A. Sánchez González[d], J.S. Casas[d] and J. Sordo[d]

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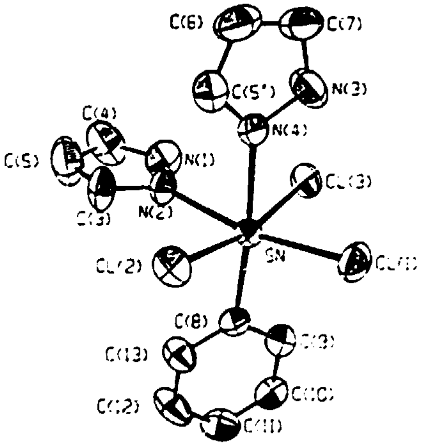
The title compound was obtained when we attempt the recrystallyzation of [$SnPh_2Cl_2(HPz)_2$] (HPz = Pyrazole) in chloroform.

The structure of trichlorophenylbis(pyrazole)tin(IV) was determined by X-ray diffraction. The crystal consists of discrete [$SnPhCl_3(HPz)_2$] units with the metal coordinated to three Cl atoms [Sn-Cl(1) = 2.423(2), Sn-Cl(2) = 2.461(2), Sn-Cl(3) = 2.453(2) Å], one phenyl group [Sn-C(8) = 2.150(7) Å] and two pyrazole ligands [Sn-N(2) = 2.284(6), Sn-N(4) = 2.224(6) Å] giving a distorted octahedral structure.



Crystal data: $C_{12}H_{13}Cl_3N_4Sn$; M = 438.31; Monoclinic, $P2_1/n$; a = 8.750(1), b = 13.152(1), c = 14.051(2) Å; ß = 97.72(1)°; Z = 4; U = 1602.3(6) $Å^3$; D_c = 1.82 $g{\cdot}cm^{-3}$; R = 0.032, R_w = 0.035.

LAICM2154P **86, Mon. 13**

SYNTHESIS AND CRYSTAL STRUCTURE OF DIBROMODIETHYLBIS[2(3H)-IMIDAZOLINETHIONE]TIN(IV)

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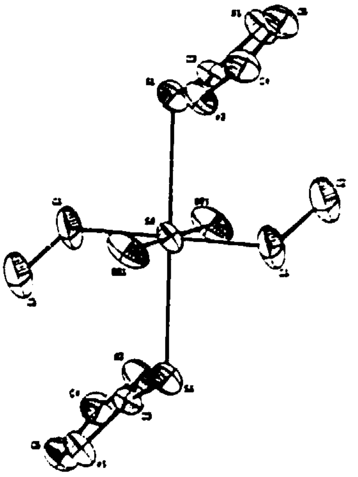
As part of our studies on the coordination of imidazole-derived ligands with diorganotin(IV) dihalides[1], the title compound was synthesized by reacting dibromodiethyltin(IV) with 2(3H)-imidazolinethione (Himt) in dichloromethane.

The structure of dibromodiethylbis[2(3H)-imidazolinethione]tin(IV) was determined by X-ray diffraction. The crystal consists of discrete $[SnEt_2Br_2(Himt)_2]$ units with the metal atom octahedrally coordinated to two Br atoms [Sn-Br(1) = 2.759(3) Å], two ethyl groups [Sn-C(1) = 2.158(7) Å] and two Himt ligands [Sn-S(1) = 2.772(2) Å] in an all-trans configuration with the Sn atom at a centre of symmetry.

Crystal data: $C_{10}H_{18}Br_2N_4S_2Sn$
M = 536.9, Triclinic, $P\bar{1}$
a = 8.641(1) Å
b = 7.236(1) Å
c = 7.337(1) Å
α = 107.0(1)°
β = 97.72(1)°
γ = 96.8(1)°
U = 437.7(3) $Å^3$
Z = 1, D_c = 2.05 $g \cdot cm^{-3}$
R = 0.041, R_w = 0.040



LAICM2156P **87, Mon. 13**

PROTODEMETALATION REACTIONS OF DIPHENYLTHALLIUM(III) COMPOUNDS WITH DICYCLOHEXYL DITHIOPHOSPHINIC ACID. II. CRYSTAL STRUCTURE OF TRIS(DICYCLOHEXYLDITHIOPHOSPHINATO)THALLIUM(III) CHLOROFORM SOLVATE.

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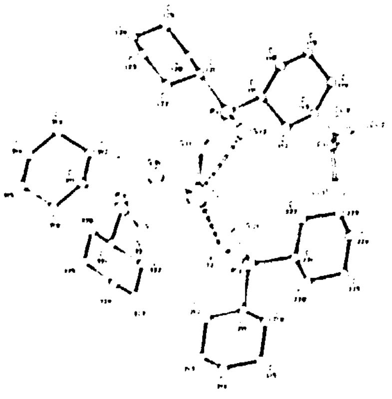
[a] *Departamento de Química Inorgánica, Universidade de Santiago de Compostela, Spain.*

The reaction of $[TlPh_2(S_2PCy_2)]$ with HS_2PCy_2 in $CDCl_3$ was monitored using ^1H and ^{205}Tl NMR spectroscopy. When the complex:acid mole ratio is ≤ 1:1 the monophenylthallium(III) dithiophosphinate forms. Mole ratios ≥ 1:1.5 lead to the cleavage of the two Tl-C bonds according to the equation:

$$[TlPh_2(S_2PCy_2)] + 2HS_2PCy_2 \dashrightarrow 2HPh + [Tl(S_2PCy_2)_3]$$

giving the thallium(III) derivative. The structure of this compound was solved by X-ray diffraction. Crystal data: $a = 15.539(1)$Å, $b = 16.23(3)$Å, $c = 10.556(1)$, $\alpha = 103.13(1)°$, $\beta = 91.71°$, $\gamma = 111.56°$, $V = 2392.2(4)$Å^3 and $R = 0.052$.



As is shown in the Figure, $[Tl(S_2PCy_2)_3]$ crystallizes as a chloroform solvate. Thallium is coordinated to the sulphur atoms of an isobidentate [Tl-S(31) = 2.667(3) and Tl-S(32) = 2.658(3) Å] and two anisobidentate [Tl-S(11) = 2.471(2), Tl-S(21) = 3.217(2), Tl-S(21) = 2.475(2) and Tl-S(22) = 3.107(3) Å] ligands.

LAICM2157P 88, Mon. 13

DIPHENYL(DICYCLOHEXYLDITHIOPHOSPHINATO) THALLIUM(III): SYNTHESIS, CRYSTAL STRUCTURE AND SPECTRAL BEHAVIOUR.

J.S. Casas[a], E.E. Castellano[b], A. Sánchez[a], J. Sordo[a], E.M. Vázquez-López[a] and J. Zukerman-Schpector[b].

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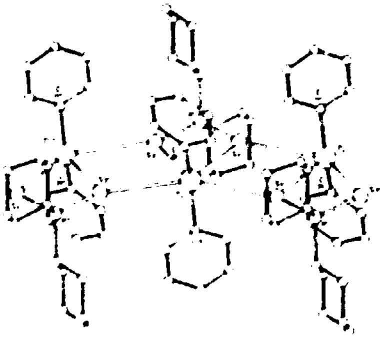
[b] *Instituto de Fisica e Quimica de São Carlos, Universidade de São Paulo, São Carlos, SP Brasil.*

The title compound was synthesized by reacting $TlPh_2Br$ with $[Et_4N][S_2PCy_2]$ in chloroform; monocrystals suitable for X-ray measurements were obtained as one of the several products formed when HS_2PCy_2 and $TlPh_2OH$ interact in $CDCl_3$. *Crystal data*: $C_{24}H_{32}PS_2Tl$, M= 619.99, triclinic, space group P1, a= 10.141(1)Å, b= 10.315(2)Å,c= 11.913(2)Å, α= 94.46(1)°, β= 101.45(1)°, γ= 91.01(1)°, V= 1219.9(6)Å^3 and R= 0.050.



The thallium atom is coordinated (see Fig.) to the carbon atom of the phenyl groups and to the sulphur atoms of a slightly anisobidentate dithiophosphinate ligand. Two weak additional Tl...S intermolecular interactions form molecular chains along the b axis.

The spectral properties of the complex (IR, Raman, and ^1H, ^{13}C and ^{205}Tl NMR spectra) are discussed in the light of this structural information.

LAICM2158P **89, Mon. 13**

PROTODEMETALATION REACTIONS OF DIPHENYLTHALLIUM(III) COMPOUNDS WITH DICYCLOHEXYL DITHIOPHOSPHINIC ACID. I. CRYSTAL STRUCTURE OF PHENYL [BIS(DICYCLOHEXYLDITHIOPHOSPHINATO)]THALLIUM(III).

J.S. Casas[a], E.E. Castellano[b], A. Sánchez[a], J. Sordo[a], E.M. Vázquez-López[a] and J. Zukerman-Schpector[b].

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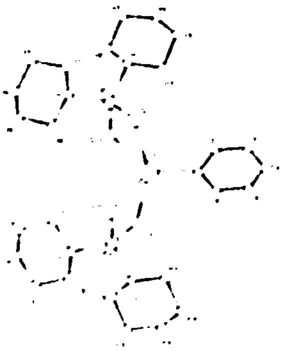
[b] *Instituto de Fisica e Quimica de São Carlos, Universidade de São Paulo, São Carlos, SP Brasil.*

The reaction of diphenylthallium(III) bromide with dicyclohexyldithiophosphinic acid carried out in DMF/$CHCl_3$ afforded the title compound together with diphenylthallium(III) and thallium(III) dithiophosphinates. The monophenylthallium(III) derivative, that arises from a protodemetalation reaction

$$TlPh_2Br + 2HS_2PCy_2 \dashrightarrow [TlPh(S_2PCy_2)_2] + HPh + HBr$$

was studied by X-ray diffraction. Crystal data: $C_{30}H_{49}P_2S_4Tl$, M= 804.30, triclinic, space group P1, a= 9.442(1)Å, b= 10.809(2)Å, c= 18.256(2)Å, α= 80.41(1)°, β= 86.95(1)°, γ= 72.52(1)°, V= 1752.3(5)Å^3 and R= 0.049.

The crystal structure of the complex is shown in the Figure. The thallium atom is bound to the phenyl group and to the sulphur atoms of the anisobidentate dithiophosphinate ligands [Tl C(1)= 2.13(2), Tl-S(11)= 2.879(3), Tl-S(12)= 2.547(4), Tl-S(21)= 2.547(4) and Tl-S(22) = 2.863(3) Å].



LAICM2173P **90, Mon. 13**

TITANIUM μ_3-ALKYLIDYNES

Román Andrés, Mijail Galajov and Miguel Mena.
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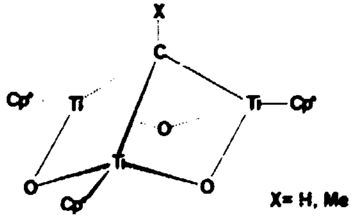
OrganoMetallic Oxides (OMO) are of a considerable interest as hydrocarbon-soluble models for metal oxide surfaces and help to provide a basic understanding of catalyst-to-support interactions in heterogeneous catalytic processes.[1]

We have previously described a variety of titanium cluster oxides with the highly solubilizing pentamethylcyclopentadienyl (η^5-C_5Me_5=Cp*) ligand, including $(Cp^*TiX)_3(\mu\text{-}O)_3$ (X=Cl, Br, I, Me) and $(Cp^*Ti)_4(\mu\text{-}O)_6$,[2] and have found that $(Cp^*TiCl)_3(\mu\text{-}O)_3$ is a versatile starting material for the preparation of many interesting complexes containing the "Cp*TiO" moiety.

We are investigating the reactivity and stability of these electron-deficient metal centers connected by oxo groups and will report the mechanism of formation of Ti_3O_3 clusters, $(Cp^*TiO)_3(\mu_3\text{-}CX)$ (X= H, Me), by thermolysis of $(Cp^*TiR)_3(\mu\text{-}O)_3$ (R= Me, Et). We propose that CX groups are capping the triangle containing the three titanium atoms



We thank DGICYT(PB90-0294) and Universidad de Alcalá de Henares for support.

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[1] Bottomley, F., *Polyhedron*, **1992**, *11*, 1707. Pope, M.T.; Müller, A., *Angew. Chem. Int. Ed. Engl.*, **1991**, *30*, 34. Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

[2] Gómez-Sal, M.P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147.

LAICM2174P **91, Mon. 13**

CARBONYL INSERTIONS INTO METAL-NITROGEN BONDS OF GROUP 4 DIALKYLAMIDO COMPLEXES.

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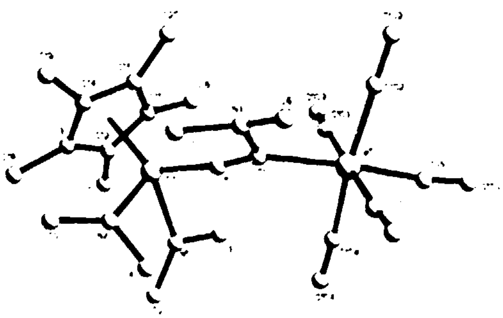
Paul R. Raithby
University Chemical Laboratory, University of Cambridge ENGLAND

The reactivity of the metal-nitrogen bond occupies a central place in the chemistry of amido derivatives of the early transition metals. These compounds have been shown to undergo insertion reactions with molecules containing polar multiple bonds.[1]

We have found that dialkylamides $MCp^*(NMe_2)_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M= Ti, Zr) are unreactive toward carbon monoxide at room temperature, while react at 30-35°C with metal carbonyl complexes $L_nM'(CO)$ [$L_nM' = Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$ and $Fe(CO)_4$], without CO evolution, to give oxicarbene compounds of the general formula $Cp^*(NMe_2)_2M(OCNMe_2)M'L_n$. At 80°C, in the case of M= Ti and $L_nM' = Fe(CO)_5$ we can obtain the new heterodimetallacyclic product $Cp^*(NMe_2)Ti(OCNMe_2)_2Fe(CO)_3$.

All compounds have been characterized by elemental microanalysis, mass spectrometry, IR, ^1H-, ^{13}C-NMR spectroscopy. The structure of the complex $Cp^*(NMe_2)_2Ti(OCNMe_2)W(CO)_5$ was established by single-crystal X-ray diffraction.



We thank C.A.M. (C198/91) and Universidad de Alcalá de Henares for support.

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[1] Lappert, M.F.; Power, P.P ; Sanger, A.R.; Srivastava, R.C., *Metal and Metalloid Amides: Syntheses, Structures, and Physical and Chemical Properties*, Ellis Horwood Publ. 1980.

LAICM2180P **92, Mon. 13**

REACTIVITY OF TERTIARY SILANES AND STANNANES WITH AN EDGE-BRIDGED TRIRUTHENIUM CARBONYL CLUSTER COMPLEX

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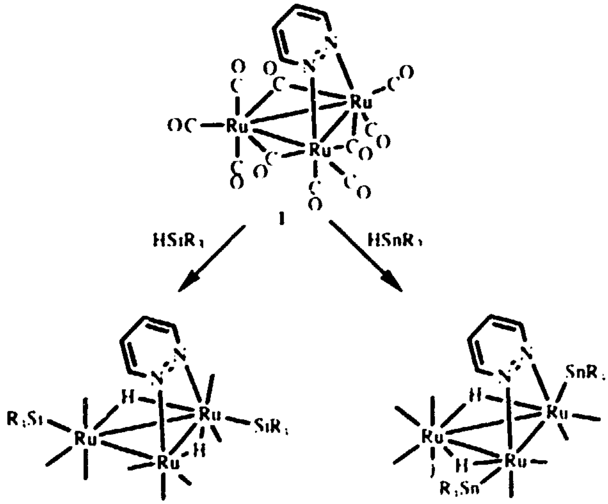
The edge-bridged cluster complex $[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}CO)_3(CO)_7]$ (**1**) ($C_4H_4N_2$ = pyridazine) reacts with tertiary silanes and stannanes to give the trinuclear derivatives $[Ru_3(\mu\text{-}H)_2(ER_3)_2(\mu\text{-}C_4H_4N_2)(CO)_8]$ (ER_3 = $SiEt_3$, $SiPh_3$, $Si(OMe)_3$, $SnBu_3$, $SnPh_3$). Their spectroscopic data indicate that the silyl derivatives are asymmetric (C_1), whereas the stannyl derivatives are symmetric (C_S). The structure of the compound with ER_3 = $SiEt_3$ has been stablished by an X-ray diffraction study.



LAICM218SP **93, Mon. 13**

DIFFERENT COORDINATION MODES OF DMIT LIGAND IN GOLD(I) CHEMISTRY

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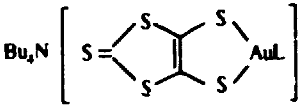
[c]Institut für Anorganische und Analytische Chemie der Technischen Universitat, Hagenring 30, 3300 Braunschweig, Germany.

Materials containing transition metal complexes of dmit (4,5-dimercapto-1,3-dithiole-2-thione) have been extensively studied as possible candidates for high conductivity in the solid state. Despite of the work done in this area, the usual coordination mode of dmit is as bidentate ligand in homoleptic square-planar complexes (e.g. $Q_n[M(dmit)_2]$) but nowdays results point out to better conducting materials when asymmetrical molecules are used.

With a good selection and/or with different ratio of the precursors, $dmit^{2-}$ and gold(I) complexes, mono, di or tri-nuclear gold(I) derivatives (1-4) can be prepared with the dmit ligand acting either as bidentate or as μ^2 and μ^3 bridging ligand.



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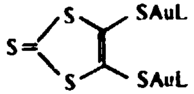

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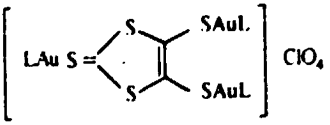

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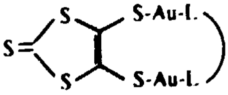

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The reaction of some of this complexes with TCNQ or $(TTF)_3(BF_4)_2$ and the X-ray structures of these complexes: $[dmit(AuPPh_3)_2]$, $Bu_4N[dmit(AuPPh_3)]$, $[dmit(AuPPh_3)_3]ClO_4$ and $Bu_4N[(dmit)Au_2\{CH_2PPh_2CH_2\}]$ will be described.

LAICM2186P **94, Mon. 13**

TRIGONAL AND TETRAHEDRAL SILVER(I) COMPLEXES WITH DIFFERENT BIDENTATE OR TRIDENTATE PHOSPHINE LIGANDS.

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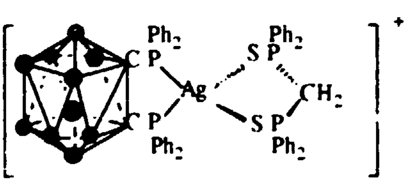
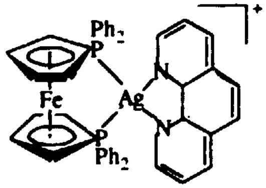
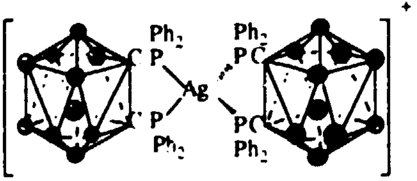
The reaction of $AgCF_3SO_3$ or $AgClO_4$ with the diphosphines $Fe(C_5H_4PPh_2)_2$ or $B_{10}H_{10}C_2(PPh_2)_2$ gives the three coordinated $[AgX(P_2)]$ (X= CF_3SO_3, ClO_4), while with the triphosphine $(Ph_2P)_3PCH$ affords the tetra coordinated $[AgX(P_3)]$.

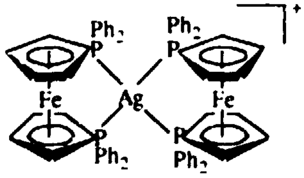
In these complexes the triflate or the perchlorate ligand is weakly bonded to silver and thus can be displaced by other monodentate or bidentate ligands leading the trigonal planar or the tetrahedral silver(I) derivatives, respectively.





Homoleptic diphosphine complexes can be prepared by direct reaction of two equivalent of the corresponding ligand and $AgClO_4$.





The complexes have been studied by low temperature NMR spectroscopy, FAB Mass spectrometry and X-ray analysis on compounds $[B_{10}H_{10}C_2(PPh_2)_2Ag(SPPh_2)_2CH_2]ClO_4$, $[Ag\{(PPh_2C_5H_4)_2Fe\}_2]ClO_4$ and $[Fe(C_5H_4Ph_2P)_2Ag(phen)]ClO_4$.

LAICM2187P **95, Mon. 13**

DINUCLEAR ASYMMETRICAL BRIDGED GOLD(I) AND GOLD(II) COMPLEXES

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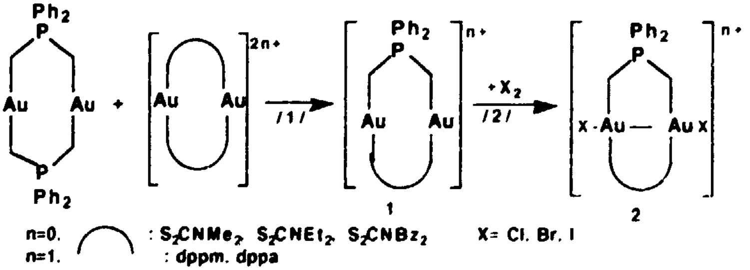
[b]Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig (Germany)

In recent years, extensive studies have been carried out on dinuclear gold complexes. Special attention has been focused on the formation and stability of gold(II) derivatives.

We described (eqn. 1) a general procedure for the synthesis of dinuclear derivatives with two different bridges.



It is well established that metal-metal bonded Au(II) complexes bridged by two ylide anion ligands are very stable. On the contrary gold(II) complexes with sulfur ligands as dialkyldithiocarbamates or dithiophosphinates are only stables at low temperature (-78°C), and disproportion into $[Au^{III}(S\text{-}S)_2][Au^{I}X_2]$ takes place at higher temperature. It is noteworthy that asymmetrical bridged complexes of type 1, even when L-L is a disulfur ligand, give stable gold(II) derivatives when oxidative addition reactions are carried out (eqn 2).

The X-ray structures of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(S_2CNEt_2)]$ (type 1) and $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(S_2CNBz_2)Br_2]$ (type 2) confirm the dioctauracycle of gold(I) and gold(II) nature.

LAICM2195P 96. Mon. 13

ORTHO METALATION REACTIONS IN DIRHODIUM(II) COMPOUNDS. FURTHER EVIDENCE OF AN EQUILIBRIUM PROCESS INVOLVING METALATION-DEMETALATION REACTIONS OF A $P(o\text{-}ClC_6H_4)Ph_2$ LIGAND.

A PRELIMINARY KINETIC STUDY.

A. Garcia-Bernabé[a], P. Lahuerta[a], E. Peris[a], M.A. Ubeda[a], S. Garcia-Granda[b], P. Pertierra[b], M. Martinez[c], G. Gonzalez[c]

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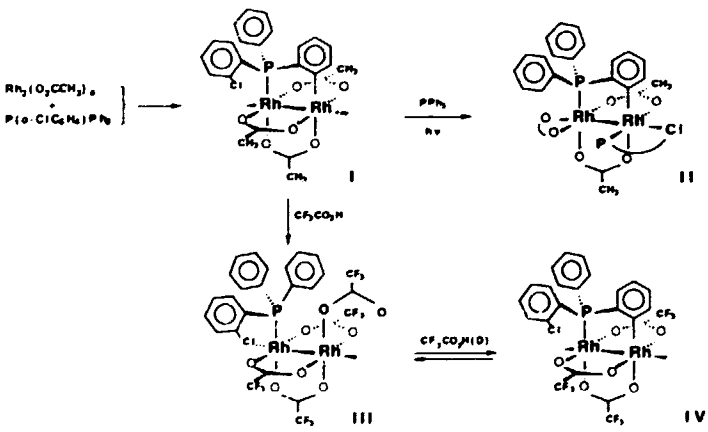
[c] Dpto. Quimica Inorgánica, Divisió de Ciencias Experimentals i Matemàtiques, Diagonal 647, E-08028 Barcelona, Spain.

In the course of our investigation of ortho metalation reactions in dirhodium(II) compounds we have found that $Rh_2(O_2CCH_3)_4$ and $P(o\text{-}ClC_6H_4)Ph_2$ show an interesting reactivity with reversible metalation-demetalation processes. Scheme 1 summarizes the observed reactivity.

Scheme 1



Compounds III and IV are in a reversible equilibrium. Preliminary kinetic studies on this reaction have been carried out. The following reaction sheme and derived rate law are proposed:

$$\mathrm{IV} + CF_3CO_2H_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{III.H}^+ \overset{Ka}{\rightleftharpoons} \mathrm{III} + H^+$$

$k_{obs} = [k_1 + k_2/(Ka + [H^+])]\,[H^+]$ where $[H^+]$ represents any solvated proton presents in solution. For reactions performed at 313K in chloroform solutions, the same rate constants were observed for the metalation and demetalation processes, in good agreement with the proposed reaction scheme.

For values of the concentration of added acid (CF_3CO_2H) between 0.1 and 6.0 M the observed rate constants are in the 1-10 $\times 10^{-4}$ s^{-1} range. When deuterated acid was

LAICM2201P **97, Mon. 13**

THE SYNTHESIS AND REACTIVITY OF THE BINUCLEAR RUTHENIUM COMPLEX $[Ru_2(\mu - PPh_2)(\mu - OH)_2(p - cymene)] PF_6$ WITH VARIOUS POTENTIAL PROTON DONORS

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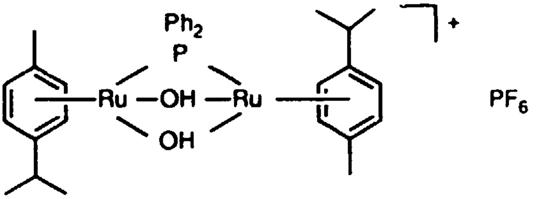
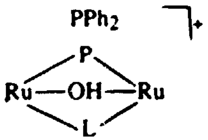
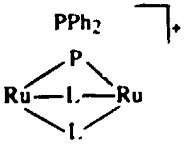
33071 Oviedo, Spain

The reaction of the binuclear ruthenium hydroxo complex $[Ru_2(\mu\text{-}OH)_3(p\text{-cymene})]PF_6$ with PPh_2H affords the bridged diphenylphosphine complex $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(p\text{-cymene})]PF_6$.



The reaction of the latter complex with carboxylic acids, alcohols, thiophenols and amines results in the protonation of one or both hydroxo groups to form aqua intermediates and the consequent replacement of the water by the respective conjugate bases to form either the monosubstituted or the disubstituted complexes respectively.





L = conjugate base
(Note that the p-cymene molecule has been omitted for clarity)

LAICM2202P **98, Mon. 13**

HYDROFORMYLATION OF N-ALLYL SUBSTRATES BY RHODIUM CATALYSTS.

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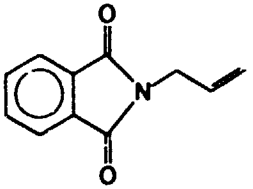
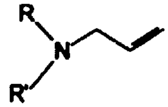
Bellaterra, 08193 Barcelona, Spain

We have previuosly reported on the rhodium catalyzed hydroformylation of allyl and vinyl cyclic ethers (*Organometallics*, 1992, *11*, 3525). We have established the crucial influence of the size of the phosphorous co-catalyst in the regioselective control of the reaction.

We report here the results on the hydroformylation of N-allylic substrates. This reaction could provide a ready entry to α-aminoacids.

Three different types of substrates have been explored in order to analyze the influence of the basicity of the substrate, as well as their steric hindrance:





The substrates are readily hydroformylated in mild conditions in the presence of rhodium-phosphorus complexes. Two different catalytic systems have been used. $RhH(CO)(PPh_3)_3$ produces mixtures of the β and γ aldehydes, while the catalytic system prepared from $[Rh_2(\mu\text{-OMe})_2(ccd)_2]$ (cod= 1,5-cyclooctadiene) plus $P(OPh^*)_3$ (Ph^*= *o-tert*-butylphenyl) behaves as a extremely regioselective catalyst. The influence of pressure, temperature, the nature of the phosphorous co-catalyst and the phosphorous ligand/rhodium molar ratio on the regioselectivity will be discussed.

ENANTIOSELECTIVE HYDROFORMYLATION CATALYSTS WITH CHIRAL THIOLATO RHODIUM COMPLEXES

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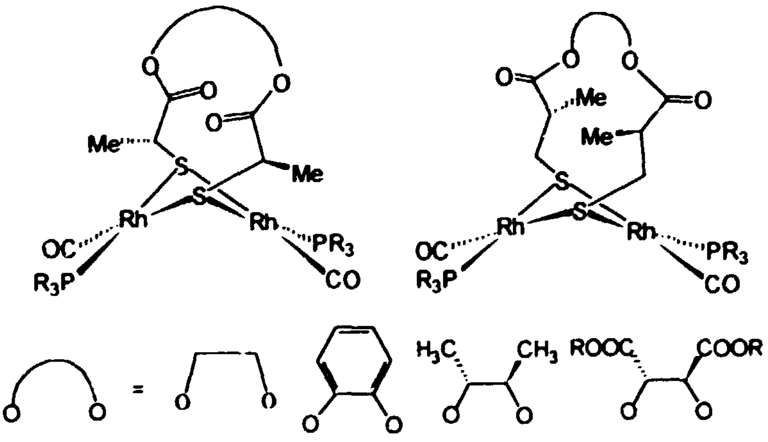
Bellaterra, 08193 Barcelona, Spain

Dinuclear rhodium thiolato complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ behave as very active catalysts in the hydroformylation of olefins in mild conditions. An advantage of these type of catalysts is the possibility of introducing changes in the thiolato bridge in order to prepare enantioselective systems.
We have prepared a series of dithiolato ligands from chiral precursors lactic acid and (R)-S-acetylmertcaptoisobutyric acid plus different diols:



The catalysts has been tested in the hydroformylation of styrene. The results indicated that the regio and enantioselectivity depens on the number of atoms of the metalomacrocycle. Also low pressures and temperatures are required to obtain high selectivities in the branched aldehyde (*ca.* 90%). Enantioselectivities up to 50% have been already achieved.

LAICM2204P **100, Mon. 13**

REACTIONS OF β-KETOSULPHOXIDES WITH $Pd(OAc)_2$

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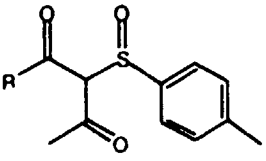
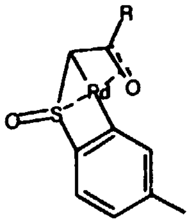
Reactions of ethyl- and phenyl-*p*-tolyl-β-ketosulphoxide with $Pd(AcO)_2$ in AcOH yield a mixture of compounds **1** and **2**.

The compound **1** results from the acetolysis of the β-ketosulphoxide's enolic form. The formation of this organic compound never take place between acetic acid and β-ketosulphoxide if $Pd(AcO)_2$ is not present.

The mycroanalitical data of compound **2** shows a 1:1 metal-ligand ratio. ^1H-NMR, ^{13}C-NMR and IR spectroscopy show that they are cyclometallated compounds and that there is an interaction between the metallic center and the sulphoxide, carbonylic and methylen groups.

This situation seems to be similar to the complexes with phenacylsulphoxide recently described.[1,2]





R = CH_2CH_3 and C_6H_5

1 **2**

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1. K.W. Chiu, J. Fawcett, W. Henderson, R.D.W. Kemmitt, D.R. Russell *J. Chem. Soc., Dalton Trans.* **1987**, 733.
2. W. Henderson, R.D.W. Kemmitt, L.J.S. Prouse, D. Russell *J. Chem. Soc., Dalton Trans.* **1990**, 781.

SYNTHESIS, CHARACTERIZATION, AND SOME CATALYTIC APPLICATIONS OF WATER SOLUBLE RUTHENIUM AND OSMIUM COMPLEXES

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The use of water soluble metal complexes in catalysis is a field of growing interest. A number of ruthenium complexes containing mono- and tri-sulphonated triphenylphosphine (TPPMS and TPPTS, respectively) are known, and some catalytic applications have been reported.

We have prepared a series of ruthenium and osmium TPPMS complexes, namely $MCl_2(TPPMS)_2$, $[MHCl(TPPMS)_2]_2$, and $MHCl(CO)(TPPMS)_3$ ($M = Ru, Os$), characterized them by ^{31}P NMR spectroscopy, and explored their catalytic properties in the biphasic hydrogenation reactions in comparison with their PPh_3 analogues in homogeneous systems.

Cinnamaldehyde can be hydrogenated under moderate reaction conditions to various proportions of cinnamic alcohol or 3-phenylpropanal depending on the catalyst and on the reaction conditions. The best selectivities for C=O vs. C=C reduction were obtained for the water soluble complexes containing the sulphonated ligand, and particularly for the osmium derivatives.

Quinoline was also cleanly reduced to 1,2,3,4-tetrahydroquinoline both in homogeneous and in biphasic conditions. The mechanism of this reaction in water using $RuCl_2(TPPMS)_2$ as the catalyst precursor was investigated in more detail, which allowed us to propose a catalytic cycle.

LAICM2213P **52, Tue. 14**

NEW 3,4,5-TRIMETHOXY,2,6-DINITROPHENYL PALLADIUM(II) COMPLEXES

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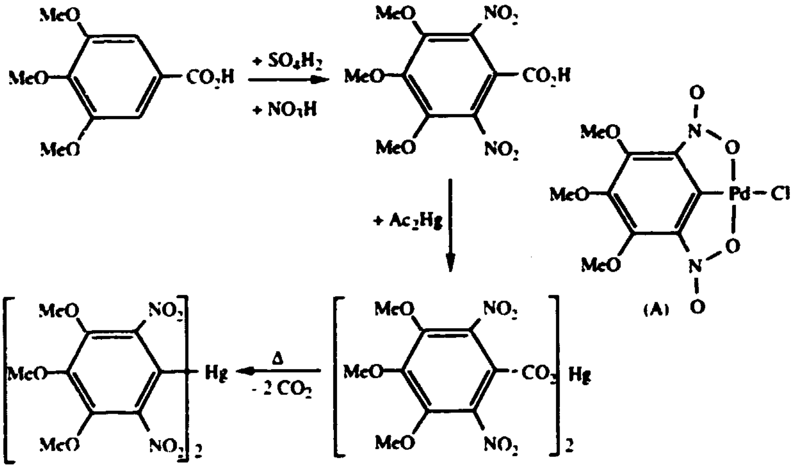
Grupo de Química Organometálica. Departamento de Química Inorgánica.
Universidad de Murcia. Apdo. de Correos 4021, Murcia 30071, Spain.

We have prepared HgR_2 [R= $C_6(MeO)$-3,4,5, NO_2-2,6] according to the following scheme:



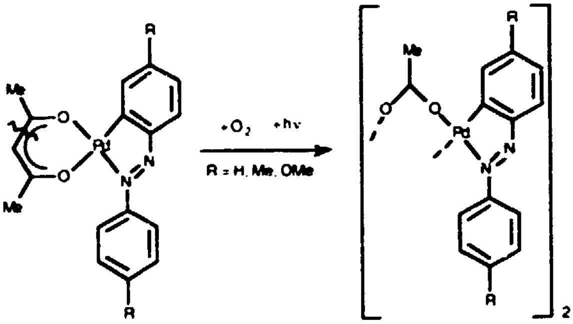
By reacting HgR_2 with $[PPh_3(CH_2Ph)]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (2:1) in refluxing acetone, the complex trans- $[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]$ crystallizes in high yield. The other reaction product, HgRCl can be isolated from the mother liquor. The dinuclear arylpalladium complex reacts with Tl(acac) giving the compound $[PPh_3(CH_2Ph)][PdClR(acac)]$ which reacts with HBF_4 yielding [PdClR] which must have two coordinated nitro group [see (A)]. [PdClR] was also obtained by reaction of trans- $[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]$ with $AgClO_4$ (1:1). The reaction of [PdClR] with PPh_3 or Py (1:2) gives trans-$[PdClRL_2]$ (L= PPh_3, Py).

LAICM2215P **53, Tue. 14**

VISIBLE LIGHT INDUCED AIR OXYGENATION OF ACETYLACETONATE LIGAND IN CYCLOPALLADATED COMPLEXES TO GIVE C-C BOND CLEAVAGE PRODUCTS

José Vicente, Aurelia Arcas, Delia Bautista and Georgiy B. Shul'pin.
Grupo de Química Organometálica. Departamento de Química Inorgánica. Universidad de Murcia. Apdo. de Correos 4021. Murcia 30071. Spain.

Investigation of oxygenations of organic compounds *via* photoinduced electron transfer is important both for synthetic chemistry and for understanding some biological processes (e.g. photooxidation of biological matter in the tissue). Such processes may occur in the presence of metal complexes and usually are induced with light of UV region. We have found a system in which a chemical reaction is stimulated by visible light (λ = 500 nm). Thus when an acetone solution of **1** (3.10^{-4}) is irradiated in air at 18°C with such light product **2** is formed with yield *ca.* 90% after 30 min.



1 2

It should be emphasize that $Pd(acac)_2$ is photoinactive even if irradiated with light of λ = 300 nm. In contrast, complex **1** combines within its molecule a chromophoric fragment (the azophenyl group acting as an "antenna" that absorbs energy of long-wavelength light), the reaction centre (metal ion which on excitation withdraws electron from substrate), and the substrate (acetylacetonate which after oxidation with excited Pd ion can add O_2 molecule to produce peroxide), and so **1** is able to be oxidized *via* a photoinduced electron transfer-peroxidation mechanism.

LAICM2216P **54, Tue. 14**

INSERTION OF CARBON DISULPHIDE IN AN Fe-H BOND. SYNTHESIS OF THE η^2-DITHIOFORMATE COMPLEX $[Fe(\eta^2\text{-}S_2CH)(dppe)_2][BF_4]$

Luísa M.D. Ribeiro, João J.R. Fraústo da Silva and
Armando J.L. Pombeiro

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,
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The lability of the chloride ligand at trans-$[FeHCl(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) was previously demonstrated and, in particular, the series of the hydride-isocyanide compounds trans-$[FeH(CNR)(dppe)_2]A$ (A=Cl or BF_4) was prepared [1] by reaction of that complex with the appropriate isocyanide in the presence of $Tl[BF_4]$.

We now report that the hydride ligand can be a reactive moiety towards a suitable acceptor substrate and the η^2-dithioformate complex $[Fe(\eta^2\text{-}S_2CH)(dppe)_2]BF_4]$ has been prepared by insertion of carbon disulphide in the Fe-H bond, according to reaction (1).

$$[FeHCl(dppe)_2] + CS_2 + Tl[BF_4] \rightarrow [Fe(\eta^2\text{-}S_2CH)(dppe)_2][BF_4] + TlCl \quad (1)$$

No evidence for the formation of the corresponding η^3- or η^1-isomers was obtained.

The ^{13}C, ^1H and ^{31}P NMR and electrochemical properties of the η^2-dithioformate complex are presented, as well as its reactivity towards base.

Reference

[1] - M.B. Baptista, M.A.N.D.A. Lemos, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Organometal. Chem., 1992, 424, 49.

Acknowledgements

This work has been supported by JNICT.

LAICM2219P **55, Tue. 14**

REACTIONS OF PHENYLDIAZENIDE COMPLEXES OF RHENIUM WITH ISOCYANIDES

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Jonathan R. Dilworth
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Organodiazenides are versatile ligands in coordination chemistry, but their reactions with isocyanides have not yet been explored.

In this work we have investigated the reactions of $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (1) with CNR (R = Me or C_6H_4Cl-4) and obtained a few mixed diazenide-isocyanide complexes, in particular $[ReBr_2(NNPh)(CNR)(PPh_3)_2]$ which, upon further reaction with CNR (for R = Me), leads to the bisisocyanide complexes $[ReBr(NNPh)(CNMe)_2(PPh_3)_2]Br$ and $[ReBr_2(NNPh)(CNMe)_2(PPh_3)]$.

Complex (1) also reacts with CO to give the dicarbonyl compound $[ReBr(NNPh)(CO)_2(PPh_3)_2]Br$.

These reactions appear to proceed *via* the formation of the paramagnetic complex $[ReBr_3(NNPh)(PPh_3)_2]$ which we have previously obtained and whose molecular structure has been authenticated by an X-ray analysis. The relevant spectroscopic properties of these complexes are also indicated.

Acknowledgements

This work has been partially supported by JNICT.

LAICM2227P 56, Tue. 14

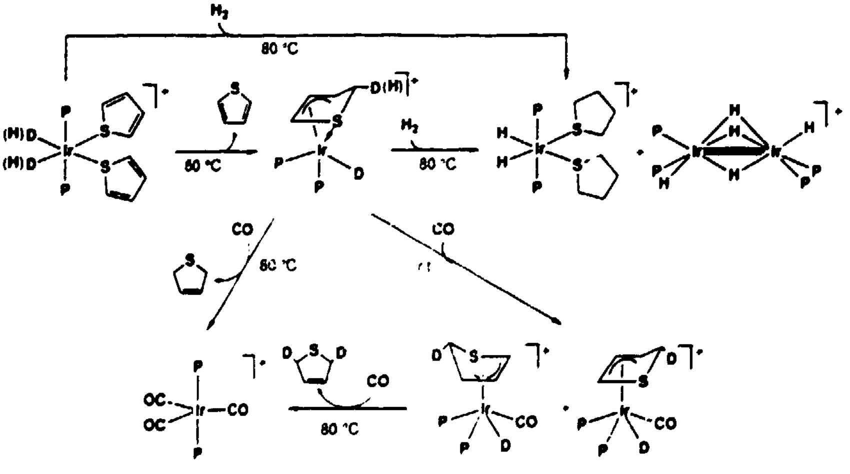
HOMOGENEOUS HYDROGENATION OF THIPHENE AND BENZOTHIOPHENE AT IRIDIUM

Claudio Bianchini, Verónica Herrera, Andrea Meli, Maurizio Peruzzini, Roberto Sánchez-Delgado and Francesco Vizza

ISSECC, CNR Firenze, Italy and IVIC, Caracas, Venezuela.

The interaction of thiophenes with transition metals continues to attract considerable interest as model chemistry for the hydrodesulfurization (HDS) reaction, which is one of the largest volume applications of transition metal catalysis.

In this communication, we report that the new complexes $[IrH_2(\eta^1S\text{-}Th)_2(PPh_3)_2]PF_6$ (Th = thiophene, benzothiophene) react with H_2 (1 atm) at room temperature in chlorinated solvents converting to the corresponding derivatives $[IrH_2(\eta^1S\text{-}ThH)_2(PPh_3)_2]PF_6$ (ThH = tetrahydrothiophene; 2,3-dihydrobenzothiophene) *via* a stepwise mechanism. Synthetic, spectroscopic and deuterium labelling studies have been carried out which have allowed us to draw out a reliable mechanism for the hydrogenation reactions as illustrated in the Scheme for the conversion of thiophene to 2,5-dihydrothiophene and tetrahydrothiophene.



LAICM2231P **57, Tue. 14**

ALKOXYDE DERIVATIVES OF BARIUM AND STRONTIUM

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Dpto. Química Inorgánica-ICMSE. Sevilla (SPAIN)

Angeles Monge, Caridad Ruiz

Facultad de Ciencias-ICMM. Madrid (SPAIN)

Metallic barium and strontium are activated by gas NH_3, at room temperature. When NH_3 is bubbled through a suspension of Ba granules, in a solution of the alkoxydes 2,6-Bu^t_2-4-X-C_6H_2OH (X = H, Me, Bu^t) in THF, the evolution of H_2 on the surface of the metal and the dissolution of the granules is observed. After several hours of stirring, all the metal granules have been consumed and a solution is obtained from which white crystals can be obtained.

NMR data obtained for these compounds, at different temperatures, suggest they present a trimetallic structure containing barium atoms in low coordination environment, with terminal and bridging OAr groups, and a molecule of THF attached to a metallic centre. Unfortunately, the crystals loose crystallinity upon drying under vacuo, probably due to lost of solvent, what, together with the high sensitivity of the compounds, has prevented the determination of their X-ray structure.

Nevertheless, reaction with HMPA (hexamethylphosphoramide) leads to the formation of good quality crystalline materials. The structure of the derivative with X = Me has been determined by X-ray and is shown in Figure 1.

On a related field, derivatives containing polypyrazolylborate ligands have been obtained by reaction of anhydrous barium iodide with KTp'. The structure, determined by X-ray, of one of these derivatives, {[HB(3,5-$Me_2pz)_3$]Ba(HMPA)I} is shown in Figure 2.

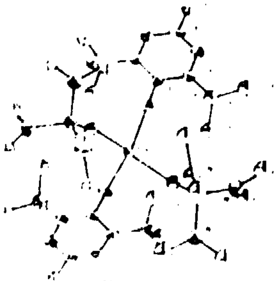

Figure 1

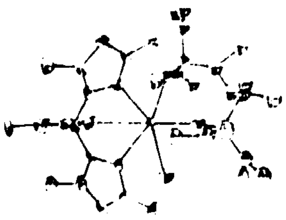

Figure 2

LAICM2233P **58, Tue. 14**

POLYPYRAZOLYL COMPLEXES OF IRIDIUM IN LOW OXIDATION STATE

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In this communication we will present some results obtained from our research in the chemistry of Ir complexes containing polypyrazolyl ligands. The bis-ethylene complex, $Tp^*Ir(C_2H_4)_2$, **1**, ($Tp^*=HB(3,5\text{-}Me_2\text{-}pz)_3$), has been found to be a very reactive molecule which readily undergoes inter- and intramolecular C-H activation processes. When complex **1** is heated at 60°C in benzene, a mixture of two compounds is obtained (*eq. 1*)

$$\underset{\mathbf{1}}{Tp^*Ir(C_2H_4)_2} \xrightarrow[\Delta]{C_6H_6} Tp^*Ir(C_6H_5)_2N_2 + [Tp^*Ir(C_6H_5)_2](\mu\text{-}N_2) \qquad (1)$$

One of them has been characterized by IR and NMR as the dinitrogen complex $Tp^*Ir(C_6H_5)_2N_2$. The other is a rather insoluble material that has been characterized by X-ray diffraction as the dimer $[Tp^*Ir(C_6H_5)_2]_2(\mu\text{-}N_2)$. The reaction of the dinitrogen derivative $Tp^*Ir(C_6H_5)_2N_2$ with donor ligands will also be presented. Reaction of complex **1** with phosphines leads to the formation of species of composition $Tp^*Ir(C_2H_4)(P)$, **2**, (P = PMe_3, PMe_2Ph, PEt_3, $^1/_2$dmpe) (*eq.2*).

$$\underset{\mathbf{1}}{Tp^*Ir(C_2H_4)_2} \xrightarrow{P} \underset{\mathbf{2}}{Tp^*Ir(C_2H_4)(P)} + C_2H_4 \qquad (2)$$

A trigonal bipyramidal structure has been found for these complexes from spectroscopic data and an X-ray diffraction study carried out on the PMe_2Ph derivative. Complexes **2** react with hydrogen in an oxidative addition process with formation of the Ir(III) species $Tp^*Ir(H)_2(P)$, **3**, (*eq.3*)

$$\underset{\mathbf{2}}{Tp^*Ir(C_2H_4)(P)} \xrightarrow{H_2} \underset{\mathbf{3}}{Tp^*Ir(H)_2(P)} \qquad (3)$$

Several related Tp (Tp = hydrotrispyrazolyl borate) complexes have also been prepared.

It was of interest to compare the effect of the isosteric but neutral trispyrazolyl methanes ($HC(pz)_3$) on the chemistry of these types of iridium complexes. To this end, the bis-ethylene derivative $HC(pz)_3Ir(C_2H_4)_2Cl$ was prepared. Reaction with H_2 in the presence of excess ethylene yielded the bis-ethyl complex $HC(pz)_3Ir(C_2H_4)(C_2H_5)_2Cl$

LAICM2234P 59, Tue. 14

BINUCLEAR NICKEL COMPLEXES BRIDGED BY PYRAZOLATE AND HYDROCARBON LIGANDS.

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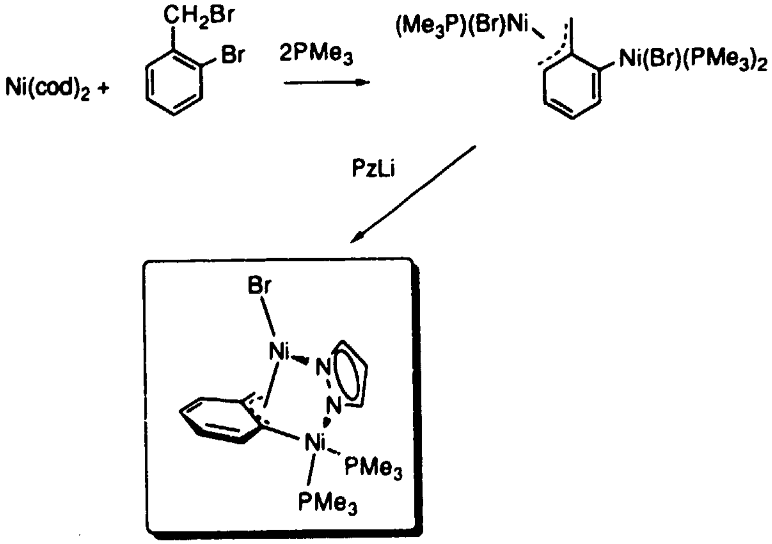
The synthesis and characterization of several binuclear Nickel complexes containing bridging hydrocarbon and pyrazolate ligands will be described. These compounds were prepared by double oxidative addition of the appropriate α,ω dibromides to Ni(0) followed by reaction with lithium or thallium pirazolate (Scheme).

The use of 3-methylpirazole leaded to a 2:1 mixture of both possible isomers. Some reactions of these compounds will be discussed.



LAICM2235P **60, Tue. 14**

ACTIVATION OF ORGANIC SUBSTRATES BY Tp*Ir-DERIVATIVES (TP* = $HB(3,5\text{-}Me_2pz)_3^-$)

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The activation of different unsaturated organic substrates by complexes containing the fragment Tp*Ir- is presented.

1.- Several complexes, containing diene ligands, have been synthesized. Treatment of the chloro-bridged dimer $[IrCl(coe)_2]_2$ (coe = cyclooctene) with the diene (represented by L_2 from now on), in the presence of KTp*, affords the expected complexes in high yields (eq 1).

$$[IrCl(coe)_2]_2 \xrightarrow[(\text{-KCl, -coe})]{1.\ L_2\ (\text{exc})\quad 2.\ \text{KTp*}} \text{Tp*Ir}L_2 \qquad (1)$$

(L_2 = butadiene, 2-Me-butadiene, 2,4-Me_2butadiene, 2,5-norbornadiene, 1,3-cyclohexadiene)

Some of these derivatives undergo unprecedented photochemical C-H activation reactions to form allyl-type species.

2.- The complex $Tp^*Ir(C_2H_4)_2$ reacts with net tiophene, at 50 °C, to form the Ir(III) species $Tp^*Ir(2\text{-}C_4H_3S)_2(SC_4H_4)$, **1**, in good yield. The S-bonded tiophene in **1** is easily displaced by donor ligands such as N_2, CO, PMe_3 and $CNBu^t$, to form the derivatives $Tp^*Ir(2\text{-}C_4H_3S)_2L$. Figure 1 shows the molecular structure, by X-ray, of the complex with L = CO.

Hydrogenation of **1** under pressure (3-4 atm), at 60 °C, produces $Tp^*Ir(H)_2(SC_4H_4)$, **2**, in almost quantitative yield, with concomitant formation of free tiophene.

Other reactions carried with 1 and 2 will be discussed.

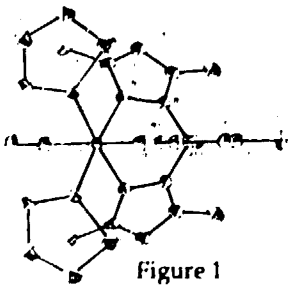

Figure 1

LAICM2238P **61, Tue. 14**

REACTIONS OF AN ANSA-BRIDGED η:σ-CYCLOPENTADIENYL IMIDO DERIVATIVE OF NIOBIUM WITH ALKYLATING AGENTS

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The reaction of $NbCl_5$ with the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ gives the ansa-bridged cyclopentadienyl imido derivative $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N]Cl_2\}$, **1**.[1] This compound is meant to be isoelectronic and isolobal with Cp_2ZrCl_2. In this communication we report some reactions of **1** with alkylating reagents.

Treatment of **1** with an excess of MeMgBr gives the binuclear compound $\{MeNb[\eta^5\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)(\mu\text{-}N){=}CH(CH_2)_2\text{-}\eta^5\text{-}C_5H_4]NbMe_2\}$, **2**. The crystal structure of **2** has been determined and shows that it contains only three methyl groups and a hydrogen has been lost from a CH_2 group adjacent to an imido nitrogen. Full ^1H and ^{13}C NMR characterization reveals that **2** is a fluxional molecule.

Reaction of **1** with 2 eqs of NaCp affords $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N](\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)\}$, **3**, which is a fluxional molecule at room temperature. Variable-temperature NMR studies indicate diverse dynamic processes including exchange between cyclopentadienyl rings.

The synthesis of $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N](CH_2C_6H_5)_2\}$, **4**, has been achieved by the reaction of **1** with 2 eqs of $C_6H_5CH_2MgCl$. In this compound at least one of the benzyl ligands is believed to coordinate in an η^2 fashion.

[1] D.M. Antonelli, M.L.H. Green, P. Mountford, *J. Organomet. Chem.*, **438**, C4 (1992).

LAICM2239P **62, Tue. 14**

Au-Au BONDING IN A PENTANUCLEAR GOLD COMPLEX CONTAINING A LINEAR Au_5 CHAIN

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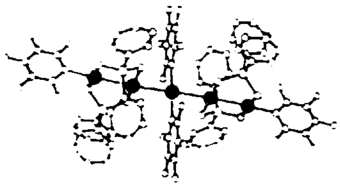
A polinuclear gold complex with a striking structure was recently described[1]. This molecule is a cationic complex with five gold atoms in a row containing a central unbridged metal atom, the two inner Au-Au lengths (2.755 Å) being longer than the outer ones (2.640 Å). The metallic frame of the molecule is formally a $(Au_5)^{9+}$ chain, though a more specific assignment of the oxidation state of each individual metal was not clear[1].



The electronic structure of this pentanuclear complex was studied by extended Hückel molecular orbital calculations, in order to understand the intermetallic bonding and assign oxidation states to the three independent gold atoms.

The calculations were made on an idealized model and the C_6H_5 and C_6F_5 groups replaced by hydrogen atoms. Based on this model and using a fragment decomposition analysis, we were able to study separately the two different Au-Au bonds, namely, the inner one between the central atom and the two external Au_2 units and the outer one between a central Au_3 fragment and the external gold atoms.

Our calculations reveal that the Au-Au bond strengths are a direct consequence of the particular coordination of each metal atom, specially the number of R groups. Therefore, the results show a weaker Au-Au interaction for the inner bond, reflecting the observed bond lengths. The different electron occupancies of the gold atoms indicate that the outer ones are electronically poorer, suggesting a succession of Au(III)-Au(I)-Au(I)-Au(I)-Au(III) formal oxidation states.

The gold-gold overlap populations were compared with others from related Au complexes. A clear dependence both on the oxidation state and on the geometry (bridged or unbridged) of the Au-Au bonds is observed.

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[1] R. Usón, A. Laguna, M. Laguna, J. Jiménez and P. G. Jones, *Angew. Chem. Int. Ed. Engl.*, **30**, (1991), 198

LAICM2240P **63, Tue. 14**

ANSA-BRIDGED η^5-CYCLOPENTADIENYL IMIDO AND AMIDO DERIVATIVES OF TITANIUM, ZIRCONIUM AND MOLYBDENUM

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An improved synthesis of the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ **1** is described. Its reaction with $TiCl_4$ gives $\{Ti[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ **2** which eliminates $SiMe_3Cl$ to give the ansa-bridged imido derivative $\{Ti[\eta^5\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)]Cl\}_2$, **3**. On the other hand, treatment of a solution of $ZrCl_4(SMe_2)_2$ with **1** gives $\{Zr[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$ **4** which, upon heating, dissociates the dimethylsulphide ligand to give $\{Zr[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl(\mu\text{-}Cl)\}_2$, **5**. The reaction of $MoCl_5$ with **1** in dichloromethane, followed by extraction in THF led to $\{Mo[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](C_4H_9O)Cl_3\}$ **6**. Treatment of this compound with trimethylphosphine causes the substitution of the THF ligand giving $\{Mo[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](PMe_3)Cl_3\}$ **7**.

LAICM2241P **64, Tue. 14**

CATALYTIC HYDROGENATION OF IMINES WITH $[Ir(\mu\text{-}OMe)(COD)]_2$ / $P(O^tBuPh)_3$. STUDY OF THE INVOLVED METALLIC SPECIES.

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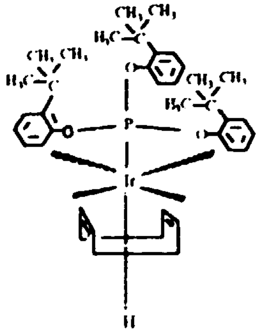
Whilst the hydrogenation of carbon-carbon double bonds is well understood and widely used, reduction of carbon-nitrogen double bonds has been less well studied. In this field has been encouraged recent work on hydrogenation of imines using rhodium and ruthenium complexes as catalysts, and occasionaly iridium[1] complexes.

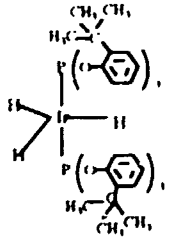
The complex $[Ir(\mu\text{-}OMe)(COD)]_2$ has been used as intermediate for synthetic purposes and as homogeneous catalyst precursor[2]. In this work the hydrogenation of imines is carried out in good yields using $[Ir(\mu\text{-}OMe)(COD)]_2$ with a bulky auxiliary ligand, $P(O^tBuPh)_3$[3].

$$\mathrm{PhHC{=}NPh} \xrightarrow[\mathrm{H_2\quad MeOH}]{[\mathrm{Ir}(\mu\text{-}\mathrm{OMe})(\mathrm{COD})]_2\ +\ \mathrm{P(O^tBuPh)_3}} \mathrm{PhH_2C{-}NHPh}$$

Furthermore, some hydride metal species, have been isolated before and at the end of the hydrogenation, which have been characterized by spectroscopic (NMR, FT-IR and X-Ray diffraction) and analytic techniques.



Before hydrogenation:



After hydrogenation:

LAICM2244P **65, Tue. 14**

MONONUCLEAR PENTACHLOROPHENYL COMPLEXES OF RHODIUM(II)

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Rhodium and iridium complexes with a d^7 electronic configuration are very unusual, especially as monomeric species[1] and, in this field, we have recently described[2] a fully characterized monomer square planar iridium(II) organometallic complex, $[Ir(C_6Cl_5)_2(cod)]$ prepared by oxidation of iridium(I). The anionic complexes $[NBu_4][Rh(C_6Cl_5)_2(L_2)]$ $[L_2$=1,5-cyclooctadiene (cod), $\{P(OPh)_3\}_2$, $(CO)_2$ and $(CO)(PPh_3)]$ are obtained by arylation of $[\{Rh(m\text{-}Cl)(L_2)\}_2]$ with LiC_6Cl_5.

$$[\{Rh(\mu\text{-}Cl)(L_2)\}_2] + 4\,LiC_6Cl_5 \xrightarrow{-2\,LiCl} 2\,Li[Rh(C_6Cl_5)_2(L_2)] \longrightarrow$$

$$\xrightarrow[-2\,LiBr]{+2\,NBu_4Br} 2\,[NBu_4][Rh(C_6Cl_5)_2(L_2)]$$

These compounds can be used as precursors to a number of rhodium(II) complexes via oxidation and substitution reactions. The oxidation with chlorine gives the neutral rhodium(II) compounds $[Rh(C_6Cl_5)_2(L_2)]$ $[L_2$= cod, $\{P(OPh)_3\}_2]$. Substitution of cod in $[Rh(C_6Cl_5)_2(cod)]$ by neutral ligands renders new neutral rhodium(II) monomer complexes. They have been studied by IR, NMR, MS, EPR, CV and $[Rh(C_6Cl_5)_2\{P(OPh)_3\}_2]$ structurally characterized by an X-ray diffraction study.

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[1] Serpone, N.; Jamieson, M. A. in *Comprehensive Coordination Chemistry* Pergamon Press, Oxford, **1987**, *vol. 4*, p. 1120.

[2] García, M. P.; Jiménez, M. V.; Lahoz, F. J.; Oro, L. A.; Alonso, P. J. *Angew. Chem.* **1992**, *104*, 1512; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1527.

LAICM2250P **66, Tue. 14**

PREPARATION OF NEW CATIONIC COMPLEXES $[CpFe(dppe)L]PF_6$ WITH SULFUR AND OTHER DONOR LIGAND

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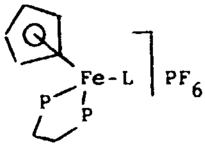
Compounds containing CpMLL'moieties (M Fe,Ru;L,L' CO, phosphines and phosphites, $Cp=\eta^5\text{-}C_5H_5$) are the among the most versatile systems in organo-transition metal chemistry. We have recently reported that the complex CpFe(dppe)I $dppe=Ph_2P(CH_2)_2PPh_2$ is a good precursor of anionic CpFe(dppe)X as well as the cationic $[CpFe(dppe)NCCH_3]PF_6$ complexes [1]. Now we report the preparation of the new complexes $[CpFe(dppe)\ L]PF_6$



1 L-a THF
b $P(n\text{-}Bu)_3$
c $C_6H_5SN(C_6H_{11})_2$
d $C_6H_5SN(CH_3)_2$
e $S_2(CH_3)_2$
f $S_2(t\text{-}Bu)_2$

The compounds 1b-f were obtained by reaction of CpFe(dppe)I with L in presence of $TlPF_6$ and in CH_2CL_2 as solvent. The complex 1a can be easily prepared from CpFe(dppe)I in THF in presence of $TlPF_6$. The compounds were characterized by elemental analyses, IR, ^{31}P and ^1H-NMR spectroscopy as well as cyclic voltammetry. The complex 1a appears to be an useful precursor for the preparation of other cationic complexes. Electrochemical one electron oxidation of some of the cationic complexes suggest the formation of stable di-cationic 17ē species.

ACKNOWLEDGEMENTS. D.T.I.(Proy.Q3280), U. de Chile.

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LAICM2251P 67, Tue. 14

HYDROFORMYLATION RHODIUM CATALYSTS WITH S-DONOR CHIRAL LIGANDS.

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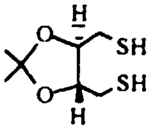
In recent years much research has been done in enantioselective catalysis. In the hydroformylation process, the enantiomeric excesses obtained are, in general, low. Rh or Pt catalysts modified by optically active phosphines possesing a C_2 symmetry axis have been mostly employed[1]. The Pt systems provide better chiral inductions but lower activity and selectivity.

Dinuclear Rh thiolate complexes are efficient catalytic precursors in hydroformylation[2] The advantage of this systems is the possibility to introduce changes into the thiolate bridging ligands. Firstly, we considered interesting to modify the Rh-thiolate systems in two ways: joining the two sulfur groups with a carbon chain and introducing a chiral center.

The chiral dithiolate ligand studied is, **1** (-)DIOS. The dinuclear neutral complex $[Rh_2(\mu\text{-DIOS})(COD)_2]$ (**2**) has been prepared. This system is active in the hydroformylation of styrene affording high selectivity of 2-phenylpropanal without phosphorous ligands. However, low e.e. are obtained.



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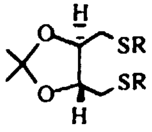

3

A further modification of the (-)DIOS system has been studied using the corresponding thioether ligands showed in **3** (-)DIOSR where R=-Me, $-{}^{i}Pr$, -Ph. In this case cationic mononuclear complexes have been obtained.

[1] K.E. Koenig, in *Asymmetric Syntheses* (Ed. J. Morrison) Vol.5, Academic Press, NY. (1988).

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LAICM2254P **68, Tue. 14**

ORGANOMETALLIC NICKEL(II) THIOMOLYBDATES AND THIOTUNGSTATES

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The tetrathiometallates MS_4^{2-} (M = Mo, W)[1] are known to act either as bidentate terminal ligands or as tetradentate bridging ligands to a wide variety of transition metal ions, but tetrathiometallate adducts of organometallic compounds are a relatively new class of compounds. Incentives for recent interest in this area follow from evidence that certain thiometallate complexes are structurally related to catalytic sites in both nitrogen-fixing enzymes and industrial hydrodesulfurization and hydrodenitrogenation catalysts.

Due to current interest in this area, we turned our attention to reaction systems containing $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ and thiometallates $MO_{4-n}S_n^{2-}$ (M = Mo or W; n = 2, 3 or 4) in order to obtain adducts of the $(C_6F_5)_2Ni$ moiety with thiometallate. By reaction of $(NBu_4)_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ [2] with $(NH_4)_2MS_4$ (M = Mo or W) in a 1:1 ratio in ethanol solution the complexes $(NBu_4)_2$-$[Ni_2(C_6F_5)_4(\mu\text{-}MS_4)]$ are obtained. When the same reaction is carried out with the bis(hydroxo)nickel complex and $(NH_4)MO_{4-n}S_n$ (n = 2, 3, 4; M = Mo and/or W) in the presence of NBu_4OH (1:2:2 molar ratio respectively) the binuclear complexes $(NBu_4)_2[Ni(C_6F_5)_2(MO_{4-n}S_n)]$ are formed. In both reactions the OH bridges of the hydroxo complex are protonated by the NH_4^+ ions and the resulting $Ni(C_6F_5)_2$ fragment is trapped by the thiometallate ligand in either 2:1 or 1:1 ratio respectively. Elemental analyses and conductance and spectroscopic (IR, ^{19}F NMR) data have been used for structural elucidation. A single-crystal X-ray diffraction study has established the trinuclearity of complex $(NBu_4)_2[Ni_2(C_6F_5)_4(\mu\text{-}WS_4)]$ containing tetradentate bridging WS_4^{2-}.

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[2] G. López, G. García, G. Sánchez, J. García, J. Ruiz, J. A. Hermoso, A. Vegas and M. Martínez-Ripoll, *Inorg. Chem.*, 1992, **31**, 1518.

LAICM2255P **69, Tue. 14**

SYNTHESIS OF PALLADIUM ENOLATE COMPLEXES

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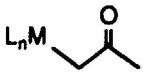
Palladium enolates have been proposed as intermediates in numerous organic transformations, especially palladium mediated aldol reactions.[1] On the other hand, hydroxo complexes of Ni, Pd and Pt have shown to be good precursors for synthetic work.[2]
Treatment of mononuclear hydroxo complexes of the type *cis*-$[L_2Pd(C_6F_5)(OH)]$ with methylketones yields the palladium carbon-bound enolates of the general formula *cis*-$[L_2Pd(C_6F_5)(CH_2COR)]$ (R= CH_3, Ph, Bu^i, Et).



The reaction of the binuclear μ-hydroxo complex $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ with acetone leads to the formation of the complex $[(C_6F_5)_2Pd(CH_2COCH{=}C(CH_3)_2)]^-$, as shown by IR and ^1H, ^{13}C and ^{19}F NMR spectroscopy, which implies a metal-aldol condensation process.

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C-H Cyclopentadienyl Activation in Anionic Zirconium(III) Species $[Cp'_2ZrH_2]^-$ ($Cp' = C_5H_4tBu, C_5H_4SiMe_3$)

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Chemical reduction of deuterated $[Cp'_2ZrD(\mu\text{-}D)D]_2$ $Cp' = C_5H_4tBu, C_5H_4SiMe_3$) with sodium naphthalenide affords E.P.R. spectrum of $[Cp'_2ZrD_2]^-Na^+$ ($Cp' = C_5H_4tBu, C_5H_4SiMe_3$) which is transformed in a few minutes into another complicated stable EPR signal analyzed by computer simulation as a mixture of $[Cp'_2ZrD_2]^- Na^+$·$[Cp'_2ZrHD]^-Na^+$ and $[Cp'_2ZrH_2]$-Na^+(35%, 55% and 10% respectively). Investigations in order to improve mechanisms by which Zr(III) hydrides exchange H/D were difficult to operate under EPR techniques. The conversion of Zr(III) species in their diamagnetic dichoride analogues allowed us to test the presence of D on cyclopentadienyl ring. EPR solutions of the above mixture $[ZrD_2]^-$, $[ZrHD]^-$and $[ZrH_2]^-$ were oxidized with HCl to $[Cp'_2ZrCl_2]$. In this dichloride series, ^2H NMR spectra show evidence of incorporation of D mainly in CMe_3 or $SiMe_3$ sites but also in a less extend in C_5H_4 ring. The H/D exchange observed in the chemical reduction of $[Cp'_2ZrD(\mu\text{-}D)D]_2$ as well as the presence of deuterated sites on Cp' confirm the C-H cyclopentadienyl activation process in Zr(III) species chemistry.

H/D exchange is also observed by EPR on hydride sites of $[Cp'_2ZrH_2]^-$ with D_2 atmosphere.

Mechanisms of these exchanges will be proposed.

Catalytic selective hydrogenation of 1,5 or 1,3 COD to cyclooctene is presented.

R. Choukroun, F. Dahan, A.M. Larsonneur, E. Samuel, J. Petersen, P. Meunier, C. Sornay, Organometallics, 1991, 10, 374.

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LAICM2262P **71, Tue. 14**

NEW η^5 - MONOCYCLOPENTADIENYLNICKEL (II) DERIVATIVES SYNTHESIS AND CHARACTERIZATION

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Our previous results on the coordination of p- substituted nitriles, bearing a donor or an acceptor group to organometallic fragments [1,2] with the aim to reinforce nitrile π deslocalization, lead us to explore the chemistry of [Ni (η^5-C_5H_5) PPh_3]$^+$ fragment. The main goal of this work are the potencial nonlinear optical properties of these compounds since the uncoordinated ligands show high values of their second harmonic generated signals.

In this communication we present the synthesis and characterization of [Ni (η^5 -C_5H_5) (PPh_3) (p- DC_6H_4CN)]$^+$ where D = donor group = NH_2, NMe_2, OCH_3 and C_6H_5.

All new compounds were fully characterized by the usual IR and ^1H, ^{13}C, ^{31}P NMR spectroscopic techniques.

In order to get an insight on the reactivity of these mono-η^5-cyclopentadienyl derivatives, their electrochemistry was studied by cyclic voltammetry, in different solvents.

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AICM2267P **72, Tue. 14**

HIGH VALENT IMIDO VANADIUM COMPLEXES CONTAINING BENZAMIDINATES AS STABILIZING LIGANDS.

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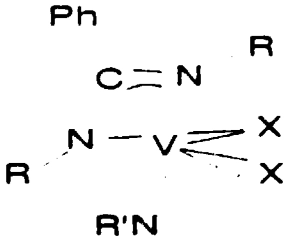
Untill now organovanadium chemistry has almost exclusively been build on bis- and mono-cyclopentadienyl derivatives. Normally the oxidation state of the metal is +3 or lower and stabilization of high valent vanadium complexes seems difficult.

We have decided to concentrate on vanadium compounds with the metal in higher oxidation state using spectator ligands other than cyclopentadienyl. Attractive candidates for this purpose are arylamidinates $PhC(NR)_2^-$ ($R=SiMe_3$, ^tBu, ^ipropyl, etc.), and alkoxysilylamides $ROSiMe_2NR^-$ ($R={}^tBu$).

We present here several new monobenzamidinate complexes of vanadium (V). $RN=VLX_2$ [1], $L= PhC(NR)_2^-$. $X=Cl$, NR_2, OR.. Their synthesis, characterization, molecular structure and chemical properties will be discussed.



1 X=Cl, OR NR2
R=SiMe3, t-Bu, p-
R'=t-Bu, p-Tol

LAICM2270P

73, Tue. 14

CATALYTIC ACTIVITY OF $[(FeBr_3)_2(DMSO)_3]$ AND $FeBr_3$ AND IN SELECTIVE OXIDATION OF ORGANIC SULFIDES TO SULFOXIDES.

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The new complex compounds $[(MX_3)_m(DMSO)_n]$, were M = 3d transition metals, X = Cl, Br, m and n = 1-3, are being studied in our research group in order to compare them with the MX_3 simple salts as catalysts in organic reactions.

We reported here the selective oxidation of a series of organic sulfides to sulfoxides by nitric acid, catalyzed by $FeBr_3$ and $[(Fe\ Br_3)_2(DMSO)_3]$, 1.

The reaction system consisted of a 10% solution of nitric acid containing either $FeBr_3$ or complex 1. Organic sulfides were solved in nitromethane in a 10:1 mol ratio substrate:catalyst.

From the organic layer, values yielded for sulfoxides ranged between 80-90% with high purity degree. Results of reactions catalyzed by 1 gave higher yields and purity than $FeBr_3$ catalyzed ones. The products were identified by ^1H NMR, IR, m.p. and mixed m.p.. Their purity was controlled by m.p., TLC and/or GLC and ^1H NMR.

In complex 1, DMSO is coordinated to the metal by the oxygen atom as shown by the 938 cm^{-1} band in the IR spectrum. Elemental Analysis and Mass Spectrum supported the proposed structure. It is a light and moist stable complex which decomposes at 190°C. Therefore, it has excellent properties to be used in place of anhydrous $FeBr_3$ whose known moisture sensibility made it difficult to handle.

LAICM2271P 74, Tue. 14

REVERSIBILITY FROM OXIDATIVE ADDITION TO ß-ELIMINATION IN METAL HALIDES CATALYZED REACTIONS

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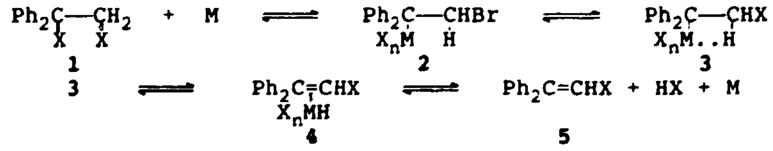
Catalyzed dehydrohalogenation of 1,2-dihalo-1,1-diphenylethanes in CCl_4 solutions afforded 2-halo-1,1-diphenylethenes, as only products. Iron, ruthenium, aluminum, and their anhydrous halides were used as catalysts. The reaction mechanism involved the participation of organometallic intermediates that were spectroscopically detected. The organometallic pathway was initiated by oxidative addition to produce intermediate **2** which decomposed by ß-elimination, as shown in Scheme I.

SCHEME I



$$\underset{\mathbf{1}}{Ph_2\underset{X}{C}-\underset{X}{C}H_2} + M \rightleftharpoons \underset{\mathbf{2}}{Ph_2\underset{X_nM}{C}-\underset{H}{C}HBr} \rightleftharpoons \underset{\mathbf{3}}{Ph_2\underset{X_nM..}{C}-\underset{H}{C}HX}$$

$$\mathbf{3} \rightleftharpoons \underset{\mathbf{4}}{Ph_2\underset{X_nMH}{C=}CHX} \rightleftharpoons \underset{\mathbf{5}}{Ph_2C=CHX} + HX + M$$

$M = FeBr_3, RuBr_3, AlBr_3$ $X = Br, Cl$

The reversibility of the oxidative addition (**1** $\rightleftharpoons$ **2**) and ß-elimination (**4** $\rightleftharpoons$ **5**) reactions, as well as equilibrium between agostic and hydride complexes (**3** $\rightleftharpoons$ **4**) are well known.

For the first time, we report here that the complete system, (**1** $\rightleftharpoons$ **5**), is reversible. As these species can be in equilibrium, we may study both reactions, dehydrohalogenation and hydrohalogenation. The influence of temperature, catalyst and oxygen on these reactions was investigated. Results provided additional evidence supporting the proposed mechanism for transition metal catalyzed dehydrohalogenations.

LAICM2272P 75, Tue. 14

STRUCTURE AND REACTIVITY OF BROMOMETALATES FORMED IN METAL BROMIDES CATALYZED DEHYDROBROMINATIONS.

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Dehydrobromination of 1,2-dibromo-1,1-diphenylethane catalyzed by iron, ruthenium and aluminium tribromides, is a reversible process with participation of organometallic intermediates. The reaction mechanism consists of an oxidative addition followed by a ß-elimination. In the course of the HBr elimination metal tribromides are turned into species that work as hydrogen bromide donors in the reverse addition reaction. We reported here the study carried out to know the structure of these compounds: potentiometric titrations, UV-V, iron determination by A. A. Spectrophotometry and ammonium salts derivatives. According to the results, HBr lost from the substrate in the ß-elimination step was captured by the metal tribromides that turned into $H_3[MBr_6]$, where M=Fe, Ru and Al. As the spectra of the $[FeBr_4]^-$ anion was identified in the decomposition of $H_3[FeBr_6]$ followed by UV-V spectroscopy, its role as an intermediate in the reaction mechanism was studied. It proved to be both HBr acceptor in the elimination reaction and HBr donor in the addition reaction. Reactions of $H_n[FeBr_{3+n}]$ formed in the dehydrohalogenation reaction and synthesized $H[FeBr_4]$ with other olefins gave also HBr addition to the double bond. In conclusion, the catalytic activity of MBr_3 in these reactions is due to their ability to coordinate the eliminated HBr to form unstable perhalometalates that according to the reaction conditions can: either lose HBr regenerating the catalytic site or transfer HBr in the addition reaction.

LAICM2274P

76, Tue. 14

SYNTHESIS OF THE PHOSPHINE-THIOLATE METALLOLIGANDS $Cp_2M[S(CH_2)nPPh_2]_2$ (M=Mo(IV), W(IV); n=1,2) AND ITS REACTION WITH Cu(I) AND Rh(I) COMPLEXES TO FORM HETEROBIMETALLIC SYSTEMS

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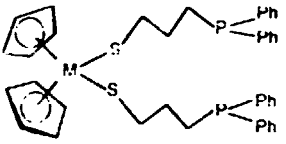
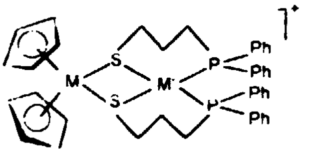
As part of our continuing interest in developing molybdenum and tungsten thiolate chemistry [1], we have undertaken the synthesis of a new family of compounds:



M = Mo (IV) W(IV)

and the study of their potential application as metalloligands.

In this communication we present the synthesis and characterization of these new ligands and some heterobimetallic complexes as well:



M = Mo (IV) , W(IV)

M' = Cu (I), Rh (I)

All the new compounds were characterized by the usual ^1H, ^{13}C and ^{31}P NMR spectroscopic techniques.

The electrochemical behaviour of these compounds was studied by cyclic voltametry, in order to get an insight on the reactivity of the compounds and to have some hints in the future development of their chemistry.

LAICM2275P **77, Tue. 14**

SYNTHESIS AND CARACTERIZATION OF NEW COMPOUNDS WITH BIPYRIDINS AND CYANOPYRIDINS COORDINATED TO MONOCYCLOPENTADIENYLRUTHENIUM (II)

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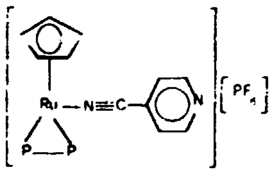
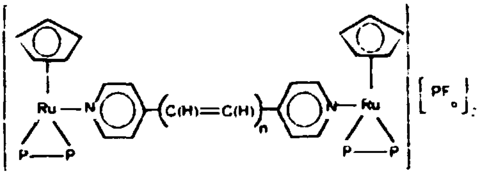
We have been developing, in our research group, during the last five years, synthesis of new mono-η^5-cyclopentadienyl(transition metal) derivatives, possessing a π-delocalised system attached to the organometallic moiety. The aim of this work is their potential nonlinear optical properties [1].

In this comunication we present a new serie of compounds with 4-cyanopyridin, 4-4'-Bipyridin and *trans*-1,2-Bis-(4-Pyridil)-ethylene, coordinated to the monocyclopentadienylruthenium(II).

This new family was synthetised in methanol, at room temperature, from the starting material [Ru(η^5-Cp)(P—P)Cl] [2]



P—P = DPPE DIOP DPOPYR



P—P = DPPE DIOP n = 0, 1

These compunds were fully characterized by the spectroscopic technics (IR, ^{1}H, ^{13}C and ^{31}P NMR). finally we present the results of the cyclic voltametric studies

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[2] - Bruce, M.I., Windsor, N.J. *Aust. J. Chem.*, 1977, 30, 1601

LAICM2276P **78, Tue. 14**

NUCLEOPHILIC ADDITION IN TRIPLE BONDS PROMOTED BY PLATINUM(II) COMPOUNDS

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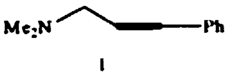
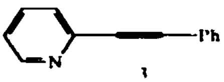
The reactions involving alkynes and transition metals compounds, mainly of the group 10 gave, in most of the cases, alkyne oligomers. However, it was observed that the reaction alkynes containing electron withdrawing groups such as carboxylate group, are easily cyclized by intramolecular nucleophilic addition of this group in the triple bond coordinated to the metal center. The functionalized alkynes(1-3) employed in this study were prepared as described in literature. This method is based in the coupling of aryls-halides with terminal alkynes, using as catalyst $PdCl_2(PPh_3)_2/CuI$.



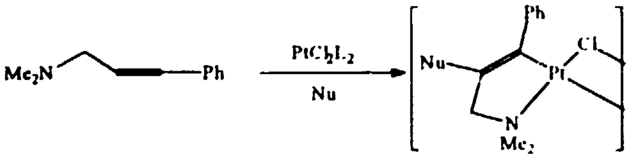
1

2



3

The reaction of alkynes (1-3) with $PtCl_2(L)_2$ L = PhCN, SEt_2 in presence of several nucleophiles such as N_3^-, $CH(CO_2Me)_2^-$, $\underbrace{CH_2CH_2CH_2COC}CO_2Me^-$ afford cycloplatinated complexes as described below.



The cyclometallated compounds synthesized were characterized by IR and NMR (^1H, ^{13}C) spectroscopy and combustion analysis.

Acknowledgments Thanks are due to the CNPq e FAPERGS for financial support

Synthesis, Structural Characterization and Catalytic Properties of a New Series of Mononuclear and Hetero-Binuclear Metal Complexes Containing the Short Bite Ph_2PPy Ligand.

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Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare, Università di Messina, Italia

Roberto Gobetto
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Italia

There is considerable interest in the synthesis of binuclear complexes due to their possible use in the catalytic transformations of organic compounds.Two metal centers in close proximity in a binuclear system can react in a cooperative manner. However, proof of such a cooperative effect is always a challenge.

These considerations led us to investigate the catalytic activity towards hydroformylation reactions of hetero-binuclear Ru-Rh and Ru-Ir complexes in which the metal centers are bridged by one 2-(bis-diphenylphosphino)pyridine, Ph_2PPy, hetero-bifuntional ligand.

We used, as catalytic test reaction, the hydroformylation of styrene since the condition used for this reaction represents usually a severe test of the stability of the bimetallic system. The hydroformylation reactions have been performed in the temperature range 45 - 100° C under 20 - 60 atm. of a CO/H_2 1:1 mixture. Almost quantitative conversion of styrene could be obtained under 80 atm of pressure at 60° C.

The binuclear derivatives reported have been obtained by "bridge-assisted" reactions starting from the cationic mononuclear ruthenium(II) complex $[Ru(Ph_2PPy)_3Cl]$ (X= Cl, PF_6). Part of the work was devoted to the synthesis, spectroscopic and X-ray structure characterization of the synthesized mononuclear and binuclear complexes containing the Ph_2PPy ligand.

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF Re(I) COMPLEXES CONTAINING NITROGEN DONOR LIGANDS DERIVED FROM TERPYRIDINE.

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[1]Departamento de Bioquímica, Facultad de Medicina, Universidad de Chile, Casilla 70086-7, Santiago, Chile.

The synthesis and spectroscopic characterization of new halocarbonylrhenium(I) complexes containing heterocyclic nitrogen ligand derived from terpyridine is reported. The ligands has been prepared from the condesation of 2-acetylpyridine with 4-pyridinecarboxaldehyde (1) and 2,6-diacetylpyridine with 2-aminobenzaldehyde (2) and 2-aminonicotinaldehyde (3)[1]. A series of complexes of type $ReX(CO)_2(NNN)$ (NNN = 1, 2, 3, and X = Br) were obtained. The complexes were characterized by elemental analysis, electronic, FT-IR, and MNR spectroscopy. The redox properties of the prepared complexes will be dsicussed.

We thank DICYT-USACH and MOLYMET-CHILE for support this research.

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LAICM2289P **81, Tue. 14**

^{19}F AND ^{31}P EVIDENCE FOR SILVER HEXAFLUOROPHOSPHATE HYDROLYSIS IN SOLUTION. SYNTHESIS OF THE FIRST PALLADIUM DIFLUOROPHOSPHATE COMPLEXES.

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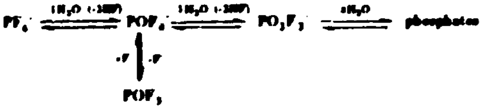
Although several PO_2F_2-complexes have been reported where the anion $PO_2F_2^-$ is generated from the partial hydrolysis of the PF_6^- group, the hydrolysis of the $AgPF_6$ reagent in organic solution has not yet been considered. Herein we report the study of this hydrolysis process and the synthesis of the first PO_2F_2-palladium complexes.

The reaction of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2$(1) with $AgPF_6$ in CH_2Cl_2 yields $[Pd(\mu\text{-}PO_2F_2)(\eta^3\text{-}C_4H_7)]_3$ (2) where the $PO_2F_2^-$ arises from the partial hydrolysis of the PF_6^- ion.

$$[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2 + 2AgPF_6 + 4H_2O \longrightarrow AgCl + 8HF + 2/3[Pd(\mu\text{-}PO_2F_2)(\eta^3\text{-}C_4H_7)]_3$$

We have demonstrated, by means of ^{19}F and ^{31}P NMR spectra that $AgPF_6$ hydrolyses completely (to phosphates) in CH_2Cl_2 in the absence of the palladium complex and the presence of **1** stops the hydrolysis process at the $PO_2F_2^-$ stage. The intermediates of the hydrolysis indicated in the following scheme are detected and a clear solvent dependence demonstrated. The hydrolysis is only observed with solvents of low coordinating ability.



2 reacts with PR_3 (molar ratio 1/3) to give the complexes $[Pd(PO_2F_2)(\eta^1\text{-}C_4H_7)(PR_3)]$ R=Cy(**3**), Ph(**4**), p-tolyl(**5**); PR_3=$PMePh_2$(**6**). A single crystal X-Ray structure determination of **3** showed unequivocally the presence of the $PO_2F_2^-$ ion.

The behaviour of **2**,**3** or **4** against several complexes as $[MPPh_3]PF_6$, M=Ag, Cu or $PdCl_2(PhCN)_2$ has also been investigated.

LAICM2290P **82, Tue. 14**

NEW NEUTRAL, ANIONIC AND CATIONIC NIOBIUM(V) ALCOXIDES.

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In the recent years, the chemistry of the early transition metals bearing ligands like that oxo or alkoxo have received considerable attention because they are models of the behaviour of metal oxides in catalytic processes.

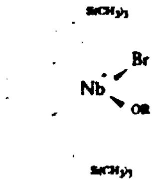
The present work was undertaken in order to explore the synthesis and structural characterization of new ionic or neutral niobium-alkoxide derivatives. In this communication we present some of the last results.

The cationic complexes can easily be obtained by reaction of the corresponding cationic niobocene halide with an excess of trimethylsilylalkoxide reagent, $(CH_3)_3SiOR$:

$$[Cp'_2NbBr_2]^+PF_6^- + (CH_3)_3SiOR \longrightarrow [Cp'_2NbBr(OR)]^+PF_6^-$$

$Cp' = C_5H_4Si(CH_3)_3$ $R = CH_3, Et, {}^iPr, Ph$

The spectroscopic properties and the conductivity measurements are accordance with the following structure for these derivatives:



We have also studied the reactions of $(CH_3)_3SiOR$ with $NbCl_5$ or $NbCl_5OPPh_3$ in order to obtain the corresponding neutral alkoxide complexes in agreement with the following reactions:

$$\begin{tikzcd}
NbCl_5 + (CH_3)_3SiOR \arrow[r] \arrow[d, "L"] & NbCl_{5-x}(OR)_x \quad x=2,3 \arrow[d, "L"] \\
NbCl_5L + (CH_3)_3SiOR \arrow[r] & NbCl_{5-x}(OR)_xL \quad x=2,3
\end{tikzcd}$$

$L = OPPh_3, SPPh_3, Cl^-, Br^-$

When Cl^- or Br^- were added, anionic compounds are isolated. Some of these compounds were early reported by us.

The spectroscopic properties (^1H, ^{13}C NMR, IR) and conductivity measurements of all complexes will be discussed.

NEW APPROACH TO THE CHEMISTRY OF TRISPYRAZOL-1-YLBORATES RUTHENIUM DERIVATIVES. APPLICATION OF SPECIAL NMR TECHNIQUES TO THE STRUCTURAL ELUCIDATION OF THESE COMPLEXES.

Félix A. Jalón, Antonio Otero and Ana Rodríguez.
Departamento de Química Inorgánica, Orgánica y Bioquímica. Facultad de Químicas. Campus Universitario. Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain.

In spite of the rich chemistry of transition metal derivatives with tris(pyrazol-1-yl)borate ligands, scarce examples have been reported in the ruthenium chemistry. Probably, the reason is the lack of suitable starting materials. That is why we have studied the reaction of the potasium salt of tris(pyrazol-1-yl)borate anion (KTp) with both the polymeric $[RuCl_2(COD)]$ **1**, an usual starting material of Ru(II) chemistry, and the less known $RuCl_2(THT)_4$ **2**. Treatment of **1** with KTp, in refluxing THF, gives **3** and **4** in a variable ratio, depending on reaction conditions, according with eq. 1:

$$[RuCl_2(COD)] + KTp \longrightarrow TpRuCl(COD)\ \mathbf{3} + RuCl_2(PzH)_2(COD)\ \mathbf{4} \quad (1)$$

4 has two coordinated pyrazol ligands and the arguments to think that pyrazol arises from the pyrolitic degradation of a not identified insoluble precursor will be discussed. **4** turns into **3** with an excess of KTp.

The reaction of **2** with KTp leads to a mixture of two (**5** and **6**) or three products dependent on the experimental conditions (eq. 2):

$$RuCl_2(THT)_4 + KTp \longrightarrow TpRuCl(THT)_2\ \mathbf{5} + Tp_2Ru(THT)_2\ \mathbf{6} + Tp_2Ru\ \mathbf{7} \quad (2)$$

3-7 have not been reported up to date. They have been independently isolated from moderate to good yields by suitable methods and characterized by polynuclear NMR techniques.

COSY correlations, difference NOE experiments and monodimensional homonuclear irradiation of ^{1}H-NMR spectra have allowed the total elucidation of the different structures on the basis of their octahedral environment.

LAICM2292P **84, Tue. 14**

SYNTHESIS AND REACTIVITY OF RUTHENIUM AND NIOBIUM COMPLEXES WITH POLY(PYRAZOL-1-YL)METHANE LIGANDS.

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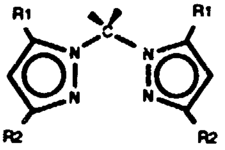
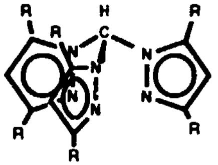
In contrast to well-developed chemistry of tris(pyrazol-1-yl)borate derivatives of transition metals, there are scarce examples where a metal is co-ordinated whith a poly(pyrazol-1-yl)methane ligand, although some bis- and tris-pyrazolymethanes complexes are readily prepared by usual methods. We have proposed to develop in the last years, the poly(pirazol-1-yl)methane coordination chemistry of early and late transition metals. We report here some of our findings in Niobium and Ruthenium chemistry.



NN: $R_1=R_2=H$; NN': $R_1=R_2=Me$;
NN*: $R_1=SiMe_3$; $R_2=H$



NNN: R=H ; NNN': R=Me

The reaction of $[NbCl_3(DME)]_n$[1] **1** (DME=dimethoxyethane) with bis(pyrazol-1-yl)methane ligands (NN, NN' and NN*) gives high yields of the chelate complexes $[NbCl_3NN]_2$, $[NbCl_3NN']_2$ and $[NbCl_3NN^*]_2$ **2,3,4**. These complexes react with diphenylacetylene to give neutral monomeric trihaloniobium alkyne bis(pyrazol-1-yl)methane complexes of the general formula $[NbCl_3(PhC{\equiv}CPh)L\text{-}L]$ (L-L=NN, NN',NN*) **5,6,7**. The same complexes can also be obtained by substitution reactions of $[NbCl_3(DME)(PhC{\equiv}CPh)]$[1] **8** with the above mentioned ligands.

The new compounds $[NbCl_3(NNN)]$ and $[NbCl_3(NNN')]$ **9,10** have been prepared by reaction of **1** with the corresponding ligands. In solution, the split of C-N bond for the complex $[NbCl_3(NNN')]$ to give the pz' has been observed.

In the ruthenium chemistry we have started from RuClH(NN)(COD) **11**. This hydride reacts easily with phospines and pyridines displacing Cl^- in presence of silver triflate salt. The following complexes are obtained: trans-$[RuH\{P(OMe)_3\}(NN)(COD)]CF_3SO_3$ **12**, cis and trans-$[RuH(PMe_2Ph)(NN)]CF_3SO_3$ **13**, cis and trans-$[RuH(Py)(NN)(COD)]CF_3SO_3$ (Py=pyridine **14**, 4-picoline **15**, 3,5-lutidine **16**).

The displacement of the NN ligand is too possible [$RuClH(PMe_2Ph)_2(COD)$ **17** is obtained] or the both ligands obtaining the fac-$[RuH(PMe_2Ph)_3(COD)]CF_3SO_3$ **18**.

All these complexes are been characterized by IR, microanalyses and polynuclear NMR techniques.

1.-Hartung J.B., Pedersen S.F., Organometallics 1990, 9, 1414.

LAICM2293P **85, Tue. 14**

KINETIC STUDIES ABOUT THE SYNTHETIC REACTIONS OF $Nb(\eta^5-C_5H_4SiMe_3)_2(H)(L)$ DERIVATIVES.

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The chemistry of transition metal polihydrides forms an expansion area by their important variety of reactions.

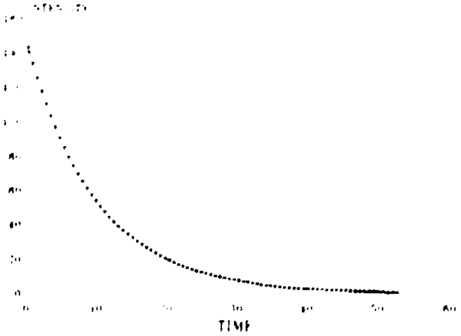
We have focused our interest on the reactions of niobocene polihydride with several ligands in order to obtain new families of hydride compounds. In fact, we have prepared the $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(L)]$ L=CO, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ and Ph-CH=CH_2 complexes, by reaction between $Nb(\eta^5-C_5H_4SiMe_3)_2(H)_3$ and the ligand L in THF or toluene during two days at room temperature or three hours at 65°C.

In this communication, we show the mechanism proposed for this reaction, from the trihydride complex, which it has been based on an initial equilibrium for the molecular hydrogen elimination to give an 16 electrons unsaturated complex that, in presence of a ligand L, forms the $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)(L)]$ complexes:

$$Nb(\eta^5-C_5H_4SiMe_3)_2H_3 \xrightleftharpoons[+H_2,k_{-1}]{-H_2,k_1} [Nb(\eta^5-C_5H_4SiMe_3)_2H]' \xrightarrow[k_2]{L} [Nb(\eta^5-C_5H_4SiMe_3)_2(H)(L)]$$

We have used the ^{1}H-NMR spectroscopy technic to follow the disappearance of the starting complex in the reaction, in order to find both the constant rate of the process and his dependence with the nature and concentration of the ligands.

In this way, we have studied the reactions with $P(OMe)_3$ and Ph-CH=CH_2 as ligands, at several concentrations at 35°C. The initial equilibrium has been determinated as the slow step of the reactions, as well as his independence of the nature of the ligand concentration.



Intensity of one trihydride peak vs time(s 10^3)

LAICM2294P 86, Tue. 14

REACTIVITY OF $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ TOWARDS SOME 1,2,4-TRIAZINE LIGANDS

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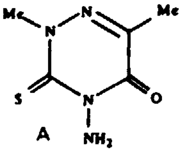
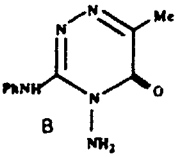
4-Amino-1,2,4-triazin-5-ones are biologically highly active substances which have been used as herbicides and alter the integrity of chloroplast by inhibiting the peroxidase-catalized lignification of the cell wall.[1] Some complexes of Ni(II), Co(II), Pd(II), Ru(II) and Rh(III) with 1,2,4-triazines have recently been reported.[2]

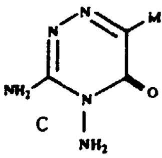
Under appropriate conditions $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ reacts with the triazines A, B and C (see below) to form the corresponding mononuclear rhodium(III) derivatives $[(\eta^5\text{-}C_5Me_5)RhCl(triazine)]Cl$. The exchange reaction of these with KPF_6 yields the hexafluorophosphate salts.



A



B



C

The new $(\eta^5\text{-}C_5Me_5)Rh$ derivatives have been characterized by elemental analyses, conductance measurements and spectroscopic (IR, ^1H and ^{13}C) methods. In every case the triazine appears to behave as a chelating bidentate ligand via the 4-NH_2 group and the 3-thioxo (A), 3-phenylamino (B) or 3-amino (C) groups, respectively. This coordination has been confirmed by a X-ray diffraction study carried out with $[(\eta^5\text{-}C_5Me_5)RhCl(triazine\ B)]PF_6$.

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[1] H. Neunhoeffer, *Comprehensive Heterocyclic Chemistry*, 1984, 2, 385. R. Muñoz, A. Martínez, A. Ros and M. A. Pedreño, *Pestic. Sci*, 1990, 30, 235.

[2] G. García, G. Sánchez, I. Romero, I. Solano, M. D. Santana and G. López, *J. Organomet. Chem.*, 1991, 408, 241, and references therein.

LAICM2296P 87, Tue. 14

PALLADIUM AND PLATINUM HYDROGENSULFIDO COMPLEXES

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The interaction of transition metal complexes with H_2S is important in the biological sulfur cycle and in hydrogendesulfurization catalysis.[1] MSH species are very likely involved in the formation of metal sulfides in aqueous solution.[2]

The reactions of the hydroxo complexes $[R_2M(\mu\text{-OH})_2MR_2]^{2-}$ (M= Pd, R= C_6F_5, C_6Cl_5; M= Pt, R = C_6F_5) and $[RLPd(\mu\text{-OH})_2PdRL]$ (R = C_6F_5 and C_6Cl_5; L= PPh_3) with H_2S yield the corresponding binuclear hydrogensulfide complexes $[R_2M(\mu\text{-SH})_2MR_2]^{2-}$ and $[RLPd(\mu\text{-SH})_2PdRL]$, respectively.

The monomeric hydrogensulfide complexes $[(C_6F_5)_2M(SH)(PPh_3)]^-$ (M= Pd, Pt) have also been prepared by reactionsof the corresponding binuclear complexes and PPh_3.

Treatment of the mixed μ-hydroxo-μ-3,5-dimethylpyrazolate complex $[(C_6F_5)_2(\mu\text{-OH})(\mu\text{-dmpz})Pt(C_6F_5)_2]^{2-}$ with H_2S leads to the formation of the mixed hydrogensulfide complex $[(C_6F_5)_2(\mu\text{-SH})(\mu\text{-dmpz})Pt(C_6F_5)_2]^{2-}$.

All the new complexes prepared exhibit a high field resonance in their ^1H NMR spectra due to SH ligand.

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2. J. Amarasekera and T.B. Rauchfuss, Inorg. Chem., 1989, 3875.

LAICM2301P **88, Tue. 14**

NEW ARYLOXO COMPLEXES OF PALLADIUM AND PLATINUM

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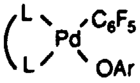
The chemistry of late transition metal alkoxides and aryloxides[1] is recently attracting growing attention because of their relevance to organic synthesis.

We have reported the synthesis of hydroxo- and methoxo- complexes[2] of the type $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OR)\}_2]$ (M= Pd, R = H; M = Pt, R = H, Me). The reactions of these hydroxo complexes with phenols lead to the formation of μ-aryloxo complexes.

$$[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]^{2-} + 2\,ArOH \longrightarrow [(C_6F_5)_2M(\mu\text{-}OAr)_2M(C_6F_5)_2]^{2-} + 2\,H_2O$$

We have also prepared aryloxo mononuclear complexes of the type



and binuclear allyl aryloxo complexes of the type $[(\eta^3\text{-}C_4H_7)Pd(\mu\text{-}OAr)_2Pd(\eta^3\text{-}C_4H_7)]$. Spectroscopic methods have been used to study the new complexes.

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2. (a) G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins and C. Miravitlles, Inorg. Chem., 1991, 30, 2605. (b) G. López, J. Ruiz, G. García, C. Vicente, R. Rodriguez, G. Sánchez, J.A. Hermoso, A. Vegas and M. Martínez-Ripoll, J. Chem. Soc., Dalton Trans, 1992, 53.

LAICM2304P **89, Tue. 14**

STUDY ON REACTIVITY OF FERROCENECARBOXALDEHYDE WITH PHENYLENEDIAMINES

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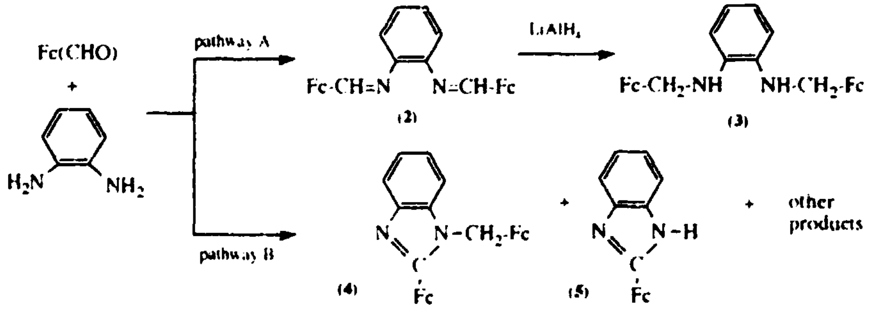
A lot of substituted derivatives of ferrocene have been synthetized and adequately characterized, but only relatively few examples of chelating and macrocyclic ligands containing one or more attached ferrocenyl groups have been reported.

We present here the study of reaction of ferrocenecarboxaldehyde (**1**) and *ortho-*, *meta-* and *para-*phenylenediamines and the characterization of the resulting products. Reaction of **1** with *ortho-*phenylenediamine shows a particular behaviour. When the reaction mixture was refluxed in benzene, the major product is the corresponding imine **2** (pathway A), which can be hydrogenated for yielding its parent amine **3**. However, in the presence of p-toluensulfonic acid (PTSA) a cyclation process takes place, yielding products showed in Scheme (Pathway B).

Compounds **2-5** have been spectroscopically characterized and their redox behaviour studied by voltammetric procedures. Additionallly, crystal structure of **4** has been solved.

Reaction of **1** with *meta-* and *para-*phenylenediamines have been carried out; in this case, only pathway A takes place.



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LAICM2311P **90, Tue. 14**

A Stepwise Synthesis of Molybdenocene, Cp_2MoX_2, and Analogue Mixed Ring Substituted Derivatives $CpCp'MoX_2$, ($Cp' = C_5H_4Me, C_9H_7$).

Cristina G. de Azevedo[1], Isabel S. Gonçalves, Eberhardt Herdtweck[2], Domitília S. Moreno, Miguel Pessanha, Carlos C. Romão and Jürgen Zühlke[2]

Instituto de Tecnologia Química e Biológica and Instituto Superior Técnico, R. da Quinta Grande 6, 2780 Oeiras, Portugal.

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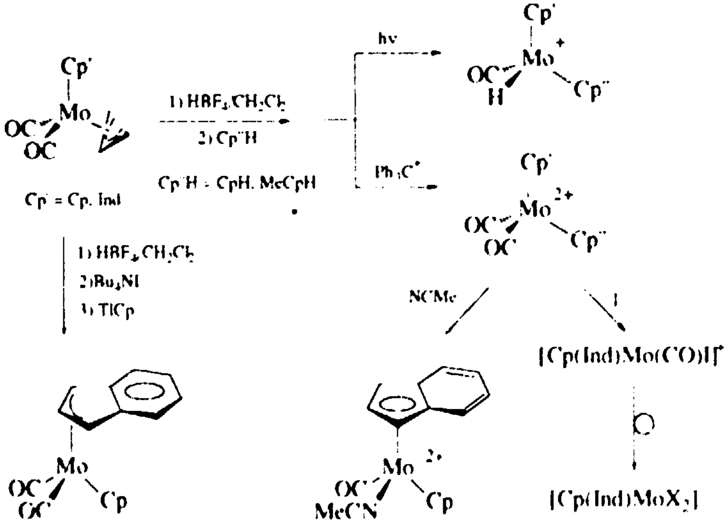
The replacement of the cyclopentadienyl (Cp) ligand by other pentahapto cyclic analogues, e.g. RCp, Cp*, Ind, has been a successful means of controlling the stability, reactivity and several other physico-chemical properties of many organometallic complexes. However, very few ring substituted metallocene derivatives of group 6 metals are known due to the difficult synthesis of Cp_2MX_2 (M = Mo, W).

Herein we report a simple stepwise preparation of molybdenocene complexes which has been extended to mixed $CpCp'MoX_2$ analogues e.g., $Cp' = C_5H_4Me, C_9H_7$. The crystal structures of the dication $[Mo(\eta^5\text{-}Cp)(\eta^5\text{-}Ind)(CO)(NCMe)][BF_4]_2$ and isoelectronic neutral $[Mo(\eta^5\text{-}Cp)(\eta^3\text{-}C_9H_7)(CO)_2]$ are presented together with some chemistry and electrochemistry of these and related complexes.



EVIDENCE FOR A THREE-COORDINATE PALLADIUM(II) SPECIES.

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Many catalytic and stoicheiometric reactions promoted by square-planar organometallic compounds of the platinum group are proposed to occur *via* an unimolecular process involving ligand dissociation in the first step of the reaction[1], and molecular orbital studies support that this three-coordinate intermediate should be T-shaped. However, only one 14e$^-$ T-shaped compound has been isolated, and the detection of this kind of intermediates is still rare, particularly if compared with the great number of pentacoordinate intermediates detected in associatively activated reactions.

We now report that spectroscopic studies on $[Pd(C_6F_5)X(Phpy_2P{=}S)]$ complexes (X= Cl, Br, I), using the pentafluorophenyl ligand as a "reporter ligand", support that the rotation of this ligand around the Pd-C_6F_5 bond occurs in a three-coordinate intermediate $[Pd(C_6F_5)(Phpy_2P{=}S)]^+$.

The X-ray structure of the complex $[Pd(C_6F_5)Br(Phpy_2P{=}S)]$ shows a typical pentafluorophenyl-palladium arrangement in which the perfluoroaril ring is almost perpendicular to the coordination plane of the metal, whereas the coordination of the ligand through the sulfur and one pyridyl group makes the two halves of the pentafluorophenyl group inequivalent.

The rotation rate of the C_6F_5 group has been measured by ^{19}F spin magnetization transfer between the two ortho fluorine nuclei. The observed rates in chloroform at different ionic strengths support the idea that the rotation occurs in a three-coordinate intermediate arising from dissociation of the halide in the starting compound. Moreover in more ionizing solvents, such as acetone, easy rotation of the pentafluorophenyl ring around the C-Pd bond is observed. Consistently with the proposed mechanism, the observed rates increase in the order Cl<Br<I.

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LAICM2333P 92, Tue. 14

INSERTION REACTIONS OF $SnCl_2$ ON Pt-Cl BONDS

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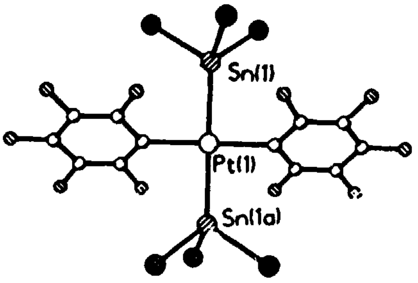
The ability of $SnCl_2$ to undergo insertion reactions in M-Cl bonds is well known, and several complexes with different geometries have been obtained.

Platinum derivatives $(NBu_4)_2[trans\text{-}PtCl_2(C_6X_5)_2]$ (X= F, Cl) react with $SnCl_2$ in 1:2 molar ratio and under mild conditions to give the insertion trinuclear complexes $(NBu_4)_2[trans\text{-}Pt(SnCl_3)(C_6X_5)_2]$ in which two Pt-Sn bonds are formed.

The complexes have been characterised by analitical and spctroscopic methods, and in the case of $(NBu_4)_2[trans\text{-}Pt(SnCl_3)(C_6F_5)_2]$ by X-ray diffraction studies (fig. 1).



The trinuclear anion contains a platinum center in a square-planar environment in which the three metallic atoms are in line, with Pt-Sn distances of 2.521 (1) Å.

Further studies on these and related reactions are in progress.

LAICM2341P 93, Tue. 14

A Stepwise Synthesis of Molybdenocene, Cp_2MoX_2, and Analogue Mixed Ring Substituted Derivatives $CpCp'MoX_2$, ($Cp' = C_5H_4Me, C_9H_7$).

Cristina G. de Azevedo[1], Isabel S. Gonçalves, Eberhardt Herdtweck[2], Domitilia S. Moreno, Miguel Pessanha, Carlos C. Romão and Jürgen Zühlke[2]

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[2] Anorganisch-chemisches Institut, T. U. München, Lichtenberg Str. 4, 8046 Garching, Germany.

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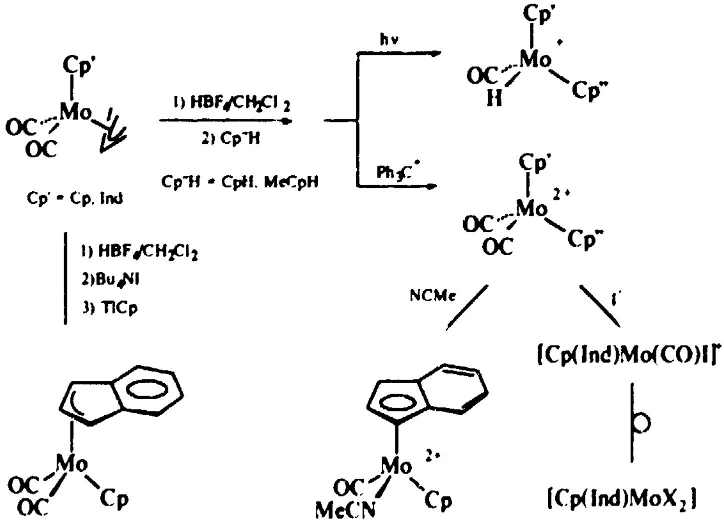
Herein we report a simple stepwise preparation of molybdenocene complexes which has been extended to mixed $CpCp'MoX_2$ analogues e.g., $Cp' = C_5H_4Me, C_9H_7$. The crystal structures of the dication $[Mo(\eta^5\text{-}Cp)(\eta^5\text{-}Ind)(CO)(NCMe)][BF_4]_2$ and isoelectronic neutral $[Mo(\eta^5\text{-}Cp)(\eta^3\text{-}C_9H_7)(CO)_2]$ are presented together with some chemistry and electrochemistry of these and related complexes.



LAICM2346P **94, Tue. 14**

CATIONIC DI-, TRI-, AND TETRANUCLEAR ARENE-RUTHENIUM COMPLEXES CONTAINING HYDRIDO OR CHLORO LIGANDS: CLUSTER BUILD-UP IN AQUEOUS SOLUTION

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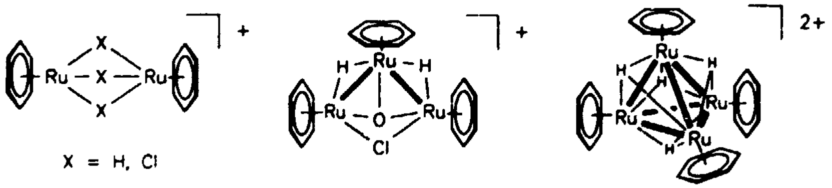
The reaction of the neutral complexes (arene)$_2$Ru$_2$Cl$_4$ (arene = benzene, p-cymene, 1,2,4,5-tetramethylbenzene) with molecular hydrogen in aqueous solution leads to water-soluble cationic arene-ruthenium species. Depending upon the reaction conditions and the nature of the counter-anions, di-, tri-, and tetranuclear cluster cations have been isolated and characterized.



The cluster build up reactions involved and the chemistry of the cationic species obtained will be discussed.

LAICM2347P **95, Tue. 14**

NEW RUTHENIUM HYDRIDES WITH DIPHOSPHINES AND ITS REACTIVITY WITH ALKYNES

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P. Noheda, Instituto de Q. Orgánica, CSIC, Juan de la Cierva 3, 28006-Madrid
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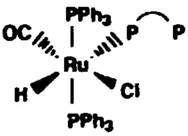
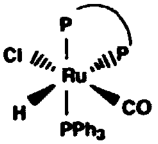
Substitution reactions of $Ru(CO)ClH(PPh_3)_3$ or $[Ru(CO)HL_2(PPh_3)_2]A$ (L=py, MeCN, $A=PF_6$) with diphosphines $Ph_2P(CH_2)_nPPh_2$ (n=1, dppm; n=2, dppe; n=3, dppp; n=4, dppb) or $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf), in different reaction conditions, give rise to the following new neutral and cationic ruthenium hydrides:



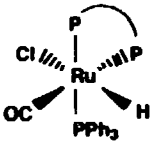
A

P⌒P= dppm.dppe.
dppp.dppb



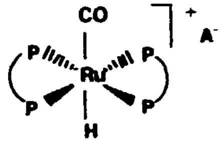
B

P⌒P= dppm.dppe.
dppp.dppb.
dppf



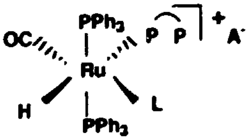
C

P⌒P= dppm.dppe



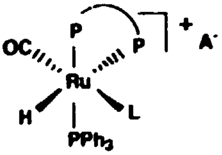
D

P⌒P=dppm.dppe.
dppp
A = Cl. PF_6



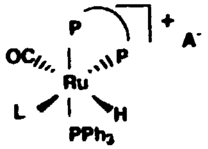
E

P⌒P = dppm.dppe
A = PF6
L = MeCN



F

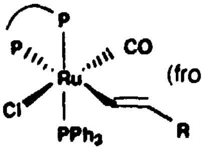
P⌒P=dppe.dppf
A = PF6
L = MeCN. py



G

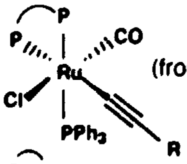
P⌒P = dppe
A= PF6
L = MeCN

Only the hydrides of type **A** and **B** (dppp, dppb, dppf) are reactive towards 1-alkynes to give alkenyl- or alkynyl complexes



(from A)

P⌒P = dppm.dppe
R = tBu. Ph. p-tolyl



(from B)

P⌒P = dppe.dppp.dppb.dppf
R = p-tolyl

Other alkenyl and alkynyl complexes were also prepared by substitution reactions from alkenyl- or alkynyl complexes with diphosphines

LAICM2357P **96, Tue. 14**

SYNTHESIS AND ELECTROCHEMICAL STUDY OF $(\eta^5\text{-}C_5Ph_4H)Co(CO)_2$ AND $CH_2[(C_5Ph_4)Co(CO)_2]_2$.

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R.M. Medina and C. Moreno.
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28049-Madrid (Spain).

The reaction of tetraphenylcyclopentadieno and bis(tetraphenylcyclopentadienil)methane with $Co_2(CO)_8$ in THF gives rise to $(\eta^5\text{-}C_5Ph_4H)Co(CO)_2$ (I) and $CH_2[(C_5Ph_4)Co(CO)_2]_2$ (II) respectively. Both compounds have been characterized by elemental analysis, IR and ^1H NMR spectroscopy.

The electrochemical results indicate that the charge transfer reactions of the compounds I and II lead to currents around 30 times smaller than the expected for the concentration used. The only possible explanation found for that effect, since the cyclic voltammetric wave is diffusion controlled, should be that both compounds approach the electrode with the ligands oriented towards the electrode surface, with the result that the cobalt atom adopts a position situated at more distance from the electrode surface than the corresponding to a normal outer Helmholtz plane (OHP). The consequence is that the tunneling step, forming part of the whole charge transfer process, becomes rate determining, giving rise to a smaller value of the standard rate constant and, consequently, of the current values.

The steric effect to which the decrease in current is attributed can indirectly be demonstrated by studying the voltammetric behaviour of the ligands used. With the ligands forming part of compounds I and II, the oxidation peak corresponding to them becomes more accentuated. The more negative is made the potential value, while the current peak of the compound remains inaltered. This has been interpreted as the consequence of the orientation and adsorption of more phenyl groups on the electrode surface induced by the larger negative charge accumulated on its surface, wich gives rise to the oxidation of a higher number of the phenylic group forming part of the ligands.

It was also possible to stablish a correlation between the molecular orbitals of the complex, as determined by studying UV and visible spectra, and the electrochemical transitions (oxidations and reductions) observed.

URACIL AND THIOURACIL COMPLEXES OF DICYCLOPENTADIENYL MOLYBDENUM AND TUNGSTEN

A. R. Dias, M. Helena Garcia, Ana Saudade Lopes, M. Matilde Marques, Dante Masi*, Carlo Meali* and M. Margarida Salema

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Lisboa, Portugal
* CNR - Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazioni, Firenze, Italy

We recently synthetised and fully characterized a series of bis- cyclopentadienyl derivatives of Mo with uracils and thiouracils, which are the first reported organometallic complexes with these ligands. Electrochemical studies were done by cyclic voltammetry and the X-ray structures were determined. We now report the synthesis and characterization of some complexes of W with thiouracils: [WCp_2(2TU)] [PF_6] (2TU = 2-thiouracil), [W(Cp_2(4TU)] (4TU = 4-thiouracil), [PF_6] [WCp_2(2MTU)] [PF_6] (2MTU = 2-methylthiouracil) and [WCp_2(4MTU)] [PF_6] (4MTU = 4-methylthiouracil). Molecular structures have been determined for these compounds and they seem to be isostructural with the Mo analogs. All the ligands are bidentate and experimental evidence shows the following preference for binding atoms in these systems: =S>=O, N(3)>N(1). We also studied the reactions of $MoCp_2Cl_2$ with 3MU (3-methyluracil) and 1,3 DMU (1,3-dimethyluracil). In such ligands, one or two usual coordination sites, N(3) or N(1) and N(3), respectively, are blocked. The experimental evidence is that only 3MU coordinates to the metal atom and in a monodentate way. We explain these facts by stereochemical reasons, based on the structural data of this series of complexes.

MECHANISM OF THE INSERTION REACTION OF ALKYNES WITH PHOSPHONICKELOCYLES.

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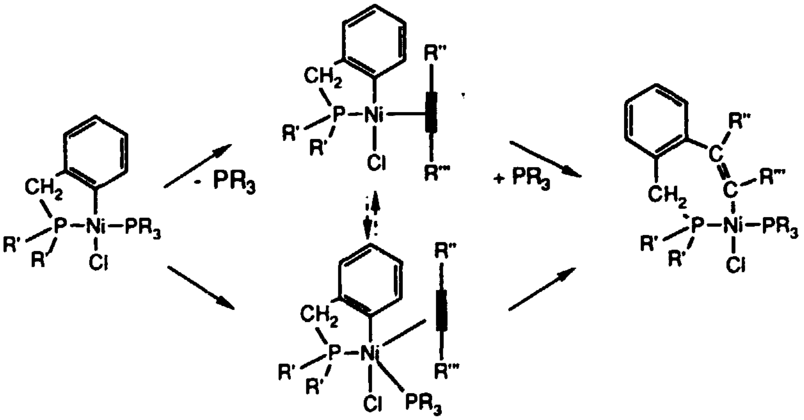
There is an increasing interest on the studies of the insertion reactivity of alkynes with phosphonickelocycles.[1] Even so, the mechanistic information concerning these type of reactions is extremely scarce. [2] In order to increase the information available for these processes we have studied the reaction:



as a function of the differents groups (PR_3, $BzPR'_2$,R"CCR"), temperature, and alkyne concentration.

The kinetic activation parameters obtained are examined in view of the two possible intermediates for the reaction depicted in the scheme above. It is accepted that the reaction occurs *via* the formation of a intermediate species, where the phosphine has been substituted by an alkyne. Nevertheless, according to the results obtained, the existence of a pentacoordinate species containing both the phosphine and the alkyne as an intermediate for the process can not be ruled out.

1- G.Muller, D.Panyella, M. Rocamora, J. Sales, M.Font-Bardía, X. Solans, J. Chem. Soc., Dalton Trans., in press.

2- E. G. Samsel, J. R. Norton, J. Am. Chem. Soc., 1984, 106, 5505.

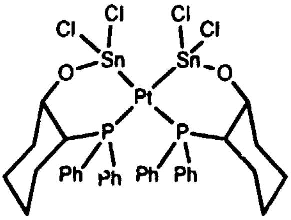
LAICM2364P **99, Tue. 14**

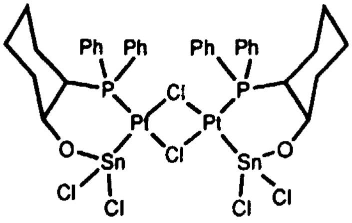
COMPLEXES OF PLATINUM WITH $PPh_2(ROH)$ LIGANDS. REACTIONS WITH $SnCl_2$

Núria Clos, Guillermo Muller, Daniel Sainz. Departament de Química Inorgànica, Universitat de Barcelona. Diagonal 647. 08028-Barcelona.

Complexes containing platinum and tin are active precursors in the catalytic hydroformylation of olefins. The lability of the $SnCl_3^-$ ligand is the main responsible for the deactivation of that system[1]. Therefore, a possible way to stabilize the Pt-Sn bond would be the inclusion of the tin atom as a coordinating end of a chelate.

A group of phosphino-alcohols PPh_2ROH and their Platinum complexes have been obtained[2]. The subsequent formation of the metallacycle containing the Pt-Sn bond can be achieved by several ways. It is possible to introduce the $SnCl_2$ group in Platinum-alcoxo complexes, or to perform the cyclization on a previously prepared compound that already contains the $-SnRCl_2$ or $-SnR_2Cl$ fragments.





Preliminary catalytic results for the hydroformylation of 1-pentene using these compounds as precursors, without added $SnCl_2$, showed better activity than the standard system $[PtCl_2(PPh_3)_2]/SnCl_2$.

1)- Gómez M., Muller G., Sainz D., Sales J., Solans X., Organometallics 10(1991)4036

2)- Alcock N.W., Platt A.W.G., Pringle P.G., J. Chem. Soc. Dalton Trans. (1989)139

LAICM2365P **100, Tue. 14**

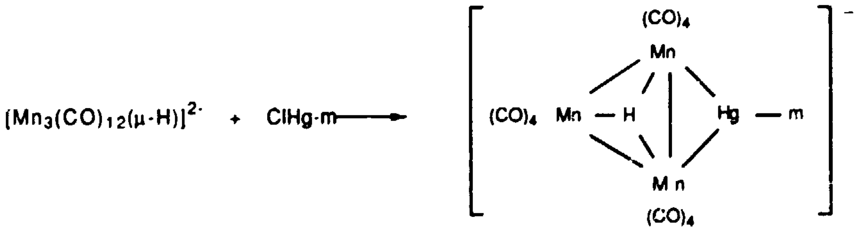
$(PPh_4)[Mn_3(CO)_{12}(\mu\text{-}H)(\mu\text{-}Hg\{Mo(CO)_3Cp\}]$: The first example of a mercury-containing planar triangulated rombohedral metal cluster.

Santiago Alvarez, Oriol Rossell, Miquel Seco, Gloria Segalés
Departament de Química Inorgànica. Universitat de Barcelona
Maria Angela Pellinghelli, Antonio Tiripicchio
Istituto di Chimica Generale ed Inorganica. Università di Parma.

One interesting class of mercury-containing transition metal clusters includes species resulting from the interaction between a mercury atom and a M_3 metal triangle. For this metal system, an edge bridged linkage with a three center-two electron mercury transition metal bond giving a butterfly geometry is the only found up to date.

In this communication, we report the first examples of triangulated M_3Hg metal clusters displaying a planar rombohedral metal framework.

The reaction between $(PPh_4)_2[Mn_3(CO)_{12}(\mu\text{-}H)]$ and ClHg-m (m = metal fragments) gives the pentanuclear clusters $(PPh_4)[Mn_3(CO)_{12}(\mu\text{-}H)(\mu\text{-}Hg\text{-}m)]$ according to the equation:



m = Fe(CO)2Cp; Mo(CO)3Cp; W(CO)3Cp; Co(CO)4; Mn(CO)5

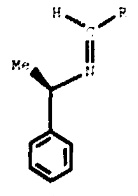
Although the nature of the molybdenum complex was deduced from its X-Ray analysis, the hydride could not be localized. However, nmr data are in agreement with its presence and theoretical calculations suggest that this ligand lies on the center of the plane of the Mn_3 triangle.

LAICM2367P **51, Thu. 16**

EXOCYCLIC CYCLOPALLADATED IMINES DERIVATED OF THE (R)-α-METHYLBENZYLAMINE.

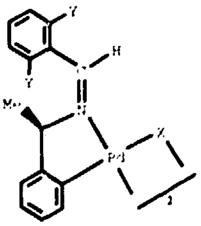
Joan Albert[a], Jaume Granell[a], Joaquim Sales[a] and Xavier Solans[b].
[a] Departament de Química Inorgànica,[b] Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, 08028 Barcelona, Spain.

It is known that cyclopalladation of N-benzylidenebenzylamines gives regioselectively endocyclic compounds. Exocyclic cyclopalladated compounds can be formed when the ortho positions of the benzal ring are blocked with chlorine atoms or methyl groups. We present here, as an extension of these reactions, the cyclopalladation of homoquiral imines of general formula R-CH=N-CH(Me)-C_6H_5, R = 2,6-$Cl_2C_6H_3$ (**1a**), 2,6-$F_2C_6H_3$ (**1b**) and 2,4,6-$(MeO)_3C_6H_2$ (**1c**) (figure I). These imines were obtained by condensation of the appropriate aldehyde and (R)-α-methylbenzylamine. The action of palladium acetate in acetic acid on the imines **1a**, **1b** and **1c** and subsequent treatment with LiCl, LiBr or KI gives the corresponding exocyclopalladated halogen bridge dimers. For imines **1a** and **1b**, these dimers consist of two stereoisomers in a aproximately ratio of 2 to 1 which are easily separated by column chromatography. The major one, contains the imine ligands in the Z form (figure II), whereas the minor one, contains the imine ligands in the E form (figure III). Otherwise, for imine **1c**, these dimers consist of only one single stereoisomer in which the imine ligands are in the E form (figure IV). Work is in progress to apply these compounds to diastereoselective formation of carbon-carbon or carbon-heteroatom bonds.



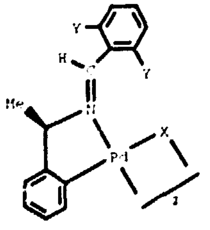
R=2,6-$Cl_2C_6H_3$ (1a)
R=2,6-$F_2C_6H_3$ (1b)
R=2,4,6-$(MeO)_3C_6H_2$ (1b)

I



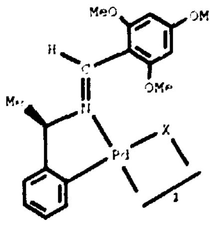
Y=Cl or F
X=Cl, Br or I

II



Y=Cl or F
X=Cl, Br or I

III



X=Cl, Br or I

IV

LAICM2368P **52, Thu. 16**

HETERONUCLEAR ORGANOMETALLIC OXIDES AS MIXED OXIDE PRECURSORS

Angel Abarca, Avelino Martín and Miguel Mena.
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Campus Universitario. 28871-Alcalá de Henares- Madrid-ESPAÑA.

Organometallic oxides may be used as precursors to prepare high surface area of mono and multicomponent oxides, without the very severe conditions of the traditional ceramics preparation technique: high temperature calcination of mixing component oxides.[1]

The major problem found with these precursors is the availability of the starting materials. We wish to report a systematic method for the preparation, in good yield, of heteronuclear organometallic titanium oxides from the trinuclear $[Cp^*TiCl]_3(\mu\text{-}O)_3$[1] ($Cp^*=\eta^5\text{-}C_5Me_5$) and different anhydrous silver oxo salts in organic solvents, with precipitation of silver chloride. The new compounds were studied by conventional spectroscopic and analytical techniques.

$$[1] + nAgX \longrightarrow [Cp^*_3Ti_3Cl_{3\text{-}n}(X)_n](\mu\text{-}O)_3$$

$$n = 3,\ X = ReO_4\ ;\ n = 1 \text{ or } 3;\ X = NO_3$$

$$[1] + AgEO_4 \longrightarrow [Cp^*_3Ti_3Cl(\mu\text{-}EO_4)](\mu\text{-}O)_3$$

$$E = Cr\ [2],\ S$$

$$[2] + AgX \longrightarrow [Cp^*_3Ti_3(X)(\mu\text{-}CrO_4)](\mu\text{-}O)_3$$

$$X = ReO_4\ ,\ NO_3$$

In order to study the thermal behavior of the above compounds, as precursors of mixed oxides, thermogravimetry analysis (TGA) and mass spectrometry (MS) were carried out.

We thank DGICYT(PB90-0294), C.A.M.(C198/91) and Universidad de Alcalá de Henares for support.

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[1] Kung, H.H., *Transition Metal Oxides: Surface Chemistry and Catalysis*, Elsevier Science Publishers: Amsterdam, The Netherlands, 1989.

LAICM2373P **53, Thu. 16**

SYNTHETIC UTILITY OF THE PALLADIUM CATALYZED REACTION OF FUNCTIONALIZED VINYLIC BROMIDES WITH 1-PROPENYLTRIBUTYLTIN AND 1-(E)-HEXENYL BORONIC ACID.

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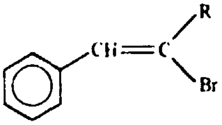
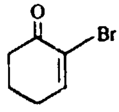
Departamento de Química, Universidad Simón Bolívar, Apartado Postal 89000, Caracas 1080A, Venezuela.

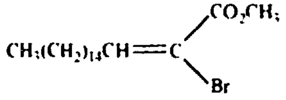
The palladium catalyzed coupling reaction between organotin compounds and organic electrophiles is an important method for the formation of carbon-carbon bonds. On the other hand, alkenylboron compounds also undergo coupling reactions with organic halides. Using vinylic halides as electrophilic partners, these coupling reactions can be applied to the synthesis of stereodefined 1,3-dienes. In this work we have examined these transformations using substituted vinylic bromides I, II and III in order to test its synthetic utility for the preparation of functionalized 1,3-dienes.



I



II



III

R CO_2CH_3, CHO, CH_2OH, H

1-Propenyltributyltin and 1-(E)-hexenylboronic acid were chosen as model compounds. In the first case, dimethylformamide was the reaction solvent while a mixture of water-tetrahydrofuran containing base (potassium carbonate or sodium bicarbonate) was employed for the latter. The catalysts employed were *tetrakis*(triphenylphosphine)palladium(0) and *bis*(acetonitrile)dichloro)palladium(II). The best yields of coupling products were obtained from the reaction with the hexenylboronic acid. Propenyltributyltin afforded significantly lower yields.

NEW ASPECTS ON THE REACTIVITY OF DIOXODIALKYLMOLYBDENUM COMPOUNDS

H. Teruel, A. Kosoy. Departamento de Química, Universidad Simón Bolivar, Apartado 89000, Baruta, Caracas 1070A, Venezuela.

Transition metal-oxo complexes have lately aroused increasing interest because of their relevance in processes of oxygen atom transfer to organic substrates. It has been shown that the Mo=O function is essential not only in most oxidation processes but also in other transition metal catalyzed reactions. Furthermore, metal oxo complexes have been widely studied as models for metal oxide surfaces used in heterogeneous catalysis.

Previous studies have shown that, in solution and under strictly anaerobic .and anhidrous conditions, dioxodialkylmolybdenum compounds of general formula $MoO_2R_2(bpy)$, decompose to yield mainly oxygenated organic products (aldehydes and alcohols) and, to a lesser extend, hydrocarbons. These results were rationalized in terms of an intramolecular oxygen transfer involving a pseudo "keto-enol" tautomerism.

In connection with these studies, we decided to investigate the behaviour of dioxodibenzylmolybdenum (VI) compounds carrying 4,4'-disubstituted bipyridine ligands. The results of the decomposition reaction in solution for these new compounds will be presented and compared to their unsubstitued analogous.

CATALYTIC CYCLOHEXENE HIDROGENATION WITH BIMETALLIC SULPHUR CLUSTERS.

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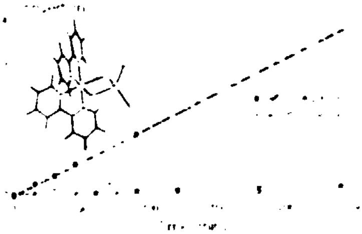
UNAM, Facultad de Química. Ciudad Universitaria, D.F. C.P. 04510. México.

In this work we report the synthesis[1], characterization and catalytic activity of the complexes $[Ru(bipy)_2S_2MoS_2]$, $[Ru(bipy)_2S_2WS_2]$, $[Ru(phen)_2S_2MoS_2]$ and $[Ru(phen)_2S_2WS_2]$ in the cyclohexene hydrogenation.



The thermogravimetric analysis, shows a similar thermal stability in the series of the phenanthroline compounds. The compound $[Ru(bipy)_2S_2MoS_2]$ decomposes at a lower temperature than the other three complexes. The thermal decomposition takes place with the lost of a diimine molecule, in all cases.

The results of the heterogeneous catalytic cyclohexene hydrogenation suggest that the complex $[Ru(bipy)_2S_2MoS_2]$ produces the most active catalytic species.

The molecular mechanic study suggests that it is easier for a bipyridine to leave that it is for a phenanthroline. Extended Hückel calculations have been performed using the program *CACAO*[2] The results point out that the molecular orbitals with high contributions to the Ru-N bonds in the complexes with bipirydine, are different from the corresponding orbitals of the clusters with phenanthroline, wich are practically equal for both complexes.

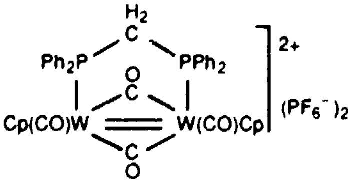
1 Tanaka T Tanaka K and Morimoto M *Inorg Chim Acta* (1981). **56**. L61
2 Mealli C and Proserpio D M *J Chem Ed* (1990). **67**. 399

LAICM2379P **56, Thu. 16**

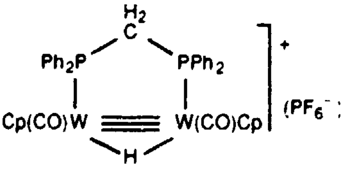
BINUCLEAR DERIVATIVES OF THE UNSATURATED CATION $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PPh_2CH_2PPh_2)](PF_6)_2$

M. A. Alvarez, E. García, V. Riera, M.A. Ruiz.
Dpto. de Química Organometálica, Universidad de Oviedo 33071 Oviedo, Spain

The unsaturated cation $[W_2Cp_2(CO)_4(\mu\text{-dppm})](PF_6)_2$ [Cp = $\eta^5\text{-}C_5H_5$; dppm = $PPh_2CH_2PPh_2$] **1** is an useful synthetic reagent due to its remarkable electrophilic behaviour. For example, complex **1** abstracts F^- from its counterion at room temperature to give the fluoro complex $[W_2Cp_2(\mu\text{-F})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](PF_6)$. Acetic acid or methanol react readly with **1** yielding related species of formula $[W_2Cp_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](PF_6)$ [X = $MeCO_2$, MeO]. Compound **1** formally abstracts an H^- ion from BH_3.thf at -30°C to give the novel unsaturated hydridocomplex $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dppm})](PF_6)$ **2**, instead of the expected (after H^- abstraction) saturated species $[W_2Cp_2(\mu\text{-H})(CO)_4(\mu\text{-dppm})(PF_6)]$ **3**. The latter, however, can be obtained from **2** and CO. Reaction of BH_4^- with **1** neither produces complex **3**, but instead the tricarbonyl cyclopentadienilidene complex $[W_2(\mu\text{-}C_5H_4)Cp(\mu\text{-H})(CO)_3(\mu\text{-dppm})]$. Thus, a high labilization of the CO ligands in **1** seems to dominate its reactions towards many different nucleophiles, under mild conditions (usually below room temperature).



1



2

LAICM2380P **57, Thu. 16**

REACTIVITY OF THE BINUCLEAR ANION $[Mn_2\{\mu-P(OEt)_2\}\{\mu-OP(OEt)_2\}(CO)_6]^{2-}$.

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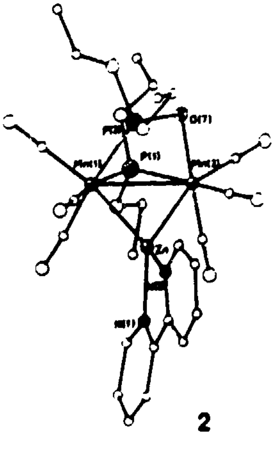
Reduction of the unsaturated dihydride $[Mn_2(\mu-H)_2(CO)_6\{\mu-(EtO)_2POP(OEt)_2\}]$ with Na(Hg) promotes an intramolecular backbone P-O bond oxidative addition of the bridging pyrophosphite ligand, giving the novel dianion $[Mn_2\{\mu-P(OEt)_2\}\{\mu-OP(OEt)_2\}(CO)_6]^{2-}$ (**1**, Na^+ salt). Dianion **1** is highly reactive, and allows the synthesis of novel heterometallic clusters through reaction with suitable halogenocomplexes. In this way, several clusters with metallic cores of the type Mn_2M (M= Zn, Cu, Ag, Au, Sn), Mn_2M_2 (M= Ag, Au) and Mn_2M_3 (M= Au) have been synthesized (ie. $[Mn_2Zn\{\mu-P(OEt)_2\}\{\mu-OP(OEt)_2\}(bipy)(CO)_6]$, **2**). Chemical oxidation of **1** generates a new unsaturation at the dimanganese centre. This, however, does not promote new P-O additions. Instead, ligand abstraction occurs (CO, generated through decomposition, or L, if added to the reaction mixture), to yield species of the type $[Mn_2\{\mu-P(OEt)_2\}\{\mu-OP(OEt)_2\}(CO)_6LL']$ (L,L'= CO or phosphine ligand; ie.: L= CO, L'= PPh_3, **3**).



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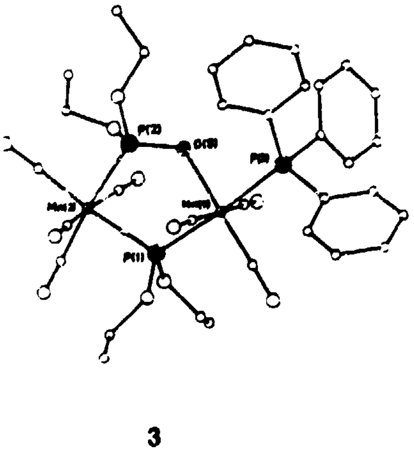

3

NEW HIGH NUCLEARITY IRIDIUM CARBONYL CLUSTERS: SYNTHESIS AND X-RAY MOLECULAR STRUCTURES

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The tetranuclear species $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (1), previously synthesized from $Ir_4(CO)_{11}PPh_2H$ (2) *via* thermolysis or the deprotonation /protonation sequence (up to 95 %) has now been obtained from $Ir_4(CO)_{11}PPh_2Cl$ (3) upon absorption on silica gel or alumina (up to 75 %). Upon varying the conditions of the chromatography, $Ir_6(\mu\text{-}CO)(CO)_{12}(\mu\text{-}PPh_2)_2$ (4) is isolated (up to 40 %) instead of (1). An X-ray analysis has shown that the structure of (4) consists of an octahedral metal frame bearing two bridging phosphido groups. Thermolysis of (1) (THF, 24 h) yields $Ir_8(\mu\text{-}CO)_2(CO)_{13}(\eta^1\text{-}Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ (5) (up to 30 %). The molecular structure of (5) was established by an X-ray analysis. The metal frame is best described as a square-based pyramid fused to an octahedron with a phosphinidene group supporting the base of the pyramid, and the phosphido ligand bridging one of the octahedron edges. This is the first high nuclearity iridium cluster heaving an $\eta^1\text{-}C_6H_5$ ligand. Compound (5) undergoes facile CO substitution with PPh_3 to yield $Ir_8(CO)_{15\text{-}n}(\eta^1\text{-}Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(PPh_3)_n$ {n = 1 - 3; (6) - (8)}, but no CO insertion into the Ir-Ph bond has been observed under a variety of conditions.

DYNAMIC BEHAVIOUR OF THE COMPLEXES $TaCp^*R_2\{\eta^2\text{-}N(Ar)\text{-}CMe_2\}$ AND $TaCp^*R(NAr)\{\eta^1\text{-}N(Ar)\text{-}C(Me){=}CMe_2\}$, ($R{=}Cl$, Me; $Ar{=}2,6\text{-}Me_2C_6H_3$) BY DNMR DATA.

Mikhail V. Galakhov, Manuel Gómez, Gerardo Jimenez and Pascual Royo.
Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain.

Reactions of alkyl monopentamethylcyclopentadienyl Tantalum(V) derivatives with isocyanides ligands lead to different organocomplexes whose synthesis, structure and reactivity have been reported separately.

The study[1] of the dynamic behaviour of these organocomplexes in solution provides additional information not only of the nature of these compounds but also about mechanism of the reactions in which they are involved.

^{13}C NMR studies in the solid state (CP MAS) show the existence of only one isomer for each compound while a process of isomerization for azatantalacyclopropane complexes and the rotation of the CMe_2 group around the C=C double bond for alkenylamido complexes is observed in solution.

According to evaluated kinetic paramaters by using DNMR data will be explained such processes and the structures of transition states will be proposed.

References.

1. a) J.M.Mayer, C.J.Curtis, J.E.Bercaw, J.Am.Chem.Soc.**1983**, 105, 2651.
   b) R.S.Berry, J.Chem.Phys.**1960**, 32, 933.

LAICM2385P

60, Thu. 16

DICYLOPENTADIENYL TITANIUM AND ZIRCONIUM COMPLEXES AS CATALYST FOR HYDROGENATION OF OLEFINES

Tomás Cuenca, Juan Carlos Flores, Pascual Royo

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The catalytic hydrogenation of 1-hexene, 4-methyl-2-pentene (65% cis), ciclohexene, styrene, isoprene, 1,3-cyclooctadiene and 1,5-cyclooctadiene has been studied by using different metallocene-type complexes of stoichiometry Cp_2MX_2, (M=Ti, Zr), containing equivalent, mixed, ansa and bridging cyclopentadienyl ligands. The dichloro complexes (X=Cl) were reduced previously with an escess of magnesium, activated by the addition of a small amount of $HgCl_2$, in the presence or ab-ence of $PMePh_2$. Cyclohexane solutions of the dialkyl derivatives [X=Me, CH_2SiMe_3, CH_2PPh_2, CH_2Ph, Ph, p-MeC_6H_4, PPh_2] were used in reactions generally carried out at 7 bar pressure of hydrogen at 90°C, with a concentration of catalyst around 10^{-3} M and [olefin]/[catalyst] molar ratio between 300 and 500

The figures show some examples of hydrogenation processes

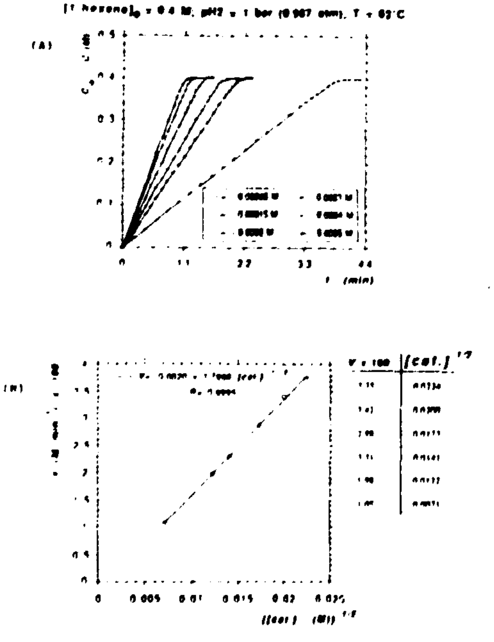

Figure Hydrogenation of 1 hexene catalyzed by T14B
(A) Olefin concentration as a function of time for different catalyst concentrations
(B) Rate of hydrogenation as a function of catalyst concentration

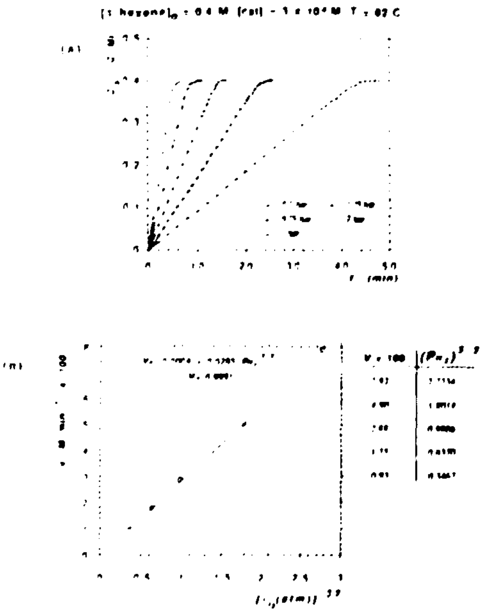

Figure Hydrogenation of 1 hexene catalyzed by T14B
(A) Olefin concentration as a function of time for different hydrogen pressures
(B) Rate of hydrogenation as a function of hydrogen pressure

LAICM2386P **61, Thu. 16**

DINUCLEAR TITANIUM METALLOCENE TYPE COMPLEXES WITH THE BRIDGING DIMETHYLSILYL BIS-CYCLOPENTADIENYL LIGAND.

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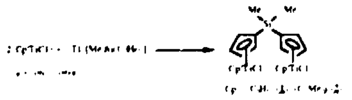
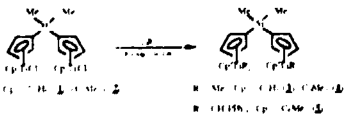
2) Centro de Graduados e Investigación. Instituto Tecnológico de Tijuana. Apdo. Postal 1166. 22000-Tijuana, B.C. (México).

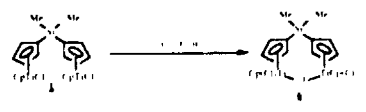
Treatment of $Tl_2[Me_2Si(C_5H_4)_2]$ with two equivalents of $Cp'TiCl_3$ ($Cp' = \eta^5\text{-}C_5H_5$; $\eta^5\text{-}C_5Me_5$) affords the corresponding chloro derivatives $[TiCl_2(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$, (**1**) and $[TiCl_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$, (**2**). **1** and **2** are metallocene type dinuclear complexes which contain the bridging dimethylsilyl-biscyclopentadienyl ligand. Compounds **1** and **2** react with LiR (R = Me, CH_2PPh_2.TMEDA) yielding the alkyl complexes $[TiMe_2(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$, (**3**) and $[TiR_2(\eta^5\text{-}C_5Me_5)]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$, R = Me (**4**); CH_2PPh_2 (**5**). Hydrolysis of **1** produces the μ-oxo derivative $[TiCl(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}O)[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$, (**6**). Compound **6** may also be obtained by reduction of **1** with one equivalent of Na/Hg and subsequent treatment with oxygen. Reduction of **1** with Na/Hg in the presence of PMe_2Ph produces compound **7**, which shows a $\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4$ ligand. All new compounds were characterized by elemental (C,H) analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. Molecular structures of **2** and **6** were determined by single crystal x-ray diffraction methods.



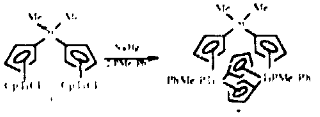
EQUATION 1



EQUATION 2



EQUATION 3



EQUATION 4

ISOCYANIDE INSERTION REACTIONS INTO Ta-Me BONDS OF $TaCp^*Cl_nMe_{4-n}$ (n=1,0) COMPLEXES.

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Maria Angela Pellinghelli and Antonio Tiripicchio
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In this communication we will describe the insertion of isocyanides CN-Ar into Ta-Me bonds of trimethyl and tetramethyl pentamethylcyclopentadienyl Tantalum(V) derivatives.

Addition of CN-Ar to $TaCp^*ClMe_3$ takes place with coordination of the isocyanide followed by the migration of the two methyl groups to give $TaCp^*ClMe(\eta^2\text{-}N(Ar)\text{-}CMe_2)$,**4**. Coordination of a new isocyanide molecule with new double migration of the methyl groups and the terminal alkyl group of the azatantalacyclopropane system, produces an intermediate which cannot be isolated because its rapidly rearranges by C-C coupling and simultaneous C-N bond breaking to give the imido alkenylamido[1] complex **5**, $[TaCp^*Cl(NAr)\{\eta^1\text{-}N(Ar)\text{-}C(Me){=}CMe_2\}]$.

The reaction of the tetramethyl tantalium(V) complex with 1 equivalent of CN-Ar produces a mixture of $TaCp^*Me_2\{\eta^2\text{-}N(Ar)\text{-}CMe_2\}$,**6**, $[TaCp^*Me(NAr)\{\eta^1\text{-}N(Ar)\text{-}C(Me){=}CMe_2\}]$,**7** (major product) and unreacted starting product. **7** is obtained in high yield as a unique product by reaction with 2 equivalents of isocyanide.

All complexes were characterized by usual methods and the results (IR, NMR and X-ray studies) will be discussed.

References.
1. a) L.R.Chamberlain, I.P.Rothwell, J.C.Huffman, J.Chem.Soc.,Chem.Commun. **1986**, 1203.
b) W.K..Chiu, R.A.Jones, G.Wilkinson, A.M.R.Galas, M.B.Hursthouse, **1981**, 2088.

NEW η5-CYCLOPENTADIENYL MOLIBDENUM IMIDO COMPOUNDS

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Organometallic imido complexes are of great interest due in part to their suspected role in different catalytic processes[1].

We have synthesized various imido compounds having the metal center in different oxidation states.

Treatment of $CpMoCl_4$ ($Cp = \eta^5\text{-}C_5Me_5$) (**1**) with ter-butyl amine affords the 17 electron, paramagnetic $CpMoCl_2(NBu^t)$ (**2**) which has been spectroscopically characterized by IR ($\nu_{M=N}$ = 1223 vs, 1206 vs) and by data of microanalysis.This compound is easily hydrolized by air yielding the well known halo-oxo derivative $CpMoO_2Cl$ and a stoichiometric amount of the corresponding ammonium salt.

Reduction of compound **2** with sodium amalgam yields a diamagnetic imido-mono-halo species for which we propose the stoichiometry of a 16 electron compound $CpMoCl(NBu^t)$ (**3**), in agreement with its elemental analysis and spectral measurements.

Analogous reduction of the imido compound **3** in the presence of isonitrile ligands CNR (R = ter-butyl, 2,6 dimethyl phenyl) yields the corresponding diamagnetic 18 electron species $CpMoCl(NBu^t)(CNR)$(**4**), spectroscopycally characterized by IR and NMR.

1.a) M. Bakir, P.E. Fanwich, R.A. Walton, Inorg. Chem., 1988, 27, 2016.
b)E.R. Maata, Y.Du, A.L.Reingold, J. Chem. Soc. Chem. Commun.,1990,756.

RHODIUM(I) COMPLEXES CONTAINING 2,5-NORBORNADIENE AND POLY(AZOL-1-YL)METHANE AS LIGANDS

P. Ballesteros[a], Concepción López[a], Carmen López[a], R.M. Claramunt[a], J.A. Jiménez[b], M. Cano[b], J.V. Heras[b], E. Pinilla[b] and M.A. Monge[c]

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Chemistry of Rh(I) complexes containing polyazolylmethane as ligands has been established. In particular $(pz)_2CHR$ (R= H, pz) and the related $(In)_2CHR$ (R= H, C_6H_5, C_6H_4N) ligands form stable Rh(I) complexes with diolefinic cooligands. In these compounds a bidentate bridge or chelate tridentate behaviour of the polyazolyl ligands has been found. In contrast with the number of species containing the above ligands and COD as diolefin, very few data have been reported for analogous complexes containing the higher π-acceptor NBD.

In this work we performed a systematic study of the reactions of $[Rh(\mu\text{-}Cl)(NBD)]_2$ with polyazolylmethane ligands shown in fig. 1, analizing the type of complex obtained depending on the ligand and on the reaction conditions. Complex structures have been characterized by ^1H and ^{13}C-NMR spectroscopy and X-Ray diffraction (fig. 2). Cationic species have been evidenced in solid state and cationic-neutral species equilibria have been established in solution.

fig. 1

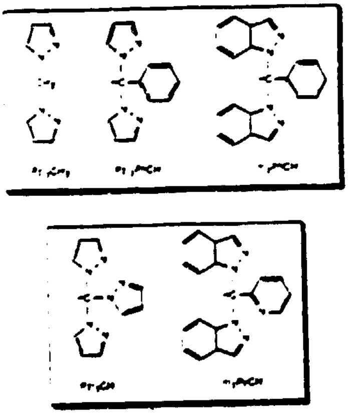
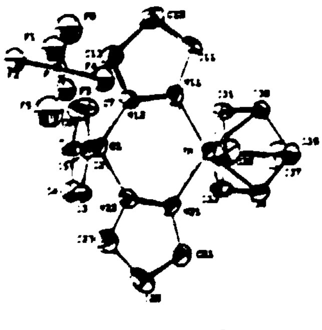


fig. 2



[RhNBD(Pz)$_2$PhCH]PF$_6$

LAICM2393P **65, Thu. 16**

REARRAGEMENT REACTIONS OF THE TRIPODAL LIGAND $[HB(Pr^iMeC_3N_2H)_3]^-$ IN SOME MOLYBDENUM NITROSYL DERIVATIVES

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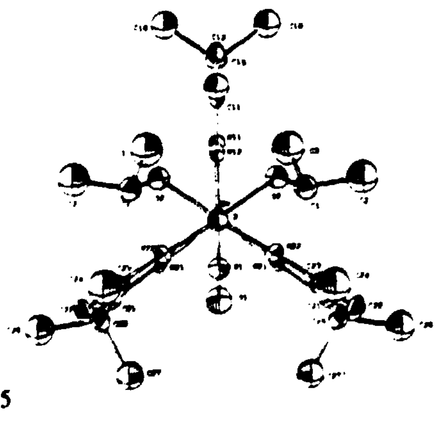
In a previous work we found that the complexes $[MoL^-(NO)(X)(Y)]$ ($L^-=[HB(Pr^iMeC_3N_2H)_3]^-$; X=Y=CO,I; X=I, Y=OR R=Me,Et,Pr,Bu^t,NHC_6H_5,NHC_6H_4-4-Me) were isolated as a mixture of isomers. These complexes undergo rearragement reactions at elevated temperature to give almost selectively a simple isomer.

Following the precedent study we have interesed in knowing the factors which control the rearragement reactions of the ligand which involve 1,2-borotropic shifts of the substituted pyrazolyl moieties.

In this work we have studied the process of formation of $[MoL^-(NO)I(OR)]$ and $[MoL^-(NO)(OR)_2]$ (R= alkoxi substituents containing (R) normal or (R) bulky groups, R= Me, Et, Pr, Bu^t) as a mixture of isomers or only one principal isomer. Monoalkoxide complexes $[MoL^-(NO)I(OR)]$ (R=Me,Et) were produced as a mixture of isomers independing of either the $[MoL^-(NO)I_2]$ complex as mixture or one isomer was used as parent compound. However one isomer could be obtained if an alkoxide group like OPr^i or OBu^t was present in the complex.

The bulkiest ligands allowed to isolate only one isomer $[MoL^-(NO)(OR)_2]$. Crystalline structure of $[MoL^-(NO)(OPr^i)_2]$ has been solved (figure). The bulky Pr^i groups in the tripodal ligand are all in the 3-position close to the OPr^i ligands. This distribution has been found in the related $[MoL^-(NO)(OEt)_2]$ complex.



LAICM2402P **66, Thu. 16**

SYNTHESIS AND CHARACTERIZATION OF RHODIUM AND IRIDIUM COMPLEXES WITH DMPE LIGAND (DMPE = $(CH_3)_2P\text{-}CH_2\text{-}CH_2\text{-}P(CH_3)_2$). STRUCTURE OF $[\{Rh\ Cp^*Cl_2\}_2(\mu\text{-dmpe})][BF_4]_2$. ($Cp^* = \eta^5\text{-}C_5Me_5$).

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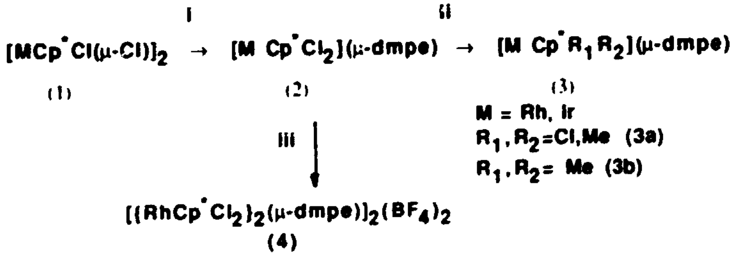
28871- Alcalá de Henares (Madrid) Spain.
F.H. Cano, I.Fonseca Instituto Rocasolano, C.S.I.C. Madrid.

We report the synthesys of μ-bis-(dimethylphosphino) rhodium and iridium complexes of the type $[MCp^*R_1R_2]_2(\mu\text{-dmpe})$ with different terminal ligands: $R_1=R_2=Cl$ (**2a,2b**); $R_1,R_2=$ Cl,Me (**3a**); $R_1=R_2=$ Me (**3b**). These compounds were preparated according to the next scheme.



Reagent: (I) = dmpe; (II) $=Al_2Me_6$; (III) = H_2S, $NaBF_4$.

We have synthesize the compound **4**, in a ~70 % yield, by the reaction of the rhodium dimer **2a** with H_2S in the presence of $NaBF_4$. The structure of **4** has been determined by X-ray analysis.

All new compounds were characterized by ^1H, ^{13}C-{1H} and ^{31}P-{1H} NMR spectroscopy and **2** and **3** (M= Rh) also by ^{103}Rh -{1H}. . All coupling spin-spin constants were obtained by simulation of experimental spectra using iteration LACON3 and PANIC programs continuing to 0.05 RMS error. We will discused some relationships between spectral and structural parameters.

LAICM2403P **67, Thu. 16**

Synthesis of Imido Derivatives of Dinuclear Molybdenum Complexes

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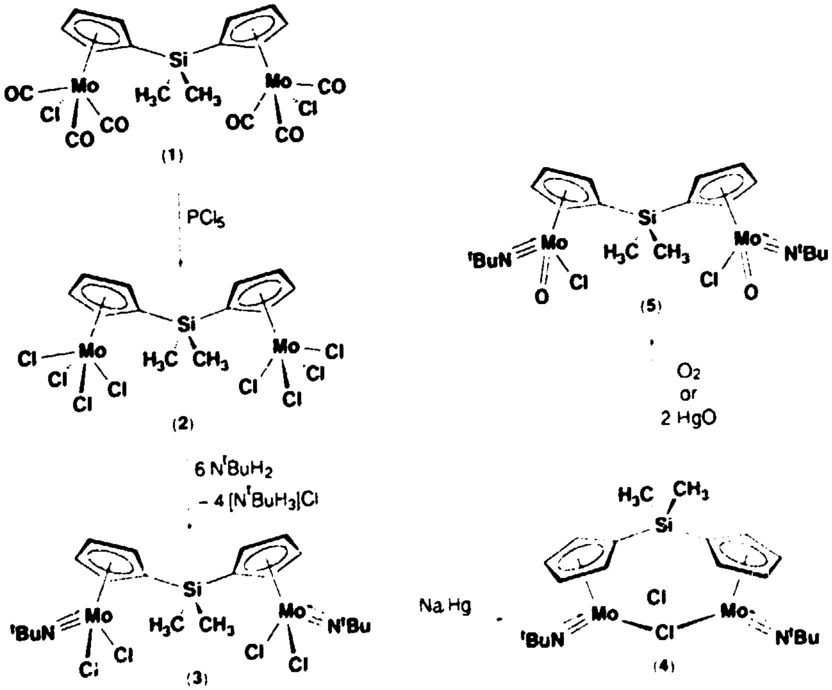
Reaction of [{(C$_5$H$_4$)$_2$SiMe$_2$}Mo$_2$(CO)$_6$Cl$_2$] (**1**) with PCl$_5$ produces [{(C$_5$H$_4$)$_2$SiMe$_2$}Mo$_2$Cl$_8$] (**2**) which reacts with *tert*-butylamine to give the imido derivative **3**. Reduction of **3** with Na/Hg gives the diamagnetic molybdenum(IV) complex **4**. In contrast to the related mononuclear species, complex **4** does not react with ligands as isocyanides. Complex **4** is oxidized by O$_2$ or HgO to give the molybdenum(VI) complex **5**.



LAICM2404P **68, Thu. 16**

COMPETITIVE CONDITIONS IN THE SYNTHESIS OF MONONUCLEAR OR DINUCLEAR ZIRCONIUM COMPLEXES WITH THE DIMETHYLSILYL BIS-CYCLOPENTADIENYL LIGAND.

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The dimethylsilyl bis-cyclopentadieny ligand $[Me_2Si(\eta^5\text{-}C_5H_4)_2]^{2-}$ is capable of cooordination to metallic centers as a chelating (I) or as a bridging group (II) (Figure 1). The chemistry of mononuclear, type I, and dinuclear, type II, compounds have important applications as catalyst in stereo- and enantioselective hydrogenation and polymerization of olefines. Whereas type I compouds have been extensively studied for group 4d metals, type II derivatives are less well known. $Li_2[Me_2Si(\eta^5\text{-}C_5H_4)_2]$ reacts with $Cp'ZrCl_3$ to give a mixture of the dinuclear $[Cp'ZrCl_2]_2[\mu\text{-}Me_2Si(C_5H_4)_2]$ ($Cp'=C_5Me_5$ 1, $C_5H_3(^tBu)_2$ 2) and the mononuclear $[Me_2Si(C_5H_4)_2]ZrCl_2$ (3) compounds. However the dinuclear derivatives 1 and 2 can only be obtained as pure compounds under appropriate conditions (temperature, reaction times and solvent). Treatment of 1 and 2 with LiMe produces the dinuclear tetramethyl derivatives 3 and 4, which under a CO atmosphere give the corresponding acyl complexes 5 and 6. The mononuclear compound 3 also reacts with RM (R=Me, CH_2Ph, $CH_2C(CH_3)_2Ph$, M=Li, MgCl, MgR) to yield the dialkyl derivatives 7, 8 and 9. These dialkyl complexes in the presence of traces of water are transformed into the μ-oxo alkyl compounds 10 and 11.

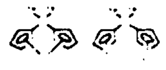
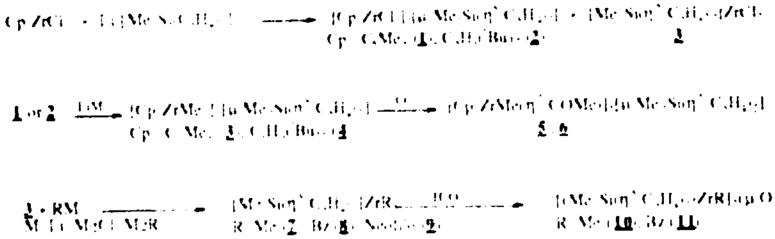


Figure 1



$Cp'ZrCl_3 + Li_2[Me_2Si(C_5H_4)_2] \longrightarrow [Cp'ZrCl_2]_2[\mu\text{-}Me_2Si(\eta^5\text{-}C_5H_4)_2] + [Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrCl_2$

$Cp' = C_5Me_5$ (1), $C_5H_3(^tBu)_2$ (2) 3

1 or 2 $\xrightarrow{LiMe}$ $[Cp'ZrMe_2]_2[\mu\text{-}Me_2Si(\eta^5\text{-}C_5H_4)_2]$ $\xrightarrow{CO}$ $[Cp'ZrMe(\eta^2\text{-}COMe)]_2[\mu\text{-}Me_2Si(\eta^5\text{-}C_5H_4)_2]$

$Cp' = C_5Me_5$ (3), $C_5H_3(^tBu)_2$ (4) 5, 6

3 + RM $\longrightarrow$ $[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrR_2$ $\xrightarrow{H_2O}$ $[[Me_2Si(\eta^5\text{-}C_5H_4)_2]ZrR]_2(\mu\text{-}O)$

M = Li, MgCl, MgR R = Me (7), Bz (8), Neofilo (9) R = Me (10), Bz (11)

LAICM2405P **69, Thu. 16**

DERIVATIVES OF TITANIUM AND ZIRCONIUM WITH THE DI-tert-BUTYL BIS-CYCLOPENTADIENYL LIGAND. SYNTHESIS AND CHARACTERIZATION.

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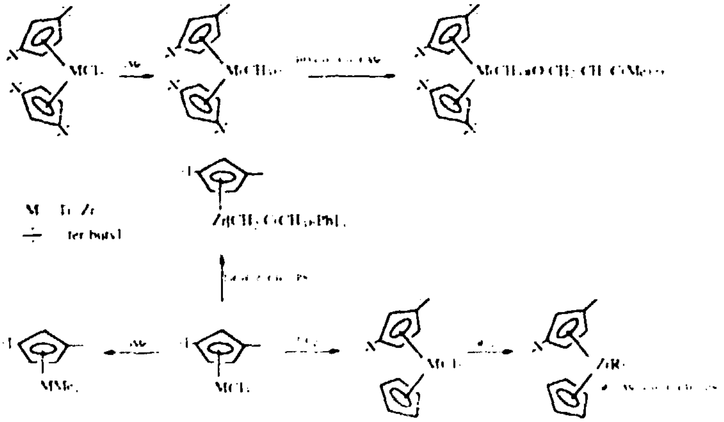
η^5-Cyclopentadienyl derivatives of group 4 metals have played an important role in structural, synthetic and catalytic organometallic chemistry. Replacement of one or more of the cyclopentadienyl ring hydrogens by alkyl or similar groups has been shown to involve important changes in reactivity, stability and other properties due to their steric and electronic effects on the metal center. In this communication we describe the shynthesis, characterization and chemical behavior of titanium and zirconium derivatives containing the 1,3-di-ter-butyl cyclopentadienyl group.



LAICM2407P **70, Thu. 16**

SELECTIVE *ANTI*-MARKOVNIKOV ADDITIONS TO TERMINAL ALKYNES CATALYSED BY RUTHENIUM COMPLEXES

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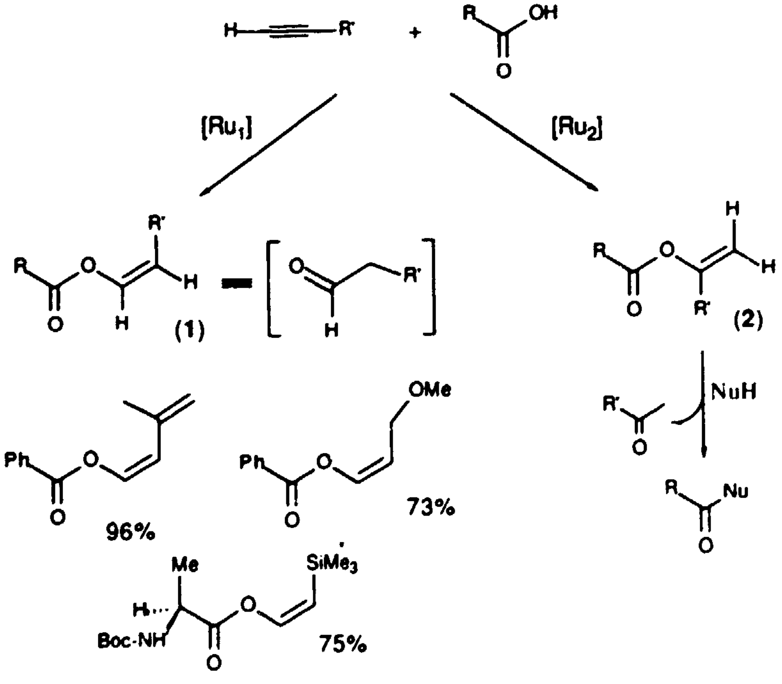
Ruthenium(II) catalysts provide the electrophilic activation of terminal alkynes towards the addition of functional groups. We have shown that specific ruthenium complexes selectively orientate the addition of carboxylic acids at C2 carbon atom of the triple bond affording unsaturated esters of type **2**.

We can now provide evidence that by using chelating diphosphine ruthenium(II) precursors, the *anti*-Markovnikov addition to terminal triple bonds selectively takes place and makes possible the synthesis of a variety of enol esters of type **1** (1).

Whereas enol esters **2** are efficient acylation reagents which react under mild and neutral conditions with amines and alcohols to produce amides and esters with formation of a volatile ketone as by-product, Z-enol esters **1** show potential in organic synthesis as masked aldehydes.



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(1) *J. Chem Soc Chem Commun (1993)*

LAICM2408P **71, Thu. 16**

FULVALENE DERIVATIVES OF TITANIUM AND ZIRCONIUM. SYNTHESIS, CHARACTERIZATION AND CHEMICAL BEHAVIOR.

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The chemistry of titanium (II) and (III) has been well developed whereas zirconium (III) is much less accessible and the reduction of zirconocene dihalides has been, for years, a tempting goal. Recently, we have demonstrated that access to, and the study of, the chemistry of low oxidation satate titanium and zirconium complexes, mainly in oxidation state (III) is facilitated by using fulvalene as ligand. The reaction of $[M(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}Cl)_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (M=Ti **1**, Zr **2**) with $LiPPh_2$ gives the titanium and zirconium (III) derivatives $[M(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}PPh_2)_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_{10}H_8)]$ (M=Ti **3**, Zr **4**). Treatment of **2** with $LiC{\equiv}CR$ permits to obtain the compounds $[Zr(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}C{\equiv}CR)_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_{10}H_8)]$ (R=Ph **5**, Me_3Si **6**). The ^1H NMR spectra of compounds **3**, **4**, **5** and **6** show broad signals for cyclopentadienyl protons at room temperature. These effects can be explained, for **3** and **4** on the basis of the behavior of relaxation time T_1. A dynamic behavior is observed between -60 C and +60 C for **5** and **6**. All the compounds synthesized were characterized by elemental analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and crystal structures of **1** and **6** were determined by x-ray diffraction methods.

LAICM2409P **72, Thu. 16**

SYNTHESIS AND CHARACTERIZATION OF PENTAMETHYLCYCLOPENTADIENYL MOLYBDENUM (IV) COMPLEXES X-RAY STRUCTURE OF $[Cp^{*}MoCl_2(PMe_3)_2][BF_4]$. ($Cp^{*}$ = η C_5Me_5)

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$Cp^{*}MoCl_3$ (**2**) has been generated by reduction of $Cp^{*}MoCl_4$(**1**) with Na/Hg. We were interested in synthesizing cyclopentadienyl molibdenum (IV) complexes in order to probe their efectiveness in further preparation of organometallic oxides.

Reaction of halo compound **2** with phospine ligands yields the corresponding diamagnetic adducts for which we propose the 16 electron stoichiometry $Cp^{*}MoCl_3L$, being L = PPh_3(**3**) or $OPPh_3$(**4**), according to their elemental analysis and spectral measurements.

The ^{1}HNMR spectrum of the adduct **3** reveals a unresolved mixture of isomers, probably due to an intramolecular rearrangement process. Attemps to obtain a single crystal from **3** affords the well know halo-oxo $MoO_2Cl_2(OPPh_3)_2$ derivative.

Treatment of **2** with PMe_3 followed by addition of $NaBF_4$, produces the four-legged piano stool Mo(IV), cis-$[Cp^{*}MoCl_2(PMe_3)_2][BF_4]$ (**5**) crystallographically characterized.

LAICM2410P **73, Thu. 16**

SYNTHESIS AND CHARACTERIZATION OF DIETHYL DITHIOPHOSPHATE DERIVATIVES CONTAINING THE FRAGMENT Cp'M (Cp'= C_5H_5, C_5Me_5; M =Mo,W).

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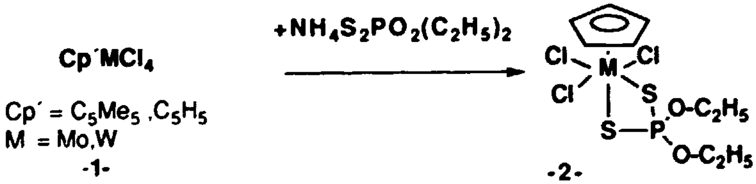
Molibdenum and tungsten compounds with the Et_2dtp ligand (Et_2dtp = OO'-diethyl dithiophosphate (-1)), have been prepared in order to explore their properties in oxygen transfer processes[1].

We report the synthesis of new complexes of the type [Cp'MCl_3 (Et_2dtp)], prepared according to the scheme:



-1- -2-

All the products are paramagnetic species and were characterized by elemental analysis and IR spectroscopy.

A X-ray investigation of (η^5-C_5Me_5)$MoCl_3$(Et_2dtp) (3) reveals a pseudo octahedral structure with a trans Cp-Mo-S arrangement.

Reaction of 3 with Na/Hg yields the diamagnetic (η^5-C_5Me_5)Mo(S_2POEt_2) or the corresponding : (η^5-C_5Me_5)Mo(S_2POEt_2)L adduct, if the reduction is carried out in the presence of the ligand (L = CNBut). In contrast, reaction of the same complex with air or H_2O_2 gives respectively halo-oxo or halo-peroxo derivatives and simultaneous elimination of the S_2POEt_2 ligand occurs.

1. S.Y. Yu and R.H. Holm, Inorg. Chem. 28(1989)4385

LAICM2411P **74, Thu. 16**

PENTAMETHYLCYCLOPENTADIENYL NIOBIUM DERIVATIVES: SYNTHESIS, REACTIVITY AND STRUCTURAL STUDY.

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Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain.

The synthesis[1] of $NbCp^*Cl_4$ in high yield permitted us to study its behaviour in the following types of reactions.

i) When $NbCp^*Cl_4$ reacts with MgClMe in appropriate molar ratio dimethyl and tetramethyl complexes can be isolated. A similar reaction with a 1:1 molar ratio of $LiPPh_2$ leads to the formation of monodiphenyl phosphido complex, but in 1:4 molar ratio produces the first oxo and phosphido-bridged diniobium(III) complex, $[(NbCp^*)_2(\mu\text{-}PPh_2)_2(\mu\text{-}O)]$ as the expected specie with a fourfold bridging phosphido ligand is extremely sensitive to air and very easily hydrolized by traces of water or by addition of the stoichiometric amount of it, with $HPPh_2$ elimination. An analogous result was obtained by using $[NbCp^*Cl_2]_2$[2] as starting material.

ii) The interaction of $NbCp^*Cl_4$ in toluene with L (L=CN-R or PR_3) yields pseudooctahedral species $NbCp^*Cl_4L$. Phosphine derivatives react with alkylating agents leading to the formation of alkylated derivatives whereas with isocyanide complexes insertion reactions occur and η^2-acylimidoyl and imido alkenylamido Niobium(V) species are formed.

All the complexes reported were characterized by usual methods (IR, NMR and X-ray studies) and the relevant structural data will also be discussed.

References. 1.J.de la Mata, R.Fandos, M.Gómez, P.Gómez-Sal, S.Martinez-Carrera,P.Royo,Organometallics,**1990**,9,2846. 2.P.A.Belmonte,F.G.N.Cloke,K.H.Theopold,R.R.Schrock, Inorg.Chem.**1984**,23,2365.

LAICM2412P **75, Thu. 16**

PENTAMETHYLCYCLOPENTADIENYL TANTALUM DERIVATIVES: SYNTHESIS AND STRUCTURAL STUDY OF ALKYL AND ISOCYANIDE COMPLEXES.

Aurora Castro, Irene de Castro, Manuel Gomez, Pilar Gómez-Sal, Pilar Nicolás and Pascual Royo
Departamento Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain

$TaCp^{*}Cl_4$[1] reacts with alkylating agents, such as LiR, {$R=Me_2N\text{-}CH_2\text{-}C_6H_4$; $CH_2SO_2\text{-}C_6H_4(p\text{-}Me)$} and $MgR'_2.(THF)_2$,{$R'=(CH_2)_2C_6H_4\text{-}o$} to give new Tantalum(V) alkyl complexes of the type $TaCp^{*}Cl_3R$,(**1**,**2**), $TaCp^{*}Cl_2(o\text{-}C_6H_4CH_2NCH_2Me)$,**3**, and $TaCp^{*}Cl_2\{(CH_2)_2C_6H_4\text{-}o\}$,**4**.

$TaCp^{*}Cl_4$ coordinates isocyanides or amines easily to give pseudo-octahedral species $TaCp^{*}Cl_4L$, ($L=CN\text{-}Bu^t$,**5**; $CN\text{-}2,6\text{-}Me_2C_6H_3$,**6**; $H_2N\text{-}Ph$,**7**). Reduction of adducts **5**-**6** or alternatively of $TaCp^{*}Cl_4$ with 2 equivalents of sodium amalgam (Na/Hg) or potassium graphite (KC_8) in the presence of the stoichiometric amount of isocyanide led to the diamagnetic pseudo-octahedral Tantalum(III) complexes, $TaCp^{*}Cl_2(CN\text{-}R)_3$,($R=Bu^t$, **8**; $2,6\text{-}Me_2C_6H_3$, **9**). On the other hand, the reduction of $TaCp^{*}Cl_4$ with 1 equiv. of Na/Hg in the presence of LiCp produces new tantalocene derivatives of the type $TaCp^{*}CpCl_2$, {$Cp=\eta^5\text{-}C_5H_4SiMe_3$, **10**; $\eta^5\text{-}C_5H_3(SiMe_3)_2$, **11**} whose reactions with oxidizing and alkylating agents will be reported.

The results obtained in the structural study (IR and NMR) of the reported complexes and X-ray crystallographic data for complexes **3** and **6** will be discussed.

References.

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LAICM2413P 76, Thu. 16

ISOCYANIDE, ACETYLENE AND DIENE PENTAMETHYLCYCLOPENTADIENYL NIOBIUM(III) COMPLEXES.

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Campus Universitario, 28871 Alcalá de Henares, Spain
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In the last years, an important number of isocyanide, acetylene and diene complexes[1] of group 5d elements have been prepared but few belong[2] to the monocyclopentadienyl type species. In this communication, we will present the results obtained in the reduction of $NbCp^*Cl_4$ with sodium amalgam in the presence of appropriate ligands.

Reduction of $NbCp^*Cl_4(CNR)$, ($R=Bu^t$,**1**;2,6-$Me_2C_6H_3$,**2**) adducts or alternatively of $NbCp^*Cl_4$ with 2 equiv. of Na/Hg in the presence of a stoichiometric amount of CNR gives diamagnetic pseudooctahedral Niobium(III) complexes $NbCp^*Cl_2(CNR)_3$, ($R=Bu^t$, **3**; 2,6-$Me_2C_6H_3$,**4**). A similar reduction of $NbCp^*Cl_4$ in the presence of acetylenes and dienes leads to isolation of new Niobium(III) derivatives $NbCp^*Cl_2(R'C{\equiv}CR'')$, ($R'=R''=Me$,**5**;$SiMe_3$,**6**; $R'=Me$, $R''=Et$,**7**; $R'=Ph$, $R''=SiMe_3$,**8**) and $NbCp^*Cl_2$(diene), (diene=isoprene, **9**; methyl metacrylate, **10**).

All complexes were characterized by mass spectrometry and IR and NMR spectroscopy and molecular structures of **2** and **4** were confirmed by X-ray diffraction methods.

References.

1. E.Singleton, H.E.Oosthuizen, Adv.Organomet.Chem.**1984**, 22, 209.
2. H.C.Aspinall, M.M.Roberts, S.J.Lippard, J.Am.Chem.Soc.**1982**, 104, 1263.

MIGRATORY INSERTION OF ISOCYANIDES INTO TANTALUM METHYL BONDS OF $TaCp^*Cl_{4-x}Me_x$ (x=1,2).

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The insertion of isocyanides into M-alkyl bonds produces intermediate iminoacyl derivatives, whose reactivity is dependent on the metal, the nature of substituents[1] and the number[2] of alkyl groups bound to the metal.In this communication, we will present the results observed in the reaction of $TaCp^*Cl_{4-x}Me_x$ (x=1,2) with isocyanides CN-Ar (Ar= 2,6-$Me_2C_6H_3$; 2,4,6-$Me_3C_6H_2$).

$TaCp^*Cl_2Me_2$ reacts with 1 equiv. of CN-Ar with the formation of the η^2-acylimidoyl complex **1**, similar to that observed when $TaCp^*Cl_3Me$ is used. However, a further instantaneous reaction produces the migration of the second methyl group to the electrophilic acylimidoyl carbon atom to give an azatantalacyclopropane complex **2**. Complex **2** reacts easily with 1 equivalent of CN-Ar which is then inserted and subsequently transformed into the imido derivative $TaCp^*Cl_2(NAr)$,**3**, with elimination of the arylimine ketene. Complex **3**. presents a three legged piano-stool disposition with a short Ta-N distance of 1.77 Å consistent with a triple bond.

References.

1. A.C.Filippou, W.Grünleitner, C.Völk, P.Kiprof, J.Organomet.Chem. **1991**, 413, 181.
2 W.K.Chiu, R.A.Jones, G.Wilkinson, A.M.R.Galas, M.B.Hursthouse, J. Chem.Soc.,Dalton Trans **1981**, 2088

PHOSPHINO AND CARBONYL DERIVATIVES OF MONOPENTAMETHYLCYCLOPENTADIENYL NIOBIUM(III).

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The chemistry of pentamethylcyclopentadienyl half-sandwich complexes of the heavier group 5d elements is receiving growing attention after the tetrahalides were prepared in high yields[1]. Here, we will describe the synthesis and characterization of new Niobium(III) derivatives containing carbonyl, tertiary phosphine and dmpe ligands and the Niobium(IV) complex of this bidentate phosphine.

The reduction of $NbCp^*Cl_4$ in the presence of dmpe $\{Me_2P\text{-}(CH_2)_2\text{-}PMe_2\}$ with 1 equiv. of Na/Hg led the paramagnetic complex, $NbCp^*Cl_3(dmpe)$,**1**, whereas monomeric and paramagnetic Niobium(III) compounds of the type $NbCp^*Cl_2L_2$, ($L=PMe_3$,**2**; PMe_2Ph,**3**; dmpe,**4**) were obtained by using 2 equivalents of the reducing agent in the presence of L. Analogous results can be observed by addition of L to toluene solutions of $[NbCp^*Cl_2]_2$,**5**, which can be prepared by reduction of $NbCp^*Cl_4$ in the absence of L. These Niobium(III) complexes reacted with CO to give pseudooctahedral diamagnetic species $NbCp^*Cl_2(CO)_2L$, ($L=PMe_3$,**6**; PMe_2Ph,**7**) and $NbCp^*Cl_2(CO)(dmpe)$,**8**

Paramagnetic complexes were characterized by ^1H NMR, EPR and magnetic measurements. The structural behaviour of all the reported compounds will be discussed.

References.

1. J.de la Mata, R.Fandos, M.Gómez, P.Gómez-Sal, S.Martinez-Carrera, P.Royo, Organometallics, **1990**, 9, 2846.

LAICM242:P **79, Thu. 16**

2,5-NORBORNADIENE RHODIUM(I) COMPLEXES WITH SUBSTITUTED PYRAZOLYL AND TRISPYRAZOLYLBORATE AS LIGANDS

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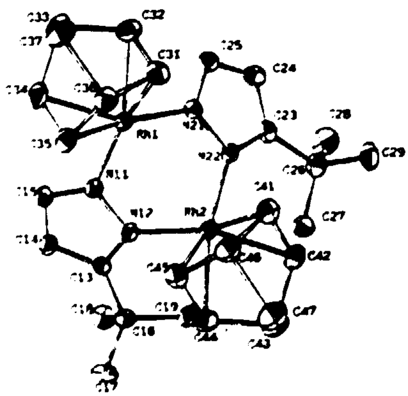
Non-rigid stereochemistry has been observed in different compounds of the type $[Rh\{HB(pz^*)_3\}(olefin)_2]$. This behaviour has been considered depending on the coordinative form and on the enviroment of the trispyrazolylborate ligand in the complexes. These studies have been generally realized in complexes containing pz* = pz, 3,5-Me_2pz and $(olefin)_2 = (C_2H_4)_2$, COD as ligands.

In this work we report the formation of related compounds containing highly demanding trispyrazolylborate $[HB(pz^*)_3]$ (pz* = 3,5-Me_2pz, 3-*t*-Bupz, 3-*t*-Bu-5-Mepz) and 2,5-norbornadiene (NBD) as ligands. Analogous reactions are also studied with substituted pyrazolyl ligands, Hpz* (pz* = 3,5-Me_2Pz, 3-*t*-Bupz, 3-(*p*-$MeOC_6H_4$)pz).

The type of compound obtained depends on the nature of the substituents on the pz rings and on the reaction medium. So, [RhCl(NBD)(Hpz*)], $[Rh\{HB(pz^*)_3\}(NBD)]$ and $[Rh(\mu\text{-}pz^*)(NBD)]_2$ complexes have been obtained and characterized.

The crystal structure of the pyrazolate complex $[Rh(\mu\text{-}3\text{-}t\text{-}Bupz)(NBD)]_2$, obtained in the reaction of $[Rh(\mu\text{-}Cl)(NBD)]_2$ with $[HB(3\text{-}t\text{-}Bupz)]_3$ or H(3-*t*-BuPz) in alcaline medium, has been solved and is shown in the figure.

A dinamic behaviour has been observed by H-NMR for some of these species.



LAICM2423P **80, Thu. 16**

SYNTHESIS OF η^3-S_2CPMe_3 COMPLEXES OF Mo AND W(0) AND SOME NEW BIS(IMIDO) DERIVATIVES OF Mo(VI).

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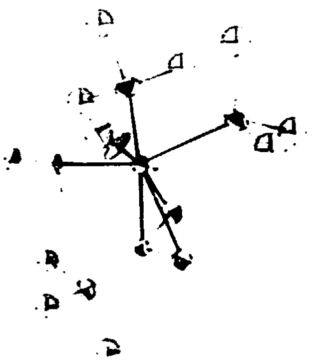
Reaction of $LiBEt_3H$ with the chlorocarbonyls $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) affords the new hydrides $MH(Cl)(CO)_2(PMe_3)_3$. These hydrides have shown reactivity with the anionic salts of bidentate groups such as xanthate or dithiocarbamate. Additionally, the interaction with CS_2 and PMe_3 gives in a stepwise reaction the dithioformate complexes $[M(S_2C(H)PMe_3)(CO)_2(PMe_3)_2]Cl$ and the phosphoniumdithiocarboxylate compounds $M(\eta^3$-$S_2CPMe_3)(CO)_2(PMe_3)_2$. This reaction constitutes an alternative route to the molybdenum derivative $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$, previously prepared in our group, and a synthetic procedure for the tungsten analog. Both complexes show an η^3-S_2CPMe_3 coordinated group, unequivocally demonstrated for the W compound by means of an X-ray crystal structure determination.



In this communication we will also report the preliminary results obtained by treatment of the bis(imido) complex $MoCl_2(=N(2,4\text{-}Me_2C_6H_4))_2(DME)$ with anionic tridentate ligands (polypirazolylborate, Kläui's ligand, etc) as well as some reactions with phosphines.

E. Carmona, A. Galindo, A. Monge, M. A. Muñoz, M. L. Poveda, C. Ruiz *Inorg. Chem.* 1990, 29, 5074.

LAICM2426P 81, Thu. 16

FACILE CONVERSION OF A *cis*–BIS(ETHYNIL)DIPHOSPHINEPLATINUM(II) COMPLEX INTO AN (η^2–BUTADIYNE)PLATINUM(0) DERIVATIVE ASSISTED BY THE TRIPHENYLPHOSPHINEGOLD(I) CATION.

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Phosphorus NMR spectroscopy measurements were performed to study the stepwise formation of the products formed during the stoichiometric and time dependent reactions between *cis*-$[Pt\{C\equiv CPh\}_2\{dppf\}]$ {dppf = 1, 1′-bis(diphenylphosphine) ferrocene} and $[Au\{PPh_3\}][SO_3CF_3]$ in tetrahydrofuran at room temperature. The two final products identified were $[Pt\{\eta^3\text{-}C\{C\equiv CPh\}\text{-}C\{Ph\}AuPPh_3\}\{dppf\}][SO_3CF_3]$, with the $Au(PPh_3)$ substituent at the 1-position of the enynyl ligand, formed when an equimolar mixture of reactants was used, and also, the zerovalent platinum diyne complex $[Pt\{\eta^2\text{-}PhC\equiv CC\equiv CPh\}\{ddpf\}]$, obtained as the main product, when two fold excess of the *cis*-bis(ethynil)platinum complex was employed. Complementary experiments have shown that the complex $[Pt\{\eta^2\text{-}PhC\equiv CC\equiv CPh\}\{ddpf\}]$ reacts with $[Au\{PPh_3)][SO_3CF_3]$ to give $[Pt\{\eta^3\text{-}C\{C\equiv CPh\}\text{-}C\{Ph\}AuPPh_3\}\{dppf\}][SO_3CF_3]$, which reacts reversely with cis-$[Pt\{C\equiv CPh\}_2\{dppf\}]$ to afford $[Pt\{\eta^2\text{-}PhC\equiv CC\equiv CPh\}\{ddpf\}]$. Such results reveal that both compounds *cis*-$[Pt\{C\equiv CPh\}_2\{dppf\}]$ and $[Au\{PPh_3\}]^+$ mediate the overall reaction. Complexes $[Pt\{\eta^3\text{-}C\{C\equiv CPh\}\text{-}C\{Ph\}AuPPh_3\}\{dppf\}][SO_3CF_3]$ and $[Pt\{\eta^2\text{-}PhC\equiv CC\equiv CPh\}\{ddpf\}]$ were isolated and characterized by microanalyses, IR, ^1H, and ^{31}P NMR spectroscopies.

LAICM2427P **82, Thu. 16**

REACTION OF $[Fe_3(CO)_{12}]$ COMPLEX WITH BIDENTATE PHOSPHINES.

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The reaction of $[Fe_3(CO)_{12}]$ complex with tertiary phosphines, generally produces the well-known mono, di or trinuclear complexes, in very poor yields. Herein, we report the synthesis of new series of iron carbonyl derivatives of bidentate phosphines ligands with various coordination modes, using trimethylamine oxide as decarbonylating agent in methylene dichloride at room temperature. Although diphosphines act as a typical bidentate ligands at a single metal centre, they can also act as bridging ligands affording dimeric species. When $[Fe_3(CO)_{12}]$, diphosphines and TMNO are used in the 1:1:2 molar ratio, the product obtained was the dark purple complex $[Fe_3(CO)_{10}](\mu,\eta^2$-diphosphines). However, in reactions using 2:1:2 molar ratio, the product is dark green, characterized as $[Fe_3(CO)_{11}]_2(\mu,\eta^2$-diphosphines), with the diphospnine acting as bridging ligand. Moreover, when the reagents are used in the 1:1:1 molar ratio, only the complex $[Fe_3(CO)_{11}]_2(\eta^1$-dppa) is obtained, where dppa (1,2-bis(diphenylphosphine)acetylene acts as a monodentate ligand. Products were obtained in the range 20-30% yield and were isolated by chromatography on silica plates (TLC), using methylene chloride/light petrolium ether (3:7, v/v) as eluant. All products were characterized by infrared, ^1H, ^{31}P, ^{13}C NMR spectroscopies and elemental analysis.

LAICM2429P

83, Thu. 16

REACTIONS OF [Ru(η^5-C_9H_7)ClL$_2$] WITH 2-PROPYN-1-OL DERIVATIVES: SYNTHESIS OF ALKENYL VINYLIDENE AND ALLENYLIDENE COMPLEXES

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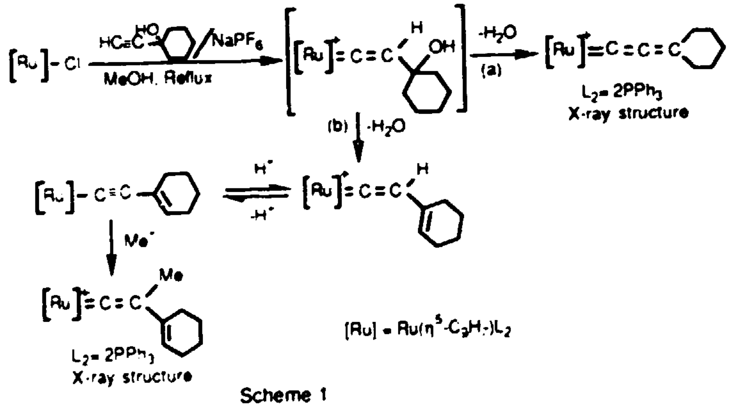
Reaction of [Ru (η^5-C_9H_7)ClL$_2$] (L_2 =2PPh$_3$, dppe) complexes with 1-ethynylciclohexanol in the presence of NaPF$_6$ in refluxing methanol leads to hydroxyvinylidene intermediates, which spontaneously dehydrate in situ to give cationic cycloalkenyl vinylidene (path a) and allenylidene (path b) ruthenium compounds (scheme 1).Deprotonation of cationic cycloalkenyl vinylidene derivatives produces enynyl complexes [Ru(η^5-C_9H_7)(C≡CR)L$_2$] (R =cyclohexenyl) which can be protonated to give exclusively the parent vinylidene compounds. The reaction with MeOSO$_2$CF$_3$ leads to the formation of cationic methylvinylidene complexes which are isolated as the triflate salts.



Scheme 1

On the other hand, allenylidene complexes [Ru(C=C=CPh$_2$)(η^5-C_9H_7)L$_2$][PF$_6$] (L_2= 2PPh$_3$, dppe, dppm) are formed exclusively when 1,1-diphenyl-2-propyn-1-ol are used.

Studies about the reactivity of allenylidene derivatives towards nucleophilic reagents (PR$_3$, KOH NaOMe, LiC≡CR) will be discussed.

LAICM2430P

84, Thu. 16

NEW INDENYL HYDRIDE RUTHENIUM COMPLEXES. SYNTHESIS OF η^2- DIHYDROGEN AND DIHYDRIDE COMPLEXES

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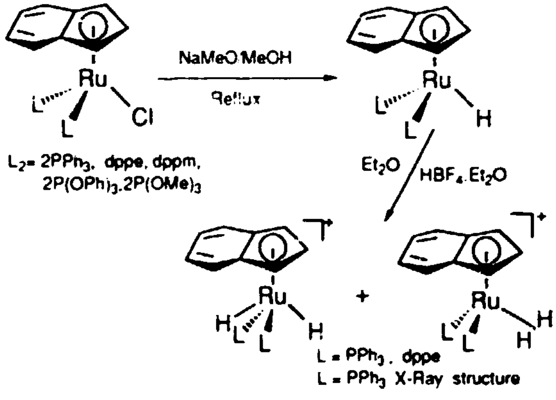
†Departamento de Química Organometálica, ††Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo (Spain)



Scheme 1

We have prepared new indenyl hydride complexes of ruthenium following the methodology developed for the synthesis of cyclopentadienyl complexes[1] (Scheme 1). We have found that the reaction of the indenyl-containing ruthenium chloride complex with methoxide ion leading to ruthenium hydride complexes takes place faster compared with the analogous Cp-containing complex, probably as a consequence of a $\eta^5 \rightarrow \eta^1$ slipping effect (Indenyl effect).

Protonation of a solution of hydride complexes with HBF$_4$.Et$_2$O gives the dihydride or the η^2 - dihydrogen complexes or a mixture of both compounds. In relation with the formation of either complex, the influence of the basicity and steric demand of the auxiliary ligands are being studied.

References

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SYNTHESIS AND REACTIVITY OF NEW ALKYNYL NITROSYL MOLYBDENUM AND TUNGSTEN COMPLEXES.

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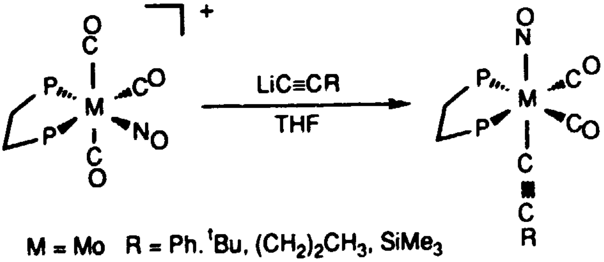
Continuing our study on the chemistry of acetylide complexes[1], we describe herein the synthesis of σ-alkynyl derivatives of Mo and W (Scheme 1). On the other hand, compound $[Mo(C{\equiv}CH)(CO)_2(dppe)(NO)]$ is prepared by adding an excess of a sodiumacetylide slurry to a suspension of the corresponding mer-tricarbonyl complex



M = Mo R = Ph, ^tBu, $(CH_2)_2CH_3$, $SiMe_3$
M = W R = Ph, ^tBu

Scheme 1

All compounds have been fully characterized by elemental analyses, NMR (^1H, ^{31}P, ^{13}C), infrared and mass spectra data. The crystal structure of $[Mo(C{\equiv}C\text{-}(CH_2)_2CH_3)(CO)_2(dppe)(NO)]$ has been determined by X-ray diffraction method.

Studies about the reactivity of these complexes towards electrophilic reagents (H^+, Me^+) with the aim of synthesizing new vinylidene derivatives will be discussed.

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1. a) M.P. Gamasa, J. Gimeno, E. Lastra, M. Lanfranchi, A. Tiripicchio, J. Organometal. Chem., 1991, **405**, 333. b) J. Díez, M.P. Gamasa, J. Gimeno, A. Aguirre, S. García-Granda, Organometalllics, 1991, **10**, 380.

LAICM2432P

86, Thu. 16

ALKYNYL COPPER (I) COMPLEXES

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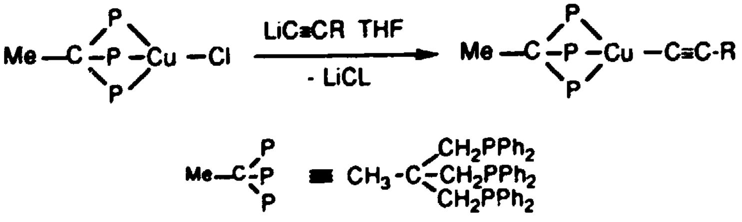
Most alkynyl copper (I) complexes are polymeric solids and their insolubility prevents a full structural characterization. We have recently described[1,2] a versatile route for the preparation of tri and tetranuclear alkynylcopper (I) complexes, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_x(\mu_3\text{-}Cl)_y(\mu\text{-}dppm)_3][BF_4]_z$ (x=2, y=0, z=1; x=1, y=1, z=1; x=1, y=0, z=2; R= ^tBu, Ph, CH_2OCH_3) and $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(L\text{-}L)]_4$ (L-L= Ph_2Ppy (P-bonded), R= ^tBu, Ph; L-L= dppm-P, R= Ph).

In this context the reactivity of different copper (I) complexes like $[Cu(bipy)(NCMe)_2]^+$ or $[CuCl(L_3)]$ (L_3=1,1,1-tris(diphenylphosphino methyl)ethane) with several lithium acetylides is explored.

Mononuclear alkynyl complexes are obtained by reaction of $CuCl(L_3)$ with $LiC{\equiv}CR$ (R= Ph, ^tBu, $(CH_2)_2CH_3$) (Scheme 1). Similar reaction using $[Cu(bipy)(NCMe)_2]^+$ and $LiC{\equiv}C^tBu$ as starting materials produces $[Cu_3(bipy)_3(C{\equiv}C^tBu)][BF_4]_2$.



Scheme 1

References

1. M.P. Gamasa, J. Gimeno, E. Lastra and X. Solans, J.Organometal. Chem., 1988,**346**, 277.

LAICM2439P **87, Thu. 16**

SYNTHESIS AND OXIDATION OF MONO AND BINUCLEAR COMPLEXES OF Fe AND Mn WITH BRIDGING $CCCH_2CH_2CN$ LIGANDS.

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The Iron alkynyl complex $[Cp(dppe)Fe\text{-}CC\text{-}CH_2CH_2\text{-}CN]$ (**1**) ($Cp=C_5H_5$, $dppe=Ph_2PCH_2CH_2PPh_2$) has been prepared from $[Cp(CO)_2Fe\text{-}CCCH_2CH_2CN]$ and dppe under UV irradiation. This compound can be protonated with HBF_4 in ether to give the cationic vinilidene complex $[Cp(dppe)Fe{=}C{=}CHCH_2CH_2CN]\ BF_4$ (**2**). The alkyne-nitrile complex $[Cp(dppe)Fe\text{-}NC\text{-}CH_2CH_2\text{-}CCH]\ PF_6$ (**3**), which has the cation isomeric of **2**, was prepared form $NC\text{-}CH_2CH_2\text{-}CCH$ and $[Cp(dppe)FeI]$ in CH_2Cl_2 in the presence of $TlPF_6$.

The alkynyl complex **1**, that has an uncoordinated -CN group, reacts with $[CpFe(dppe)I]$ and $TlPF_6$ in CH_2Cl_2 to give the cationic binuclear complex $[Cp(dppe)Fe\text{-}CC\text{-}CH_2CH_2CN\text{-}Fe(dppe)Cp]\ PF_6$ (**4**), and with trans-$\{MnBr(CO)_2(dppm)[P(OPh)_3]\}$ ($dppm=Ph_2PCH_2PPh_2$), to give the heterobinuclear derivative $\{Cp(dppe)Fe\text{-}CCCH_2CH_2CN\text{-}Mn(CO)_2(dppm)[P(OPh)_3]\}\ PF_6$ (**5**).

Following our previous studies on the redox behaviour of binuclear complexes with bridging ligands[1,2], we have studied the oxidation of the new mono and binuclear complexes with the cyano-alkynyl ligand electrochemically by Cyclic Voltammetry. The results clearly indicated that the binuclear complexes undergo two one electron oxidations, the first of which occurs always in the Cp(dppe)Fe-CC- center, and the second at the -CN-Fe(dppe)Cp or $\text{-CN-}Mn(CO)_2(dppm)[P(OPh)_3]$ centers. The potential of the first oxidations are almost identical to the potentials of the oxidation of the mononuclear complex **1**, and the potentials for the second oxidations are very close to the values observed for the oxidation of the complexes **3**, and $[Cp(dppe)Fe\text{-}NCMe]PF_6$, or $\{Mn(NCMe)(CO)_2(dppm)[P(OPh)_3]\}\ PF_6$ These data clearly indicate that the two metal centers are independent, and that in the oxidized dicationic species there is no electron delocalization.

The above observations were consistent with the results of the MO calculations at the EH level carried out in the model molecule $[Cp(PH_3)_2Fe\text{-}CCCH_2CH_2CN\text{-}Fe(PH_3)_2Cp]^+$.

1. G.Barrado, G.A. Carriedo, Carlos Diaz-Valenzuela, V. Riera. Inorg. Chem. 1991, 30, 4416.

2. G.A.Carriedo, N.G.Connelly, S.Alvarez, E.Perez-Carreño, S.Garcia-Granda. Inorg.Chem. 1993 32,272

CLUSTER SYNTHESIS BY PHOTOLYSIS OF AZIDO COMPLEXES OF PLATINUM AND GOLD. CRYSTAL STRUCTURE OF $[(dppe)PtCo_2(CO)_7]$, $[(Ph_3PAu)_4Pt(dppe)](PF_6)_2$ and $[(Ph_3PAu)_6(AuCl)_3Pt(CO)]$.

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Upon photolysis of $(dppe)Pt(N_3)_2$ and $Co_2(CO)_8$ in thf one μ_2 CO ligand of the cobalt carbonyl is substituted by a (dppe)Pt group yielding $[(dppe)PtCo_2(CO)_7]$ (**1**). It forms dark red crystals with the monoclinic space group $P2_1/n$ and $a = 1303.9(3)$, $b = 1768.1(8)$, $c = 1461.1(4)$ pm, $\beta = 102.81(1)°$; $Z=4$. In the triangular $PtCo_2$ cluster one of the CO groups binds as a μ_3 ligand.

Photolysis of **1** with excess Ph_3PAuN_3 affords the clusters $[(Ph_3PAu)_4Pt(dppe)]^{2+}$ (**2**) and $[(Ph_3PAu)_6AuCo_2(CO)_8]^+$ [1]. **2** crystallizes with PF_6^- as counterions in the triclinic space group $P\bar{1}$ with $a = 1369.1(1)$, $b = 1505.0(4)$, $c = 2773.0(8)$ pm, $\alpha = 84.74(1)°$, $\beta = 87.37(2)°$, $\gamma = 65.91(2)°$, $Z = 2$. The Au_4Pt skeleton of **2** forms a trigonal bipyramid with the platinum atom in equatorial position.

Photolysis of a mixture of Ph_3PAuN_3, Ph_3PAuCl, and $(Ph_3P)_2Pt(N_3)_2$ in thf yields after chromatographic separation with $CH_2Cl_2/EtOH$ as eluens the cluster $[(Ph_3PAu)_6(AuCl)_3Pt(CO)]$ (**3**). It crystallizes in the triclinic space group $P\bar{1}$ with $a = 2139.3(4)$, $b = 2157.1(1)$, $c = 2561.9(1)$ pm, $\alpha = 79.71(9)°$, $\beta = 80.06(6)°$, $\gamma = 66.05(5)°$, $Z = 4$. The nine gold atoms in **3** form a fragment of an icosahedron with the platinum atom in its center. The formation of the platinum bonded CO ligand is explained by participation of EtOH in the reaction:

$$(Ph_3P)_2Pt(N_3)_2 + 4\ Ph_3PAuN_3 + 5\ Ph_3PAuCl + C_2H_5OH \longrightarrow$$
$$[(Ph_3PAu)_6(AuCl)_3Pt(CO) + 9\ N_2 + 5\ PPh_3 + CH_4 + 2\ HCl$$

[1] G. Beuter and J. Strähle; J. Organomet. Chem. **372** (1989) 67.

LAICM2441P **89, Thu. 16**

SYNTHESIS OF ARYL THALLIUM(III) COMPLEXES WITH Tl-O-P, Tl-S-P OR Tl-P BONDS.

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[c]*Institut für Anorganische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Germany.*

During the last years, aryl Tl(III) chemistry has not experienced great advances and the review of H. Kurosawa[1,2] (including literature until 1982) compile most of the existing complexes. Thus, the TlR_2XL complexes, seldom show the presence of both R= aryl group and L=phosphine or phosphine oxide ligand and only eight compounds are reported: $Tl(C_6F_5)_2X(OPPh_3)$ (X= $Cl, Br, O_2CC_6F_5, O_2CCF_3$), $Tl(C_6F_5)_2X(PPh_3)$ (X= Cl,Br) and $Tl(C_6F;H)_2X(OPPh_3)$ (X= Cl,Br). None of the complexes corresponding to this stoichiometry contains neutral phosphine bidentated ligands.

We have studied the formation of aryl Tl(III) complexes, such us TlR_2XL, with R= C_6F_5, X=Cl,acac and L= $OPh_2P\text{-}CH_2\text{-}PPh_2O$ or $SPh_2P\text{-}CH_2\text{-}PPh_2S$, as well as TlR_3L derivatives with R=C_6F_5 and L=PPh_3, $OPPh_3$, dppm, OdppmO.

The reaction of $Tl(C_6F_5)_2Cl(OdppmO)$, with $Au(acac)PPh_3$ or with Tl(acac) leads to the preparation of $Tl(C_6F_5)(acac)(OdppmO)$. An X-ray crystallographic study has shown that this complex is polymeric with six coordinate tallium atoms.

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[1] H. Kurosawa and R. Okawara, Organometal. Chem. Rev. A, 6, 65(1970)

[2] H. Kurosawa, Comprehensive in Organometallic Chemistry, Vol. 1-X

LAICM2442P **90, Thu. 16**

TRIS(DIPHENYLPHOSPHINO)METHANE OR METHANIDE POLINUCLEAR COMPLEXES OF GOLD, CHROMIUM, MOLIBDENUM AND TUNGSTEN.

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The reaction of tris(diphenylphosphino)methane with different transition metal fragments shows the ability of this ligand in adopting different coordination modes. Therefore, it can act as bidentate chelating in $[(CO)_4M(PPh_2)_2CHPPh_2]$ (M = Cr, Mo, W), bidentate bridging in $[(Ph_2PCH(PPh_2AuPPh_2)_2CHPPh_2](ClO_4)_2$ or tridentate bridging ligand in $[CH(PPh_2AuPPh_2)_3CH](ClO_4)_3$ and $[(RAu)_3(Ph_2P)_3CH]$.

Some of these complexes can displace weakly coordinated ligands in gold affording polinuclear derivatives such as $[RAuPPh_2CH(PPh_2AuPPh_2)_2CHPPh_2AuR](ClO_4)_2$ or $[(CO)_4M(PPh_2)_2CHPPh_2AuX]$ (X = Cl, C_6F_5).

The methine proton of the triphosphine can be removed by reaction with bases such us $[NBu_4](acac)$ leading to methanide complexes of the types $NBu_4[(CO)_4M(PPh_2)_2CPPh_2AuX]$ or $[Ph_2PC(PPh_2AuPPh_2)_2CPPh_2]$. The latter can be synthesized by reaction of $(Ph_2P)_3CH$ and $[Au(acac)PPh_3]$. This compound is slowly oxidized by air at the free phosphorous atom and quickly with H_2O_2 to give $(O)PPh_2C(PPh_2AuPPh_2)_2CPPh_2(O)$.

Single crystal X-ray studies have been carried out for complexes $(O)PPh_2C(PPh_2AuPPh_2)_2CPPh_2(O)$ and $NBu_4[(CO)_4Mo(PPh_2)_2CPPh_2AuC_6F_5]$.

THE SYNTHESIS AND CHARACTERIZATION OF DI AND TRINUCLEAR PLATINUM COMPLEXES WITH DOUBLE ACETYLIDE BRIDGES

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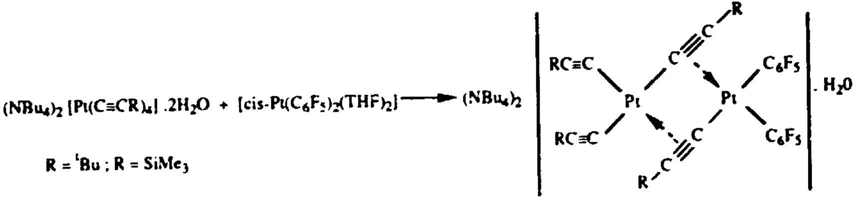
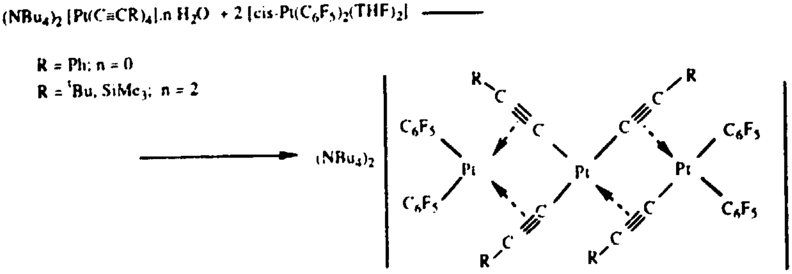
Homoleptic σ-bonded tetrakis(acetylide) complexes $(NBu_4)_2[Pt(C{\equiv}CR)_4].2H_2O$ ($R = {}^tBu, SiMe_3$) react with $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$ (THF = tetrahydrofuran) in a 1:1 molar ratio to produce binuclear derivatives $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2].H_2O$ with bridging C≡CR groups (ec. 1).



ec. 1

Similar treatment of $(NBu_4)_2[Pt(C{\equiv}CR)_4].nH_2O$ ($R = Ph$, $n = 0$; $R = {}^tBu, SiMe_3$, $n = 2$) with $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$ in a 1:2 molar ratio affords trinuclear complexes $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (ec. 2).



ec. 2

The trinuclear compound (R = Ph) has been characterized by X-ray crystallography. The structure of the anion shows two different doubly acetylide bridging systems and represent the first example of a trinuclear platinum complex where the metal centers are doubly bridged by acetylide ligands.

LAICM2444P **92. Thu. 16**

SYNTHESIS OF POLYNUCLEAR Pt, Ag ACETYLIDE COMPLEXES

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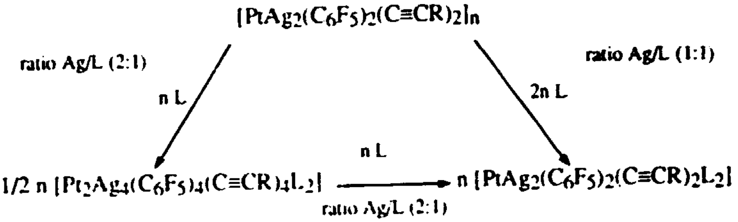
We have recently reported that the reaction between $Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ and $AgClO_4$ (ratio 1:2) affords heteronuclear complexes $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2]_n$ (R = Ph **I**, ${}^tBu$ **II**) which were thought to display a polymeric structure (1).

In this comunication we report on the reactions of **I** and **II** with phosphines (PPh_3, PEt_3) which afford novel hexanuclear $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ or trinuclear $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ complexes depending on the molar ratio Ag:L used (scheme I).



Scheme I

The structures of $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ and $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ have been established by X-ray diffraction studies. The unexpected bonding features of the acetylide ligands will be presented.

(1) Forniés J., Gómez Saso M. A., Martínez F., Lalinde E., Moreno M. T. and Welch A. J. *New. J. Chem.*, 1992, **16**, 483.

LAICM2445P **93, Thu. 16**

REACTIVITY OF [CIS-Pt(C_6F_5)$_2$(CO)(THF)] TOWARDS METAL-ALKYNYL COMPLEXES.

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Following our recent work on acetylide containing platinum complexes, we have recently shown that the reactions between [cis-Pt(C_6F_5)$_2$(THF)$_2$], containing readily displaceable molecules of OC_4H_8, with bis(σ-alkynyl)complexes have yielded homo and heterobinuclear doubly acetylide bridged complexes(1).

As a continuation of these studies we are currently interested on developing the syntetic potential of [cis-Pt(C_6F_5)$_2$(CO)(THF)](**1**) and here we describe preliminar results of the reactions between **1** and several metal alkynyl complexes. Thus, terminal organotransition metal acetylides, $L_nMC{\equiv}CR$, react with **1** to give, under alkynilation of "Pt(C_6F_5)$_2$(CO)", the μ-η^2 acetylide bridged binuclear zwitterionic complexes [(CO)(C_6F_5)$_2$Pt$^-$(μ-η^2C≡CR)M^+L_n] (ec.1) of which the phenylacetylide complex [(CO)(C_6F_5)$_2$Pt(μ-η^2C≡CPh)Pt(C≡CPh)(PPh$_3$)$_2$] has been characterized by x-ray structural analysis.

$$L_nMC{\equiv}CR \ + \ \mathbf{1} \longrightarrow [(CO)(C_6F_5)_2Pt^-(\mu\text{-}\eta^2C{\equiv}CR)M^+L_n] \qquad \text{ec.1}$$

$L_nMC{\equiv}CR$: [Pt(C≡CR)$_2$L$_2$] (R = Ph, ^{t}Bu, L = PPh$_3$, PEt$_3$), [Pt(C≡CR)$_2$(dppe)] (R = ^{t}Bu, SiMe$_3$) and Au(C≡CR)(PPh$_3$) (R = Ph, ^{t}Bu)

In contrast **1** reacts with [trans-PtH(C≡CPh)(PPh$_3$)$_2$] to afford the unexpected vinylidene-bridged complex [(CO)(C_6F_5)$_2$Pt(μ-C=C(H)Ph)Pt(PPh$_3$)$_2$] wich has been characterized by IR and ^{1}H, ^{31}P and ^{19}F NMR spectroscopy. A plausible mechanism for the formation of this complex will be discussed.

(1)J.R. Berenguer, L.R. Falvello, J. Forniés, E. Lalinde, and M. Tomás. Organometallics (1993), 12, 6.

POLYNUCLEAR HOMO- OR HETEROMETALLIC PALLADIUM OR PLATINUM PENTAFLUOROPHENYL COMPLEXES CONTAINING BRIDGING DIPHENYLPHOSPHIDO LIGANDS.

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The ability of phosphido (PR_2^-) groups to act as bridging ligands and stabilize polynuclear transition metal complexes is well known. Moreover. this type of ligands are flexible enough to bridge metal centres with or without metal-metal bonds.

Recently we have synthesized $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M=Pd, Pt)(1) and we describe now the synthesis of the tetranuclear µ-hydroxo compounds $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M=Pd, Pt) as well as the reactivity of both µ-Cl or µ-OH complexes. Several bi or trinuclear complexes with donor-aceptor metal-metal bonds are described.

The structures of the reported complexes have been established on the bases of ^{19}F and ^{31}P NMR spectroscopy. and in some cases by X-ray diffraction.

(1) J. Forniés. C. Fortuño. F. Martínez. R. Navarro and A.J. Welch *J. Organomet. Chem.*,394 (1990) 673.

LAICM2448P **95, Thu. 16**

AN UNPRECEDENT Pt-Tl CLUSTER WITH A $[PT_2TL]^{VI}$ CORE

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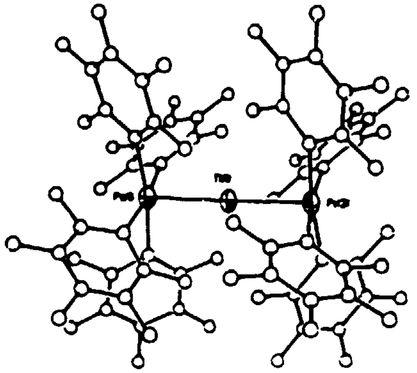
$XTl(C_6F_5)_2$ (X=Cl,Br)have been used as oxidants (1) with elimination of TlX (X=Cl,Br) and formation of pentafluorophenyl organometallic compounds.

We now report the result of the reaction between $(NBu_4)_2\{Pt(C_6F_5)_4\}$ and $ClTl(C_6F_5)_2$ that gives rise to a organometallic anionic compound with a $\{Pt_2Tl\}^{VI}$ core and where no elimination of TlCl has been detected.

The X-Ray structure of this compound has been determinated (fig.1) and proved to be isoestructural with the Pb(II) compound $(NBu_4)_2\{Pb\{Pt(C_6F_5)_4\}_2\}$(2).



The compound is paramagnetic and its EPR shows that the unpair electron is delocalised mainly over the three metal centers (Pt-Tl-Pt) witch are almost in line (angle 179°). Pt-Tl distances of 2.707(1) Å and 2.699(1) Å.

(1) R. S. Nyholm, P. Royo *Chem. Comm.* 421 (1969).

(2) R. Usón, J. Fomiés, L. R. Falvello, M. A. Usón, I. Usón *Inorg. Chem.* 1992 31, 3697-3698.

LAICM2449P **96, Thu. 16**

SYNTHESIS AND REACTIVITY OF ANIONIC PLATINUM COMPLEXES CONTAINING BIDENTATE NITROGEN DONOR LIGANDS (N-N: ORTHOPHENYLENDIAMINE, 1,8-NAPHTHYRIDINE, 2-AMINO-4,6-DIMETHYLPYRIDINE, 7-AZAINDOLE).

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Several platinate (II) complexes of the stoicheimetry $[NBu_4][Pt(C_6F_5)_3(N\text{-}N)]$ [N-N: orthophenylendiamine(**1**), 1,8-naphthyridine(**2**), 2-amino-4,6-dimethylpyridine(**3**), 7-azaindole(**4**)] and containing bidentate nitrogen donor ligands acting as monodentate have been prepared.

Taking into account that in such anionic complexes the metal center behaves as a Lewis base$^{(1)}$, the ability of the above mentioned derivatives to act as bidentate chelating ligands by using the metal centers and the free N atom of the N-N ligand have been studied.

Complexes such as $[NBu_4][(C_6F_5)_3Pt(\mu\text{-}Aza)Ag(HN{=}C(CH_3)_2)]$(**5**) $[NBu_4][Pt_2(\mu\text{-}naphthy)(\mu\text{-}C_6F_5)(C_6F_5)_4]$(**6**), $[NBu_4][Pt_2Ag(\mu\text{-}ofen)(C_6F_5)_6]$(**7**), and $[NBu_4][Pt_2(\mu\text{-}adimpy)(C_6F_5)_5]$(**8**) have been prepared and their structures have been established on the bases of ^1H and ^{19}F NMR spectra or by X-ray diffraction.

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(1) R. Uson, J. Fornies, *Inorg. Chim. Acta*, **1992**, 198-200, 165 and references cited therein.

LAICM2450P **97, Thu. 16**

SYNTHESIS AND REACTIVITY OF DINUCLEAR $\widehat{C\,P}$ CICLOMETALLATED COMPOUNDS OF Pt(II).

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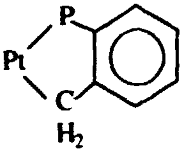
In the course of our research on organometallic intramolecular-coordination compounds of Pd and Pt we have studied the ciclometallation of tris-o-tolylphosphine to give complexes wich contain the fragment



Using the complex $[Pt(\widehat{P\,C})(\mu\text{-}Cl)_2]_2$ ($\widehat{P\,C}$ = $-CH_2C_6H_4P(o\text{-}tolyl)_2$) as starting material we have prepared intermediate species of the stoichiometry $[Pt(\widehat{P\,C})(S)_2]ClO_4$ (S : THF, NCMe).

Dinuclear compounds such as $[Pt(\widehat{P\,C})(S_2C\text{-}E)]_2$ (E : NMe_2, OEt) have also been prepared. These complexes undergo oxidation reactions with halogens to give mononuclear compounds of Pt(IV), in wich the halogen atoms are mutually "cis".

Complex $[Pt(\widehat{P\,C})(S_2C\text{-}NMe_2)]_2$ reacts with HgX_2 (X= Cl, Br, I) to give heterotetranuclear complexes $[Pt(\widehat{P\,C})(S_2C\text{-}NMe_2)HgX_2]_2$ which contain donor-aceptor Pt→Hg bonds unsuported by other bridging ligands.

The structures of the reported complexes have been established on the bases of ^1H and ^{31}P NMR spectra or by X-ray diffraction.

LAICM2452P **98, Thu. 16**

PENTAFLUOROPHENYL PLATINATE (II) COMPLEXES DISPLAYING PT→H-X HYDROGEN BRIDGING BONDS.

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The basicity of the platinum centre on pentafluorophenyl platinate complexes has allowed the synthesis of polynuclear complexes containing Pt→M (M = Ag, Sn, Pb, Hg) donor-aceptor metal-metal bonds.[1]

In this communication we report the synthesis of $[NBu_4][(C_6F_5)_3\overset{\curvearrowright}{Pt(L\text{-}H)}]$ (L-H = 8-methylquinoline, 8-hydroxyquinoline, 8-hydroxyquinaldine, 7,8-benzoquinoline) and some of them, depending on the L-H ligand, display a Pt→H bridging hydrogen interaction. The different aspects wich can influence on the formation of such Pt→H interaction (3c-4e) are discused.

The complexes have been characterized by IR, ^{1}H, ^{13}C and ^{19}F nmr spectroscopy and X-ray diffraction studies. The ^{1}H nmr provides the most valuable information about the presence of the $\overset{\curvearrowright}{Pt\text{-}L\text{-}H}$ interaction in solution.

1.- R. Usón and J. Forniés, *Inorg. Chim. Acta*, **1992**, *198-200*, 165 and references given therein.

LAICM2460P **99, Thu. 16**

Ti_8C_{12}: A POLYTOPAL MOLECULE WITH 36 TI–C BONDS

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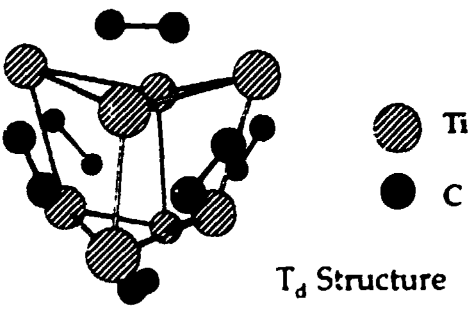
The existence of a new class of stable clusters has just been postulated from the exceptional abundance of the ionic species $M_8C_{12}^+$ (M=Ti,V) in the distribution of metal-carbon clusters obtained from reactions of the metal with hydrocarbons. It has been proposed that the prominence of the M_8C_{12} cluster arises due to its presence as a neutral species. The unusual stability of M_8C_{12} is taken as a strong argument in favor of the cagelike structure of the pentagonal dodecahedron with T_h symmetry proposed by Guo et al [1], which is reminiscent of another cage structure with exceptional stability, the famous buckminsterfullerene, C_{60}.

Although previous theoretical studies were focused on the T_h symmetry with 24 Ti–C bonds, the relaxation of the symmetry constraints leads to a remarkably stabilization of the system. Molecular orbital calculations show that seven local minima can be characterized in the potential energy hypersurface of Ti_8C_{12}, corresponding to topologically distinct conformations. All structures display 36 Ti–C bonds, but they differ each from another by the symmetry point group which they belong : T_d, D_{3d} (two times), D_{2d}, C_{2v}, D_2 and C_s. In the T_d structure, the 36 Ti–C bonds have been characterized by the existence of bond critical points in the electron density distribution.

[1] B.C. Guo, K.P. Kerns, A.W. Castleman Jr., Science 1992, 255, 1411



T_d Structure

SINGLE-POT SYNTHESIS OF THE CARBYNE COMPLEXES *trans*-$[ReX(\equiv CCH_2R)(dppe)_2][BF_4]$ (X = Cl or F) AND THEIR DEPROTONATION REACTIONS

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The routes to carbyne complexes commonly involve difficult stepwise syntheses. However, we have found that the carbyne compounds *trans*-$[ReX(\equiv CCH_2R)(dppe)_2][BF_4]$ (X = Cl or F, dppe = $Ph_2PCH_2CH_2PPh_2$) can be conveniently obtained, in a single-pot synthesis, upon treatment of the dinitrogen complex *trans*-$[ReCl(N_2)(dppe)_2]$ with the appropriate 1-alkyne, $HC\equiv CR$, and $NH_4[BF_4]$ (in the presence of $Tl[BF_4]$, for X = F) (eq. 1 for X = Cl).

The reaction proceeds through 1,2- hydrogen shift at the alkyne followed by β-protonation of the derived vinylidene species (and, in the latter case, with chloride abstraction, by Tl^+, and its replacement by fluoride).

$$trans\text{-}[ReCl(N_2)(dppe)_2] + HC\equiv CR + NH_4[BF_4] \rightarrow trans\text{-}[ReCl(\equiv CCH_2R)(dppe)_2][BF_4] + NH_3 \qquad (1)$$

The carbyne complexes undergo β-deprotonation by base, $[Bu_4N]OH$, to afford the corresponding vinylidene compounds *trans*-$[ReX(=C=CHR)(dppe)_2]$.

The spectroscopic properties of these complexes will be presented and discussed.

Acknowledgements

This work has been partially supported by JNICT and ISEL.

SOL-GEL GLASSES AND THIN FILMS

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The sol-gel process has become one of the most important methods to synthesize high purity glasses and thin films for special applications, for example in the area of optics and optoelectronics. The preparation of such inorganic materials is described in detail in the case of silica based systems, with particular emphasis on the study of the kinetics of evolution of the alkoxide precursor of SiO_2 (tetraethyl orthosilicate) to silica gel by IR and Raman spectroscopies.

Some properties of silica and silica-titania bulk gels are reviewed, such as their IR transmission and reflection and their BET surface area and porosity.

The fabrication of thin films by spin-coating of silica-based sols on glass or single crystal silicon substrates is also considered in detail, including their evolution towards the dense glassy state by appropriate heat treatments. Several properties of the films are studied, namely their thickness, refractive index, IR spectra and BET surface area and porosity (with the use of krypton). Finally, the doping of such films with rare earth elements such as Nd for active optical applications is described and recent data are presented for optical absorption, fluorescence and emmission lifetimes.

References

- R.M. Almeida and C.G. Pantano, J. Appl. Phys. (1990) 68, 4225.
- M.C. Matos, L.M. Ilharco and R.M. Almeida, J. Non-Crystalline Solids (1992) 147&148, 232.

3 SOLID STATE CHEMISTRY AND INORGANIC MATERIALS

Solid State Chemistry of Ceramic Materials: the Role of Phase Diagrams

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Phase diagrams are essential as a basis for understanding the relationships between stoichiometry, structure and properties of inorganic materials, especially complex materials which have variable composition. In materials based on solid-solution phases, it is necessary to have information on solid-solution mechanisms in order to understand the detailed crystallography and properties of the phases. This is because in many cases, properties vary dramatically with solid-solution composition. An overview is given of solid-solution equilibria, structures and properties for six ceramic systems: lithium ion conducting solid electrolytes based on Li_4SiO_4 solid solutions, Na^+ ion-conducting β-aluminas and the effect of Li/Mg additions, lanthanum zirconium tantalate ceramics, doped lithium niobate and lithium tantalate ferroelectrics, bismuth cuprate superconductors and silicon aluminium oxynitride (SIALON) engineering ceramics. As well as providing fundamental data on the stoichiometry and stability of the phases concerned, it is shown how, in each case, valuable clues regarding the likely crystallography of the solid solutions can be obtained.

HIGH NUCLEARITY SPIN CLUSTERS: A NEW DIMENSION IN MOLECULAR MAGNETISM

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In the last years there has been a large number of reports on the structure of large spin clusters, comprising 8-19 coupled spins. these compounds are very important steps towards the synthesis of nanoscale magnetic materials, wich are of interest for different that nanoscale magnetic materials show unusual effects, like large magneto-caloric effect, giant magneto-resistance, macroscopic quantum tunneling, and also can be used as models of biomineralization of iron-oxide type materials, like magnetite and ferritin. These materials are zero dimensional, because they comprise a finite number of spins, but they already show some properties which resemble those of bulk materials. Therefore they can be considered as a new dimension in magnetism.

Molecular chemistry is providing many examples of large spin clusters, and in this communication I want to report the results which we have recently obtained in Florence, in the synthesis and in the investigation of the magnetic properties of large spin clusters.

A useful classification of these materials may be made according to the nature of the metal ions forming the clusters. oxovanadium clusters have been synthesized by A. Müller in Bielefeld. Clusters comprising up to 18 oxovanadium(IV) have been reported and their magnetic properties quantitatively interpreted using a model ecploiting irreducible tensor operator techniques in order to reduce the dimension of the matrices to be diagonatized. The small spins on each centre (S = 1/2) make it difficult to observe bulk like behaviour in these materials. However it is possible to partially oxidize the compounds to yield clusters comprising both oxovanadium(IV) and (V). In these case intersting effects associated with spin delocalization (in nuce the behaviour of magnetic conductors?) are observed.

Manganese clusters provide a large variability of spins, because at least there magnetic oxidation states are available (manganese(II), S = 5/2, manganese(III), S = 2, and manganese(IV), S = 3/2). In this class of compounds we investigated the magnetic properties of a Mn_{12} cluster which at low temperature behaves like a superparamagnet. This is a unique property, which might open the way to information storage at the molecular level.

Iron(III) clusters as large as Fe_{19} have been reported, and a systematic approach to larger and larger clusters is providing a key for understanding in detail the magnetic properties of these materials which can be considered as models of ferritin.

LAICM3499S **C, Mon. 13**

FROM BIOINORGANIC CHEMISTRY TO ATOMIC BIOLOGY. RESEARCHS RESULTS FROM THE COFFE FIELD

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LAICM3493S **C, Mon. 13**

DESIGN OF NEW OPTO-MICROELECTRONIC DEVICES: III-V SEMICONDUCTOR HETEROSTRUCTURES

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APPLICATIONS OF NEUTRON POWDER DIFFRACTION IN SOLID STATE CHEMISTRY

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The use of neutron powder diffraction techniques in Solid Chemistry have long been hampered by the poor resolution of neutron diffractometers and by the low flux of neutron sources. The former point means that the structural details that could be retrieved from a diffraction pattern were of limited accuracy whereas the latter implies that long data collection times (often of the order of a day or so) were required. This situation has changed progressively over the last two decades: development of high flux sources such as the ILL reactor in France or the spallation source at ISIS (U.K.) and improvement of instruments (in particular of monochromators and detectors) heve allowed to optimize neutron powder diffractometers on theree aspects: angular resolution, volume resolution and time resolution.

The **angular resolution** of modern diffractometers, now of the order of $\Delta d/d = 10^{-3}$ or better, allows not only the accurate refinemnet but also the *ab initio* structure determination of complex crystalline structures powder data only. It also enables the investigation of the microstructure (size and strain anisotropy for instance) from the analysis of diffraction line profiles.

The high flux or modern neutron sources and the low absoption of neutrons by most element allows to probe small volumes of mater (of the order of a few mm^3) inside bulk metarials and, for instance, to study local variations of strain of texture.

Time resolution has become possible with the advent of large and efficient position sensitive detectors (PDS) that enable to mesure simultaneously large fraction of the reciprocal space of a powder sample in a few minutes or even less. Although this temporal resolution is far less spectacular than can be achieved by using synchrotron X-ray radiation, it is quite compatible with the characteristic times of many physical and/or chemical transformations in the solid state and opens the way to the investigation of the mechanism and kinetics of these transformations.

Al these instrumental improvements together with the developments of new efficient techniques of data analysis (such as multiphase Rietveld and pattern-matching profile refinement) have led to a revial of powder diffraction that is nowadays and essential tool for non-destructive investigation of the structural and microstructural aspects of crystalline materials. These recent developments in neutron powder diffraction will be illustrated by several examples in the field of Solid State and Materials Chemistry.

PHASE FORMATION AND CURRENT TRANSPORT IN HIGH T_c SUPERCONDUCTORS

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The metallurgical and current carrying capacities of most promising high T_c superconducting materials for industrial applications, e.g. Bi(2212), Bi(2223) and Tl(1223), are briefly reviewed. A particular attention is given to the compound Bi(2223), for which the fabrication procedures of tapes in view of applications at 77K are most advanced. The full characterization of Ag/Bi(2223) tapes with critical current densities up to 33,000 A/cm^2 at 77K and 0T is discussed, comprising the impurity carbon content, the grain morphology and the homogeneity of the Bi(2223) grains. Data on the temperature and field dependence of j_c, measured between 4.2 and 110K in magnetic fields up to 15T are presented.

A study of the formation mechanism at 840°C by DTA, DTG and X ray diffractometry reveals the reaction sequence Bi(2212) tetragonal → Bi-Pb(2212) orthorhombic → Bi(2223). For tapes with lower j_c values, i.e. < 10,000 A/cm^2 at 77K, 0T, characteristic kinks of $j_c(T)$ at ~80 K reflect the presence of local inhomogeneities due to unreacted Bi(2212) portions. The angular dependence $j_c(\theta)$ is inflenced by the orientation of the Bi(2223) grains and can be described by rocking angles which are always around 10°.
The observed linear dependence of $j_c(T)$ cannot be described by a SIS behavior, the current transport in c axis direction can thus not be explained by the "brick wall" model. Based on SEM observations showing frequently small angle c axis grain boundaries, a new model is proposed attributing the c axis current transport in a Bi(2223) tape to a "small angle network" structure.

Actually, the highest j_c value for short tapes obtained by pressing steps is 66'000 A/cm^2, which is much higher than for long tapes (> 100 m), obtained by cold rolling processes, ~ 12'000 A/cm^2. New developments at the DPMC comprising hot rolling and other advanced developments yield improved values, reaching 20'000 A/cm^2 at 77K. The future perspectives for the application of HTSC tapes are briefly reviewed.

DESIGN AND SYNTHESIS OF NEW INORGANIC SOLIDS: APPLICATIONS TO THE TAILORING OF SPECIFIC PROPERTIES

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With the discovery of high T_c superconductors, the interest for the design of new materials grew considerably contributing not only to the area of superconductors but also to other areas such as magnetism, catalysis and electrocatalysis.

J.B. Goodenough [1] uses the term "molecular engineering of oxides" to describe the whole process for designing new metallic oxides and emphasizes the importance of building bridges between the engineers and materials scientists, where the role of the latter involves the design of new materials having particular properties. Among the inorganic solids, the transition metal oxides may be the most interesting family of solids due to their great variety of structures and properties.

Among the metallic oxides, the complex oxides have one of the largest probabilities for the successful tailoring of specific properties due to the wide variety of cations combinations that can be made.

In the present work is described the whole process of the design and synthesis of new inorganic solids, using solid solutions of perovskite type oxides as model systems to tailor electrical, magnetic and catalytic properties.

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LAICM3249S **C, Tue. 14**

CRYSTAL CHEMISTRY IN THE NINETIES : FACTS, FEATURES & PROSPECTIVES

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The recent trends of crystal chemistry are reviewed and a prospective overview on future developments is presented. **Cation coordinations** deserved attention since the early pioneering works on the crystal chemistry of ionic compounds. **Bond valence calculations** recently emphasized the rôle of anion coordinations. Time is now arrived for switching to the search on the **cationic environment of anions,** once powerful X-ray spectroscopic techniques opened promising perspectives in the sense of probing the electronic state of individual elements. The cationic and the anionic structural fractions have identical importance; if anions are the major species in most oxygen compounds where cations usually control the crystal chemical behaviour, the reverse situation is likely to occur in metal-excess phases.

An unified approach to crystalline compounds based on spectroscopy and diffraction data taken alltogether is therefore necessary. It will allow for a deeper understanding of the **morphotropic domain** (chemical population) inherent to a given **structure type** and of the eventual polymorphism characterizing some isotypic compounds. The purpose of such approach should be the assignment of an **energetic configuration** which, along with the well recognized **geometric pattern** - given by the space group symmetry, occupied sets of equivalent positions, values of axial ratios and angles, and positional free parameters - could configurate the actual **crystal structure**. Examples of features that must be taken into account are : 1) the **bonding percolation** process in passing from mono-atomic (eutactic arrays) to multi-atomic structural units in group (0-D), chain (1-D), sheet (2-D), and framework (3-D) arrays within the set of isopointal structures ; 2) the reciprocal event when generating a **close-packed analogue** through the isosymmetric interconversion of plane networks ; 3) the case of polymerization or n-dimensional connection of the elementary "building units" to form the immediate superior level of structural complexity ; 4) the nature of these structural units, ranging from isolated poly-cationic or poly-anionic to bulk polymeric when formed of polyhedral building units.

GLASSES AND GLASS-CERAMICS CONSIDERED AS BIOMATERIALS.

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Both types of the very known materials, such as glasses and glass-ceramics, have shown recently they can be very useful as biomaterials for bone implants. Recent an increasing investigations, all from the Hench (1) and Kokubo (2) first experiments are demonstrating the possibilities to design fluorapatite glasses and glass-ceramics which promising applications.

It is possible to obtain conventional glasses with phosphate surface layers or, what is better for mechanical properties, original phosphate glasses which can be crystallized homogeneously to produce glass-ceramics with composition, microstructure and properties similar to bones. Otherwise, it has been demonstrate also the capabilities of the glass-ceramics processing for obtaining bioglass-ceramics containing several crystalline phases such as fluorapatite/wollastonite and composites glass-ceramics with improved mechanical properties with respect the more conventional hydroxiapatite ceramics.

Therefore, compositional systems, chemical compositions, several ways of processing, properties and microstructures for this new type of biomaterials are reviewed and discussed. Initial own research from the Glass-Ceramics Research Group at the Glass and Ceramic Institute (CSIC), Spain, is also included (3).

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LAICM3501S **C, Thu. 16**

SCIENCE, TECHNOLOGY AND APPLICATIONS OF BIOCERAMICS: STATE OF THE ART AND FUTURE PERSPECTIVES

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Biomaterials, are assuming a precise strategic value either in term of market development perspectives, or of national benefits due to the synergy between technological industrial research and medical research.

Today, skeletal implants in general and joint endoprostheses in particular can be manufactured in compact or porous form from three classes of mechanically and chemically different materials: (1) metals and alloys, (2) polymers, (3) inert and bioactive ceramics.

Metals and polymers were the materials most used for skeletal implatns. The greatest problems encountered were first the mechanical durability and secondly the corrosion of these metals and their alloys and the degradation of polymers in the biological environment. This would result in toxic reactions to the constituents released from an implant.

Particularly of great interest are bioceramics fo which only some have the required mechanical strength but all have a very good surface behaviour.

This means not only excellent tribological properties for articulating surfaces, but also specific surface characteristics which favour the fixation of implants to bone and tissue.

If the mechanical properties do not allow heavy load bearing, inert and bioactive ceramicas can be used as coatings, for ex. metal implants to provide fixation to bone. Nobody, today, could be sure to know the suitable materials for the different prothesic substitutions.

Thanks to the materials science and to the physico-chemical bioprocesses, with a specific interdisciplinary approach, asking a contemporary contribution by materialists, technologists, biologists and surgeons, it is possible to obtain the right knowledges since the bioceramics are mechanically suitable and biocompatible.

The lecture will treat such biomaterials from the scientific, technological and industrial point of view, with some interesting perspectives particularly for the ceramic field in a specific research among the scientists of the materials and of the medicine.

LAICM3467S **C, Thu. 16**

Molecular Design of Advanced Ceramics

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The hydrolysis and condensation of metal alkoxides $M(OR)_z$ allows the formation of advanced ceramics from solutions under mild conditions. The molecular design of alkoxide precursors provides a chemical control over the formation of condensed phases so that tailor made materials can be obtained. This can be conveniently performed via the chemical modification of alkoxides by complexing species XOH such as carboxylates or β-diketones. Chemically controlled condensation can be performed with two chemical parameters ; the hydrolysis ratio $h=[H_2O]/[M]$ and the complexation ratio $x=[XOH]/[M]$. Hydrolysis provides M-OH groups which favor the formation of more condensed speces. Complexation leads to M-OX groups which cannot be easily hydrolyzed preventing condensation. Molecular clusters, chain polymers or colloidal particles can be obtained instead of precipitates. Homogeneous multi-component materials can be obtained at low temperature by mixing precursors at a molecular level and creating M-O-M' bonds in the solution. Moreover organic species can be embedded or even chemically bound to the oxide network leading to the formation of hybrid "organic-inorganic" materials. This opens a new field for material science in which organic and inorganic components are intimately mixed.

This paper addresses the sol-gel chemistry of transition metal alkoxides. Discussion will be mainly focussed on the formation of heterometallic oxides and hybrid organic-inorganic networks in the solution via inorganic polymerization reactions.

BIOMATERIALS FOR HARD TISSUE SUBSTITUTION

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Keywords: Metals; Ceramics; Polymers; Composites.

ABSTRACT

During the last thirty years an increase at a very fast rate in the use of different kind of prostheses and implants sushtitutive of hard tissues in dental, orthopaedic and traumatological clinical applications has been taking place. At present there is a great variety of biomaterials which may be used in such applications, which includes metals and alloys, ceramics and glasses, polymers and composites. It is usually accepted that the main requirement that such materials must fulfil is to be biocompatible. However, biocompatibility is difficult to define and depends on a large number of parameters, which include the chemical composition, the surface composition and microstructure, the corrosion or degradation resistance of the material, its resistance to wear, its mechanical properties, including fracture and fatigue behaviour, all of which are related to its microstructure. All these material features will play a role on its ability to allow cell and tissue growth in, on or around it and to create a long lasting stable and functional interface.

The best interface expected between the biomaterial and the tissue should provide some kind of chemical link in order to achieve a stable fixation during the life in service of the implant. An alternative is that the material should be as inert as possible. A second alternative would be that the material degrades and transforms into healthy new tissue.

Metals and alloys are required to be inert and those which combine good corrosion, wear and fatigue resistance are the best candidates. Amongst ceramics and glasses and polymers and composites, it is possible to find specific materials which behave according to each one of the different alternatives outlined. The elaboration of new materials, able to adjust to any one of the different alternatives, and showing a good compromise amongst the different factors which affect biocompatibility, is being requested both by industry and by science. Composites, or even mixtures, of the ceramic-ceramic and ceramic-polymer types and coatings and modified surfaces seem to show the greatest potential for development in the next future.

LAICM3063S **C, Thu. 16**

SYNTHESIS, CRYSTAL GROWTH AND CHARACTERIZATION OF SUPERCONDUCTING COMPOUNDS AT THE ARGENTINE ATOMIC ENERGY COMMISSION LABORATORIES.

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A review of the activities involving synthesis, single crystal growth and characterization of high Tc superconductor oxides, at the Argentine Atomic Energy Commission (CNEA) Labs., will be summarized.

In this area several studies have been performed in order to understand the mechanisms involved in the HTc superconducting phase transition.

We considered that due to the important rol played by the Cu-O planes and chains , one of the most promising ways to contribute to the understanding of the subject was to introduce chemical substitutions in the oxygen sublattices.

In order to correlate electrical transport properties, granularity and changes in the number of carriers in $La_{2-x}Sr_xCuO_4$ compounds, introduction of Cl for oxygen was carried out through chlorinated precursors like LaOCl or $Sr_2CuO_2Cl_2$. The effects in resistivity of systematic variations of Cl and Sr contents allowed us to determine the roles played by Cl on the electrical transport properties.

In the BiSrCaCuO system a new method of synthesis was developed using double oxides as precursors. The 2212 superconductor was obtained as a monophase, confirmed by x-ray powder diffraction analysis. The reaction path was discussed. These samples showed higher purity, higher conductivity and higher critical currents than those prepared from simple oxides following the same processes.

In order to avoid contamination problems, chemical inhomogeneities and the appearance of secondary non-superconductor phases, another alternative method of synthesis was used for the $YBa_2Cu_3O_7$ system; through the use of metallic alcoxides as precursors we are looking for the obtention of more homogeneous bulk superconductors and thin superconductors films by the sol-gel technique.

Considerable effort was also devoted to single crystal growth, since the availability of single crystals is the basis of reproducible studies of these anisotropic compounds. $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O$ single crystals of high crystalline quality were grown by different methods: flux melt for LaSrCuO and YBaCuO system; directional solidification for BiSrCaCuO 6 K and 80K system. Characterization by X-Ray diffraction, optical and scanning electronic microscopy, decoration techniques, chemical analysis and electrical and magnetic measurements, were performed to assess the crystalline quality related to the physical properties of single crystal samples.

LAICM3500S

C, Thu. 16

ZEOLITE CHEMISTRY: CATALYTIC APPLICATIONS

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DETERMINATION OF POLYMERIC SULFUR STABILITY BY DSC

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Characterization of insoluble sulfur is based mainly in the determination of two parameters: phase-composition and stabilitity versus temperature. The aim of the present work is to describe a new method to determine sulfur stability, which would be suitable for plant control. This is in order to obtain readily and with enough precision some information comparable to that yielded by the laborious traditional method, involving extraction with CS_2. Differential Scanning Calorimetry (DSC) has already been applied to characterization of sulfur [1,2]. For this work, DSC experiments have been performed on insoluble sulfur samples with different stabilities versus temperature. The thermograms obtained in the temperature range 303-473 K show two characteristic effects: a) a complex effect in which at least two processes are involved (a strong endothermic due to the melting of the polymer inmediately followed by an exothermic reversion of the melt to S_8 molecules); and, b) an endothermic effect (due to polymerization of the liquid). Partial integrations of the thermograms yield parameters which are reasonably correlated ($r = 0.98$) to the corresponding stability values, determined by the traditional method. Then, a calibration pattern can be represented. In a very simple way, just refering to that pattern the information extracted from a DSC experiment of a sample whose stability is unknown, its corresponding stability value is obtained, being the result accurate enough for the purposes in plant control. The results of the application of this method will be presented. Its reproducibility and precision will also be discussed.

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LAICM3017P **102, Mon. 13**

Surface characterization and hydrogenation properties of several potassium-doped nickel / α -alumina catalysts.

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Abstract

Studies of the chemical preparation, activation energies of reduction, Temperature Programmed Reduction, X-ray diffraction, X-ray Photoelectron Spectra and catalytic activities for the hydrogenation of 1,6-hexanedinitrile of potassium-doped nickel / α - alumina catalysts were carried out. The catalytic reaction was performed in a continuous process at 1 atm pressure, 443 K, and in the absence of ammonia. Activation energies of reduction for the potassium-doped non-stoichiometric NiO/α -alumina precursors were higher than those obtained for the potassium-free NiO/ α -alumina and for the unsupported non-stoichiometric NiO. TPR results show an inhibiting effect of the NiO reduction by α-alumina and potassium [1]. XRD measurements show the presence of α-alumina, NiO and Ni phases, the latter being present in larger quantities at higher reduction temperatures and lower potassium contents. XRD spectra also show fairly constant nickel particle sizes along all catalysts tested. XPS results confirm the inhibiting effect of potassium upon the reducibility of NiO [2]. The XPS intensity ratios of surface Ni/NiO match the BET area ratios Ni/NiO of the same samples. Conversions of the catalyzed reactions decrease with increasing potassium contents of the catalysts because of poisoning of the latter with a Thorpe cycling formation of an enamine at high basic K_2O contents. Selectivities toward 6-aminohexanenitrile (which may reach 100% values at 85% conversion, thereby showing to be of potential interest for the manufacture of nylon-66) increase with potassium content of the catalysts. The less selective catalysts also yield 1,6-diaminohexane and azacycloheptane. The lack of adsorbed organics and oligomerization reactions is observed.

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LAICM3020P **103, Mon. 13**

CRYSTAL FIELD EFFECTS ON THE MAGNETIC SUSCEPTIBILITY OF RARE EARTH (Pr, Nd) MIXED OXIDES.

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A comparison between the experimental and calculated magnetic susceptibility of Pr^{3+} and Nd^{3+} compounds in a wide group of materials, scheelite-type $Na_5RE(MoO_4)_4$, S.G. $I4_1/a$ (No 88), cubic $RE_3Sb_5O_{12}$, S.G. I43m (No 217), monoclinic $RE_2Te_4O_{11}$, S.G. C2/c (No 15) and hexagonal $RE_3WO_6Cl_3$, S.G. $P6_3/m$ (No 176), is presented.

Structural studies have shown that, in all cases, the rare earth occupies *one single* crystallographic position, whose point symmetries are S_4, S_4, C_1 and C_s, for $Na_5RE(MoO_4)_4$, $RE_3Sb_5O_{12}$, $RE_2Te_4O_{11}$ and $RE_3WO_6Cl_3$, respectively.

The magnetic susceptibilities have been measured in the temperature range 4,2 - 500 K. In every case, an expression of the wavefunction associated to each energy level in the corresponding $4f^2$ and $4f^3$ configurations, previously obtained from crystal field analysis of the experimental spectroscopic data on pure and doped materials, was used in the simulation of the magnetic susceptibilities and its evolution vs. temperature.

Satisfactory correlations, especially in Nd-compounds, were obtained between the experimental and calculated magnetic susceptibilities when the approximate D_{2d} (near S_4) and C_{2v} and/or C_s (close C_1) potentials were considered. The observed deviation from Curie-Weiss behaviour at low temperature reflects the splitting of the ground state associated with these cations under the influence of the crystal field.

SIMPLE AND MULTICOMPONENT IRON OXIDES GENERATION BY THE PYROSOL METHOD.

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The pyrosol method is an important technique for ultrafine powder production. It involves atomizing the mother solution by an ultrasonic generator into very small droplets (aerosol). These droplets pass through a tubular furnace in which the solvent evaporates and the precursor reacts to form a powder which is collected by using an electrostatic filter. By this method, simple (α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4) and multicomponent oxide powders ($BaFe_{12}O_{19}$ and $BaFe_{12-2x}Co_xTi_xO_{19}$) have been synthesized.

In the same way, both structure and texture can be controlled, modifying the characteristics of the mother solution and the surrounding atmosphere used for the aerosol carrier: α-Fe_2O_3 is obtained from the $Fe(NO_3)_3.9H_2O$ solution (in both, air and nitrogen) and the spinel structure, γ-Fe_2O_3 or Fe_3O_4, is obtained by using the $FeC_6H_5O_7.4H_2O$ solution in air and nitrogen, respectively. A single step is necessary to obtain simple oxides.

On the other hand, the introduction of Ba^{2+} ions into the mother solution used for iron oxide production, in the stoichiometric amounts (1Ba:12Fe), allows the $BaFe_{12}O_{19}$ synthesis. Since the residence time of the precursor in the high temperature zone is only about two seconds, an ulterior annealing of the samples in order to obtain a single phase is necessary. In this case, both nitrate and citrate mother solutions lead to $BaFe_{12}O_{19}$, lower temperatures being needed when citrate salts are used.

In all cases, the powders synthesized are formed by hollow spherical particles. Small spheres (0.1-1.5 μm) are obtained starting from nitrate salts. The average size increases by using citrate salts as mother solution (0.2-2.2 μm) decreasing the sphere's thickness.

The oxide particles prepared by the pyrosol method are constituted by nanocrystals as shows the study by electron diffraction. In the case of $BaFe_{12}O_{19}$, these nanocrystals grow up with the thermal treatment, well formed hexagonal platelets, characteristic of this material, being obtained.

STATISTICAL MODEL FOR HYDROGEN SOLUTION IN TiC_z ($z = 0.26$) OF HCP (HEXAGONAL CLOSE PACKED) STRUCTURE

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Abstract

Equilibrium P-T-C (pressure - temperature - composition) relationships were reported for H solution in hcp $TiC_{0.26}$ lattice (700^0 C < T < 850^0 C) by Rexer and Peterson [1]. H solubility in Ti lattice seemed to be enhanced by the presence of C in Ti lattice.

We analysed P-T-C data for $TiC_{0.26}H_x$ in terms of statistical thermodynamics on the basis of a model in which C atoms distributed over O-sites (octahedral interstitial sites) and H atoms over T-sites (tetrahedral interstitial sites) around O-site occupied by C atom.

Several possible atomic configurations are compared and plausible model for atomic configuration is identified.

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SPECTOSCOPIC STUDIES ON FRAGMENTS OF AMPHORAE RECOVERED IN THE SICILIAN AREA.

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The spectroscopic tecniques represent a remarkable help in the study of archaeological artifacts. Preliminary results obtained by FTIR and ^{57}Fe Mossbauer studies on amphorae fragments recovered in the Sicilian area (Agrigento paleochristian necropolis, Himera and Monte Adranone) are here reported

The Mossbauer spectra at room temperature point out the presence of a doublet whose Mossbauer parameters of isomeric shift, I S , and quadrupole splitting, Q S , lie in the range 0 12-0 27 mmsec^{-1} and 0 64-1 11 mmsec^{-1} respectively, furthermore the presence of the components of a magnetic sextet, not always clearly evident, appears. The quadrupole doublet is attributable both to Fe(III) in silicates or replacing the aluminium in aluminosilicates, both to grains of ferric oxides of small size, tipically α-Fe_2O_3 an α- and β-FeOOH presents in clays [1]

As far as the FTIR data are concerned, the far-infrared (200÷700 cm^{-1}) vibrations of various minerals presents within the amphorae fragments have been analyzed. In particular with regard to fragments recovered in the necropolis of Agrigento the IR spectra reveal mainly the presence of bands attributed to Quarz α-SiO_2, vitreous Silica a-SiO_2, Inosilicates Pyroxenes $(Ca,Mg,Fe)_2$, Si_2O_6, Microcline Feldspar $KAlSi_3O_8$, Haematite α-Fe_2O_3, Calcite $CaCO_3$ and Muscovite Mica $KAl_2(Si_3AlO_{10})(OH,F)_2$ [2]

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INFRARED CHARACTERIZATION OF ZIRCONIA-SUPPORTED GROUP 6 METAL CARBONYLS

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There is current interest on supported transition metal carbonyls as heterogeneous catalysts or catalyst precursors because these systems can potentially combine advantages from both homogeneous and heterogeneous catalysis; they also provide a convenient route to highly dispersed low-valent metals.[1]

Zirconium dioxide can easily be prepared in the high surface area form, and it shows good thermal stability and resistance to chemical attack which are desirable properties for a good catalyst support. A few studies have appeared on zirconia-supported cobalt, molybdenum and rhodium carbonyls[2] as catalysts for CO hydrogenation and for olefin metathesis and hydrogenation. However the primary interaction between metal carbonyl and support is not known in detail. We report here an IR study of the interaction of Group 6 metal carbonyls with dehydroxylated active zirconia.

Adsorption of the three metal carbonyls takes place via O-bonding between a CO ligand and Lewis acid sites on the zirconia surface. Two kinds of surface sites (with different Lewis-acid strength) have been identified using CO as a spectroscopic probe. Formation of surface adducts between the zirconia support and the metal carbonyls was found to labilize CO ligands. Reversible decarbonylation of the adsorbed metal carbonyls was observed when pumping at room temperature. Subsequent admission of CO into the IR cell regenerates the hexacarbonyl surface adducts. The stability of these adducts (towards decarbonylation) was found to follow the order $W(CO)_6 > Cr(CO)_6 > Mo(CO)_6$.

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FORMATION AND CHARACTERIZATION OF ALKOXY-DERIVED SPINELS

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Spinels are versatile materials which possess many technological applications. One of these applications concerns the field of heterogeneous catalysis. Several spinels containing transition metal cations find usage as catalysts, and magnesium spinel ($MgAl_2O_4$) is currently been used both as a sulphur transfer catalyst (for reducing SO_2 emissions) and as a catalyst support.

For catalytic applications, the solid must have a large surface area and a convenient spectrum of pore size. The classic route for spinel preparation involves high-temperature solid state reaction between the parent metal oxides. This method leads to low surface area materials, due to thermal and reaction sintering. We report on a novel route, based on double-alkoxide precursors, which was shown to yield high-surface-area spinels (*ca.* 250 m^2g^{-1}) with pore diameters in the 5-7 nm range. $MgAl_2O_4$ and Al_2O_3-$MgAl_2O_4$ solid solutions were prepared from the corresponding heterometal alkoxides. Details will be given on i) the preparation procedure, ii) crystallographic characterization by X-ray powder diffraction, iii) determination of specific surface area and porosity by nitrogen adsorption at 77 K, and iv) surface characterization by low temperature IR spectrometry of adsorbed CO.

STRUCTURAL AND THERMAL STUDY OF NEW PRASEODYMIUM SELENITES

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Crystal growth of a new praseodymium hydrogenselenite of composition $Pr_2(HSeO_3)_2(SeO_3)_2$ has been carried out by pseudo-hydrothermal synthesis, taking as precursor a glass of composition $12SeO_2:Pr_2O_3$. The thermal decomposition of this compound mainly occurs in three steps giving rise to three new anhydrous praseodymium selenites, two of them isolated as tiny single crystals ($Pr_2Se_4O_{11}$ and $Pr_2Se_3O_9$) and the last one, Pr_2SeO_5,as microcrystalline powder.

The structure of $Pr_2(HSeO_3)_2(SeO_3)_2$ has been determined by X-ray single crystal method and refined down to R=0.052. It crystallizes in the orthorhombic system, space group $Pbc2_1$, with a=7.0503(6), b=8.349(1) and c=19.009(2) Å. This compound has been characterized too by IR spectroscopy and magnetic measurements.

A preliminary single crystal study of $Pr_2Se_4O_{11}$ and $Pr_2Se_3O_9$ were carried out, concluding that they belong to the monoclinic system. Otherwise, a crystallographic study of Pr_2SeO_5 was performed by analysing its X-ray powder diffraction pattern by a pattern matching procedure, without the previous knowledge of the structure. This compound possess an orthorhombic type of symmetry, with a Pmma space group.

TEMPERATUE EVOLUTION OF STRUCTURE OF DOPED AURIVILLIUS OXIDES

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Polycrystalline samples of general compositions $Bi_{2-x}Sb_xSrNb_2O_9$ ($0 \leq x \leq 1$) and $Bi_{2-y}Te_ySrNb_{2-y}Ti_yO_9$ ($0 \leq y \leq 0.5$) were prepared, as single phases, by solid state reactions.Their Aurivillius-type structures were studied by X-ray powder diffraction methods, from room temperature up to 800 °C.

The room temperature $Bi_{2-x}Sb_xSrNb_2O_9$ oxides must be indexed in an orthorhombic unit-cell, with $a \approx 5.51$, $b \approx 5.50$, $c \approx 25.2$ Å and space group $A2_1am$. However, the high temperature X-ray powder diffraction patterns of $Bi_{1.5}Sb_{0.5}SrNb_2O9$ and $BiSbSrNb_2O_9$ suggest one symmetry change, from 440 to 690 °C, and from 220 to 470 °C, respectively. In fact, all the reflections of these high temperature patterns can be indexed in a tetragonal unit-cell, with $a \approx 3.9$ and $c \approx 25.4$ Å, which involves a rearrangement into the structure framework (Figure 1), likely related to a change in the ferroelectric behaviour of the materials.

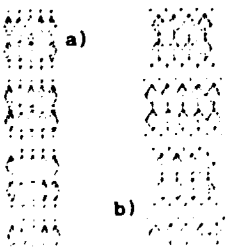

Figure 1
Projection onto (100) plane of the unit-cells of $Bi_{2-x}Sb_xSrNb_2O_9$ at a) room temperature; b) high temperature.

A similar study of $Bi_{2-y}Te_ySrNb_{2-y}Ti_yO_9$ phases will be given.

AN ATTEMPT OF COPPER SUBSTITUTION BY MAGNESIUM ON La_2CuO_4

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La_2CuO_4 is one of the most studied compound on the system with K_2NiF_4 structure (1) which can be related to the perovskite structure.

The partial substitution of copper by magnesium ions on La_2CuO_4 was essayed in order to discuss the possibility of an "s" metal ion stabilize the K_2NiF_4 srtucture.

The samples of $La_2Cu_{1-x}Mg_xO_4$ system ($x = 0$; 0.1; 0.2; 0.3) were prepared by the sol-gel method and the structural characterization was done by XRD on powdered samples.

(1)
J.B.Goodenough;A.Manthiram,*J.Solid State Chem*.88, 115(1990)

LAICM3076P **112, Mon. 13**

SYNTHESIS, SOLID STATE PROPERTIES AND CRYSTAL STRUCTURE OF THE BIS(3-AZA-1,5-PENTAMETHYLENEDIAMMONIUM) DISODIUM DIPHOSPHOPENTAMOLYBDATE(VI) PENTAHYDRATE

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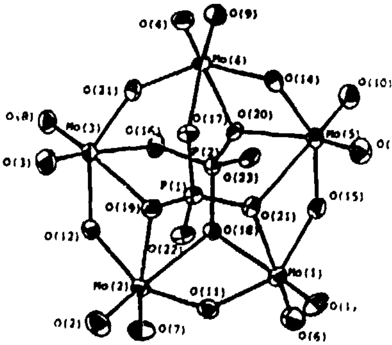
A new organoammonium diphosphopentamolybdate(VI) with the formula $Na_2(H_2dien)_2[P_2Mo_5O_{23}].5H_2O$ (dien = diethylenetriamine), has been prepared by adding diethylenetriamine on a water solution of $Na_2MoO_4.2H_2O$ and Na_2HPO_4 at room temperature. The solution was acidified with HCl (pH= 3) and after three weeks, blue crystals of the compound were obtained. The compound has been characterized by means of elemental analysis, FT-IR spectroscopy, thermal analysis (TG, DTG and DTA) under argon-oxygen and argon atmospheres, and X-ray single crystal diffraction data. The heteropolymolybdate crystallizes in the monoclinic space group I2/a, M_r = 1256.05, a = 20.330(2), b = 16.754(2), c = 21.606(3) Å, β = 95.11(1)°, V = 7330(1) $Å^3$, Z = 8, D_x = 2.28, D_o = 2.27(1) $Mg{\cdot}m^{-3}$, λ = 0.71069 Å, μ = 18.328 cm^{-1}, F(000) = 4928, T = 298. From 4493 reflections, only 3633 with $I > 3\sigma(I)$ were used for structure solution and refinement. The full-matrix weighted least-squares refinement led to R = 0.047 and wR = 0.045 for 465 parameters. The structural analysis reveals that the crystal consists of discrete $[P_2Mo_5O_{23}]^{6-}$ anions, sodium and 3-aza-1,5-pentamethylene-diammonium cations, and water molecules held together by electrostatic forces and an extensive network of hydrogen contacts. The $[P_2Mo_5O_{23}]^{6-}$ polyanion is built up of a ring of five MoO_6 octahedra, sharing four edges and one corner, and two PO_4 tetrahedra, each one linked to the opposite side of the ring by three oxygen atoms (Fig. 1).



LAICM3077P **113, Mon. 13**

SYNTHESIS AND CRYSTAL STRUCTURE OF THE ISOPOLYVANADATE(V), $[(CH_3)_3CNH_3]_4[H_2V_{10}O_{28}]$

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The title compound, tetrakis(*t*-butylammonium) dihydrogendecavanadate(V), has been prepared following the reactions 1 and 2.

$$5V_2O_5 + 6(CH_3)_3CNH_2 \xrightarrow[\text{pH} = 5\text{-}6]{H_2O,\ 100°C} [(CH_3)_3CNH_3]_6[V_{10}O_{28}] \qquad (1)$$

$$[(CH_3)_3CNH_3]_6[V_{10}O_{28}] + Na_2HPO_4 + HCl \xrightarrow[\text{pH} = 3\text{-}4]{H_2O,\ 25°C} [(CH_3)_3CNH_3]_4[H_2V_{10}O_{28}] \qquad (2)$$

The compound crystallizes in the monoclinic space group $P2_1/n$, $Z = 2$, $a = 16.244(1)$, $b = 11.336(1)$, $c = 11.871(1)$ Å, $\beta = 108.625(3)°$, $V = 2071.5(1)$ Å^3, $M_r = 1253.98$, $D_x = 2.014$, $D_o = 2.012(5)$ Mg·m^{-3}, $F(000) = 1256$, $\mu = 21.701$ cm^{-1}. The crystal structure was refined by weighted least-squares analysis up to discrepancy indices of $R = 0.048$ and $wR = 0.048$ for 9201 observed reflections $[I > 3\sigma(I)]$.

The structural analysis reveals that the crystal is composed of discrete dihydrogendecavanadate(V) anions, $[H_2V_{10}O_{28}]^{4-}$, and *t*-butylammonium cations, $[(CH_3)_3CNH_3]^+$, linked together by an extensive network of hydrogen contacts of types: N–H···O and C–H···O (N···O = 2.749(2)–3.282(4) Å; C···O = 3.362(6) Å).

The centrosymmetric dihydrogendecavanadate(V) anion is formed by ten distorted octahedra VO_6 sharing corners and edges. Bond order calculations for oxygen atoms in the anion have been carried out, the results show that the hydrogen atom is attached to O(6) being its bond order of 1.18 lower than those calculated for the rest of oxygen atoms (1.56–1.97). The protonation produces that the V(1)–O(6) and V(2)–O(6) distances, 1.993(1) and 1.974(2) Å, respectively, are longer than the others V–O_b (b = bridge between two vanadium atoms) which are in the range 1.680–1.933 Å.

LAICM3089P **114, Mon. 13**

CYCLIC VOLTAMMETRY STUDY OF HEXACYANOFERRATE COMPLEX IMMOBILIZED ON SILICA GEL SURFACE CHEMICALLY MODIFIED WITH PYRIDINIUM ION

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The chemically modified silica gel with pyridinium ion chloride, $\equiv Si(CH_2)_3^+NC_5H_5Cl^-$(hereafter denoted as $SiPy^+Cl^-$), was used to immobilize hexacyanoferrate ion complex, *i.e.* $SiPy^+/HCF(HCF= [Fe(CN)_6]^{3-/4-})$, by means of an ion exchange reaction. The immobilized electroactive species showed the following mid point potential: E^o_s= 172mV in 1.0M NaCl solution; E^o_s= 222mV in 1.0M $NaClO_4$ solution. This influence was explained considering the reaction:

$$SiPy^+/[Fe^{III}(CN)_6]X + e \rightleftarrows SiPy^+/[Fe^{II}(CN)_6] + X^-$$

where the surface potential is dependent on the affinity of the anion X^- for $SiPy^+$. The immobilized electroactive species was able to mediate electrocatalytic oxidation of ascorbic acid, H_2AA:

$$2SiPy^+/[Fe^{III}(CN)_6] + H_2AA \rightarrow 2SiPy^+/[Fe^{II}(CN)_6] + 2AA + 2H^+$$

$$2SiPy^+/[Fe^{II}(CN)_6] \rightarrow 2SiPy^+/[Fe^{III}(CN)_6] + 2e$$

where AA is the dehydroascorbic acid. The carbon paste electrode made with this material was very stable and the amount of the electroactive species which leached from the surface after various redox cycles was very small.

LAICM3090P **115, Mon. 13**

CYCLIC VOLTAMMETRY STUDIES OF COPPER AND NICKEL HEXACYANOFERRATE IMMOBILIZED ON TITANIUM(IV) OXIDE COATED ON SILICA GEL SURFACE.

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The cyclic voltammetric behavior of copper and nickel hexacyanoferrate complexes immobilized on silica gel surface coated with titanium(IV) oxide, indicated a good chemical stability for the cooper complex film and that the nickel film undergoes a structural change along the time. The surface potential of the redox reaction,

$$\equiv Ti^{+}M[Fe^{III}(CN)_6]^{-} + C + e \rightarrow \equiv Ti^{+}CM[Fe^{II}(CN)_6]^{-}$$

(where M = Cu^{2+} and Ni^{2+}, C = K^{+}, NH_4^{+}, Na^{+} and Li^{+}; and $\equiv Ti$ denotes titanium(IV) oxide substrate on silica gel surface) is dependent on the reticulation degree and affinity of C by the transition metal hexacyanoferrate solid film. The cyclic voltammetry waves in Li^{+} and Na^{+} as supporting electrolyte solution were broadened for $\equiv Ti^{+}Cu[Fe^{II/III}(CN)_6]$. suggesting that the diffusion of these cations through the zeolitic cavity of the surface complex was hindered due to the larger hydrated ionic radii compared with those of K^{+} and NH_4^{+}[1]. The midpoint potential changes with electrolyte concentration showing a sub-nernstian behavior during the redox process. The $\equiv Ti^{+}Ni[Fe^{II/III}(CN)_6]$ cyclic voltammetry waves depend on the interaction capacity of the electroactive species on the Ti(IV) oxide surface with the cationic species of the supporting electrolyte. In this case the reticulation occurs slowly, showing a lower affinity between nickel and hexacyanoferrate compared with the copper case.

[1] Lin, C. & Bocarsly, A.B.; *J. Electroanal. Chem.*, 1991, (300), 325.

SYNTHESIS, CHARACTERIZATION AND CHEMISORPTION INVOLVING MERCAPTO AND OXIDIZED MERCAPTO SILICA

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Silica gel(Sil) surface was anchored with 3-mercaptopropyltrimethoxysilane(-SH) in organic solvent(Sil-SH-1 and SH-3) and aqueous medium(Sil-SH-2 and SH-4), and then oxidized with $KMnO_4$ in acid medium($Sil-SO_3H-1$, SO_3H-2 and SO_3H-3). These surfaces were characterized by elemental analysis, infrared, solid state ^{13}CNMR, surface area and thermogravimetry(TG). A new method based on TG data showed that elemental analysis of surface, is comparable to those obtained from classical elemental analysis, providing the presence of a medium value of 1.0mmol of sulphur/gram of silica. The maximum adsorption values($10^{-4}molg^{-1}$) obtained through batch technique for divalent cations(water, ethanol and acetone) are:a)Sil-SH-1 - Co(0.66±0.05; 0.23±0.05 and 0.24 ±0.05), Ni(0.49±0.05 and 0.51±0.05), Cu(0.30±0.05; 0.40± 0.05 and 0.41±0.05) and Hg(8.55±0.01 and 7.46±0.01) and b) $Sil-SO_3-H-1$ - Co(1.65±0.01; 1.30±0.01 and 1.38±0.01), Ni (1.62±0.05 and 0.12±0.05), Cu(0.94±0.05; 0.30±0.05 and 0.31 ±0.05) and Hg(5.21±0.01 e 4.15±0.01). Hg^{2+} is the cation most highly adsorbed on both surfaces. However, by using Langmuir equation, the data showed that these cations have a high affinity for the oxidized surface. Primary amines RNH_2(R=methyl, ethyl, n-butyl and benzyl) were adsorbed through batch process, giving the maximum adsorption values ($10^{-4}molg^{-1}$, quoted deviation 0.01) in aqueous medium on Sil-SH-1 and Sil-SH-Hg surfaces: methylamine (0.80;4.60), ethylamine (2.40;6.40), n-butylamine (2.50;5.80) and benzylamine (2.60;4.00), which indicate that the presence of mercury increases the adsorption of these amines on SH-1 silica surface.

LAICM3104P **117, Mon. 13**

THERMAL EVOLUTION OF $(Zr,Ti)O_2$ GELS SYNTHESIZED AT DIFFERENT BASIC pH

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ABSTRACT : In the reported chemical preparation of powder materials based on Ti and Zr small amounts of hydrogen peroxide were added. However, little attention have been devoted until now to investigate the effect of hydrogen peroxide on sol-gel processing of the $(Zr,Ti)O_2$ system.

In this work, $(Zr,Ti)O_2$ gels as precursors of zirconium titanace (ZT) powders were prepared by the sol-gel method. The method involves the hydrolysis of $ZrClO_2$ + $TiCl_4$ in the presence or not of hydrogen peroxide, in the ranges 8-9 or 11-12. The thermal evolution of these precursors has been studied by Differential Thermal Analysis (DTA), nitrogen adsorption, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Differences in DTA thermograms, surface area and morphology were observed. In particular, ZT prepared at pH= 8-9 with hydrogen peroxide was purer, more homogeneous and presented a different morphology as compared with ZT processed at pH= 11-12; Hydrated hydroxylated Zr-Ti species were formed to a greater extent in that latter case. Addition of hydrogen peroxide in the chemical processing of these gels plays a key role in controlling the crystallization temperature of ZT.

MICROSTRUCTURAL CHARACTERIZATION OF A 7075 ALUMINUM ALLOY BY TRANSMISION ELECTRON MICROSCOPY.

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In the present work, characterization of a 7075-T6 aluminum alloy, based in a serie of parameters measured on transmision electron micrographs, is detailed.

Aluminum alloys of the 7XXX series with the T6 treatment are very susceptible to stress corrosion cracking (SCC). This problem is especially important in materials which have to be used under strong and constant tensions and corrosive atmospheres, as in the Aeronautic Industry. This is the case of the 7075-T6 aluminun alloy, material with a high strength but also with a high susceptibility to SCC. Several solutions to these problems have been developed, like overaging the materials in the T7 temper. or the so-called Retrogression and Reaging (RR) treatment.

In this work, a 7075 aluminum alloy, in its starting T6 temper, is characterized using Transmission Electron Microscopy. Measurements are based on the following parameters:

-Density of dislocations.
-Size and shape distribution of precipitated phases.
-PFZ studies.
-Grain size of the matrix.
-Intergrain precipitates. Size and shape distribution.

Measurement of these parameters is important because its variations with the heat treatments applied to improve the alloy susceptibility to SCC, help us to a better knowledge of the material itself and their cracking processes.

COMBUSTION SYNTHESIS AND CHARACTERIZATION OF M-TYPE BARIUM HEXAFERRITES

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Fine particles of barium hexaferrites are materials of great importance due to their use in permanent magnet systems and in high density magnetic recording [1]. Several procedures have been used in their preparation, such as co-precipitation, hydrothermal synthesis, hydrolisis of organometalic complexes and the organometalic precursor method.

We have used the combustion method [2], a fast and simple way of preparing submicrometric particles, from a solution of the corresponding metal nitrates and oxalic acid dihydrazide (ODH) which is used as a fuel. The combustion of this solution promobes the rapid formation of a bulky mixture of oxides, which is then calcined generating particle agglomerates of $BaFe_{12}O_{19}$.

By X-ray diffraction and Mössbauer spectroscopy particles have been characterized, which after thermal treatment below 750°C, show α-Fe_2O_3 and $BaFe_2O_4$ as minor phases($< 10\%$), whereas over 750°C they are only $BaFe_{12}O_{19}$. By TEM it has been shown that they are platelets with size between 0.05 μm, for those treated at 700°C, and 0.5 μm, for those treated at 1100°C.

The magnetic characteristics have been studied by VSM and SQUID magnetometry in the temperature range of $4 < T(K) < 300$. The coercitivy at room temperature are in the range $4000 < Hc(Oe) < 5500$, depending on the stucture, size and shape of the particles.

[1] K. Haneda and A.H. Morrish; *IEEE Trans. on Magn.* 25(May 1989)3, p. 2597.
[2] K. Suresh, N.R.S. Kumar and K.C. Patil; *Adv. Mater.* 3(1991)3, p. 148.

X-RAY PHOTOELECTRON SPECTROSCOPY OF LITHIUM COMPOUNDS

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Host-guest intercalation compounds arising from the insertion of lithium in lamellar transition metal disulfides are often used as electrodes in secondary lithium batteries. The potential of such electrodes is mainly determined by guest-host charge transfer associated to the topotactic intercalation process. In order to investigate the real oxidation state of lithium intercalated in MoS_2, the Li(1s) electron binding energy of this compound was determined by X-ray photoelectron spectroscopy. Since there is not any clear description of the different oxidation states of this element in its compounds, the binding energies in a series of compounds with different ionic character were also determined.

Measurements were performed in an AEI 200 Spectrometer. Probe surfaces were sputtered by an argon ion gun, specially in the case of moisture sensitive compounds. Binding energies were determined respect to that of $4f_{7/2}$ gold electrons.

Li(1s) binding energies depend on the nature of the lithium environment in the compound. Relatively high binding energy values are observed in $LiBF_4$ (59.4 eV) and in LiF (59.9 eV). In species in which lithium is surrounded by chelate ligands $E_b(Li_{1s})$ values in the range 56.7-57.2 eV are observed. These figures are intermediate between those for ionic compounds commented above and that observed for $LiNH_2$ (55.8 eV). For metallic lithium a value of 55.2 eV was estimated. Binding energy observed for lithium intercalated in molybdenum sulfide, 55.5 eV, is relatively near to that of the metal. A description a such a kind of intercalation compounds considering lithium atoms located between MoS_2 layers appear to more reasonable than that assuming lithium ions intercalated in a polyanionic matrix.

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NEW MOLECULAR MATERIALS BASED ON C_{60}.

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Despite the discovery of bulk cooperative phenomena such as superconductivity or ferromagnetism in C60 based materials, there still exist very few families of well characterized fullerene materials. We are investigating the synthesis of new salts of C60 with a variety of organic cations by means of the electrocrystallization technique, so successful in the field of pre-C_{60} organic conductors.

A material of formulation $(P\Phi_4^+)_3(C_{60}^-)(Cl^-)_2$ was reported by Wudl and coworkers some time ago [1]. Despite setting the first reported example of the $C_{60}^{-\bullet}$ radical, it lacked definitive chemical and physical characterization. Using the electrocrystallization, we were able to prepare as a monocristalline solid a $P\Phi_4^+/C_{60}^-$ salt using $\Phi_4P.I$ as starting material. Detailed physical characterization of this material will be presented, including ESR, bulk magnetic susceptibility and single-crystal electrical conductivity.

Reference:

1. P.M. Allemand et al., *J. Am. Chem. Soc.*, 113 (1991) 2780.

EFFECTS OF THE PROCESSING TECHNIQUES ON THE STRUCTURE AND MECHANICAL PROPERTIES OF METALLIC GLASSES.

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Rapid solidification process (RSP) is a subject of high interest to many material engineers and scientists because it shows great promise for the manufacture of high performance materials. Some alloys may exhibit enhanced yield strength and fracture thoughness at high temperature or improved magnetic properties.

The preceding methods allowed to extend the field of metallic glasses formation and they also allowed to obtain a whole series of new non-crystaline solids. When some material can be prepared by different ways, the main question is whether the structure and properties of these materials differ according to the kind of formation.

Metallic glasse belong to the category of ultra-high strength alloys that have strength greater than 125 Kg^*mm^{-2} . For instance, the strength of Fe-bassed glasses has been found to be about 350 Kg^*mm^{-2}

In this work the hardness, tensile strength, Young's module and roughness of Fe-based metallic glasses are studied When Fe is partially replaced by Cr, the change in strength and hardness is important. The mechanical behavior of metallic glasses thermal treated is analogous to those commonly observed in crystalline solids.

LAICM3167P **123, Mon. 13**

π-π INTERACTIONS IN COMPLEXES OF THE BIS(1,2-DITHIOOXALATO-S,S')METALLATE(II) ANION CONTAINING PLANAR CATIONS

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Structural studies of square-planar complexes of bis(1,2-dithiooxalato-S,S')metallate(II) anions, (M(II) = Ni, Pd y Pt), and aromatic organoammonium cations, show columnar stacked crystal structures with interesting electric and magnetic properties. Complex anions and organic cations are stacked in mixed sheets almost parallel, which suggests the existence of significant π-π interactions. Previous X-ray reports about the structures containing $[M(S_2C_2O_2)_2]^{2-}$ anions have demonstrated that the nature and size of the organic counterions play an important role in the crystal packing of this type of compounds.

The compounds were prepared by reaction between the potassium salts of the anion $[M(S_2C_2O_2)_2]^{2-}$ and the hydrochloride of the organic cation in aqueous solution with stirring at room temperature. Insoluble microcrystalline powders were recrystallized in DMF solution in order to get suitable single crystal for X-ray diffraction studies.

Three type of interactions have been found:

1) For polycyclic cations and 4-aminopyridinium cation, the aromatic rings lie up and down the MS_4 plane (M–aromatic ring distance 3.4-3.5 Å), and their best planes form an angle of almost 90° with the metallic d_{z^2} orbital (1). This arrangement indicates the existence of an interaction between their π-systems and the metal d_{z^2} orbital.

2) For other planar cations as: 2-methylpyridinium, 3-aminopyridinium, and 2-amino-3-methylpyridinium, the π-π interactions between the dithiooxalate groups and the π-systems of the aromatic cations generate interstacking distances of 3.2-3.6 Å (2).

3) For 4-aminopyridinium and quinolinium cations, π-π interactions between aromatic parallel cations with interstacking distances of ca. 3.4 Å (1).

These π-π interactions and an extensive network of hydrogen bonds together with the electrostatic atractions stabilize the crystal structures.

ELECTROCHEMICAL STUDIES OF IRON PHTALOCYANINE IMMOBILIZED ON TITANIUM(IV) OXIDE COATED ONTO SILICA GEL SURFACE.

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Electrochemical studies of iron tetrasulfonated phtalocyanine(FeTsPc) immobilized on silica gel modified with titanium(IV) oxide, were performed in acid solutions($pH \leq 2.0$). Cyclic voltammograms recorded in different supporting electrolyte solutions presented a redox process which became better defined under acidification. The position of the peak potentials ($\approx$0.35-0.45V vs SCE) and its invariance with solution pH, indicated that such redox process can be assigned to the Fe(II)TsPc/Fe(III)TsPc redox couple, which feature is similar of that observed for FeTsPc adsorbed on graphite surfaces. The nature of the supporting cation does not shift the midpoint potential(E_m) of the redox process, but increases in the peak current in the order $K^+ > Na^+ > Li^+$, as these cation are used. In contrast, th supporting anion has a strong effect, *i.e.*, the E_m shifts toward more positive values in the order $NO_3^- > Cl^- > SO_4^=$. From the viewpoint of Nernstian behavior for adsorbed species for scan rate(v) higher than 5mV/s, the peak currents became linear with $v^{1/2}$. Although the reason for such deviation from ideality is yet unexplained, it may be attributed to (*i*) the ion transport to-and-from or through the electrode interface to hold the charge compensation and/or, (*ii*) the influence of pure resistance on the shape of the current-potential wave.

SYNTHESIS OF ZINC FERRITE FROM GOETHITE INDUSTRIAL RED MUDS.

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The glass-ceramics processing is a useful method for synthesis of inorganic compounds. This processing is based on controlled nucleation and crystallization of crystalline phases from an adequate original glass (1). Usually, the composition of the original glass is designed from the phase equilibria diagrams taking into account the crystalline phase to be synthesize. On the other hand, in the recent years the vitrification of industrials or urban wastes has shown to be a very valuable method for waste recycling.

On this research it has been probed that it is possible recycling of goethite hydrometallurgical wastes by synthesizing a zinc ferrite crystalline phase into a glassy matrix (2).

The procedure included: 19 mixture of red mud with glass cullet and volcanic rocks; 2) melting at 1450°C; 3) pouring and 4) crystallization thermal treatments between 650°-1100°C for several times. Mineralogical and microstructural characterization has been carried out by XRD and SEM. The final composition of this zinc ferrite which contains other cations such as lead has been determined by energy dispersive X-ray microanalysis.

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LAICM3181P **101, Tue. 14**

BIOGLASS FROM THE $MgO\text{-}CaO\text{-}P_2O_5\text{-}SiO_2$ SYSTEM: MICROSTRUCTURE CARACTERIZATION AND MICROANALYSIS.

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Phosphate glass-ceramic materials may be an adequate matrix for possible biomaterial use. As a consequence several investigations have been carried out in order to aproach the bones composition from glass-ceramic synthesis (1,2).

In the present work we have synthetized a glass of composition in weight: 4.6 MgO, 44.7 CaO, 16.2 P_2O_5, 34.0 SiO_2 in which the crystallization agent was 0.5 % of F_2Ca. This material has been synthetized from melting at T = 1500 °C from the starting reagents during two hours. Starting glass material has been studied by means of DTA analysis in different heating conditions as well as in isothermal mode (TTT curves). Two exothermic peaks are presented at 850 °C and 950 °C indicating the formation of two different crystalline phases. TTT data indicate that at temperatures lower than 700 °C no glass crystallization is observed, although this one becomes evident from X-Ray diffraction data only after long thermal treatments at this temperature. Wollastonite (SiO_3Ca) and fluorapatite ($Ca(PO_4)_3F$) crystals appear after thermal treatment at T = 800 °C for 4 h,also at T = 900 °C during two hours is observed a devitrification of the original raw glass material. A microstructural characterization by means of SEM and TEM (at 200 kV) as well as EDX microanalysis has been performed in the obtained glass-ceramic material.Biocompatibility studies have also been performed and they are still in progress in order to further improve biocompatibility properties of synthetized glass-ceramic materials.

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INFLUENCE OF THE SYNTHETIC METHOD ON THE HYDROXYAPATITE TEXTURE AND MORPHOLOGY

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Calcium hydroxyapatite is the principal mineral phase of the human bone and is the more biocompatible material between all the known ceramic materials (1), and with bone integration ability, wich depends on the morphology and particle size.
Pure hydroxyapatite in powder form can be obtained in many ways. A careful microstructural characterization of the hydroxyapatite compound is important in order to understand and improve his properties and biocompatibility performances, wich depend strongly on the initial synthesis, stoichiometry (ratio Ca/P), sintering process, morphology, cristallinity and porosity.
We have prepared hydroxyapatite in powder form by following two different methods:

a) By coprecipitation method. $Ca(NO_3)_2.2H_2O$ and KH_2PO_4 were used as starting reagents.

b) By pyrolisis of an aerosol generated by ultra high-frequency spraying (2) precursor solution of $CaCl_2.2H_2O$ (0.1 M) and $(NH_4)H_2PO_4$ (0.06M).

The products have been studied by chemical analysis, IR, X-ray, SEM and EDAX. Such a characterization indicates that the synthesized hydroxyapatite samples are stoichiometric.Morphology and particle size depend on the synthetic method. Spherical particles (1-1,5μm) are obtained by b), while crystalline aggregates (5-30μm) with heterogeneous shape are produced by a).

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LAICM3191P STRUCTURAL INCORPORATION OF MnO IN CaO-SiO_2 AND Al_2O_3-SiO_2 SYSTEMS PREPARED BY THE SOL-GEL METHOD

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In the present work 0.5MnO-99.5SiO_2 (Mn), 5CaO-95SiO_2 (Ca), 5Al_2O_3-95SiO_2 (Al), 0.5MnO-5CaO-94.5SiO_2 (Mn-Ca) and 0.5MnO-5Al_2O_3-94.5SiO_2 (Mn-Al) gels and gel-derived glasses were prepared by using tetraethilorthosilicate (TEOS) and manganese, calcium and aluminium nitrates as starting materials. The structural incorporation of Mn in the samples was related with the corresponding composition and heat-treatment by optical absorption in the UV-VIS-IV_p, powder X-ray diffraction (XRD) and scanning electronic microscopy (SEM).
Samples were heat-treated in the range 60 to 850°C under ambient air conditions. The analysis of samples colour, UV-VIS-IVp spectra, XRD diagrams and SEM micrograph consents to conclude that:

*In all the samples heat-treated at 60°C and containing Mn this is incorporated as Mn^{2+} ions. Mn^{2+} ions are probably present in the gels as hexaquo ions $[Mn(H_2O)]_6^{2+}$. Because the majority of Mn^{2+} octahedral complexes have spin-forbidden as well as parity-forbidden transitions the samples are colorless [1].

*Samples containing Al (Al and Mn-Al samples) and heat-treated at 250 and 500°C have the same brown colour. The brown colour is due to the presence of a great amount of NO_2 (gas) in these samples. NO_2 is obtained by thermal decomposition of NO_3^- ions present in the samples.

*The colour difference between Mn-Ca and Mn-Al samples treated at 700°C is due to a behavior difference between the incorporation of Ca^{2+} and Al^{3+} in the silica network. During the hidrolysis and the polymerization processes the aluminium is captured by the silica network and is continuously transformed into normal 4-coordinated aluminium [2]. On the contrary Ca^{2+} ions filling empty spaces in the silica network. Therefore manganese, in Ca brown-rosy samples, is mainly incorporated as Mn^{3+} ions in octahedral coordination and in colorless Mn-Al samples Mn^{2+} ions are preferably present because AlO_4 tetrahedra produce an excess unit charge.

*The introduction of Ca and Mn as nitrates preventing Mn^{3+}-to-Mn^{2+} reduction.

*XRD and SEM indicate that devitrification occur at 850°C in all the samples.

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ELECTRIC PROPERTIES OF MIXED OXIDES WITH SPINEL TYPE STRUCTURE.

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Recently, many systems have been studied to search high lithium ion conductivity solids, since the solid lithium conductors are a promising separator for high energy battery systems. In this work, solid oxideslithium conductors based on the spinel structure have been examined.

The orthorhombic $LiCuVO_4$ is composed by CuO_6 octahedra, which share opposite O-O edges to form infinite one dimensional chains which are parallelto the a-axis. The cooperative ordering of the elongated Cu-O axis is expected by the strong Jahn-Teller instability of Cu^{2+} ions in the high spin configuration d^9 state. The V^{5+} ions are occupying the tetrahedral sites (1). This spinel shows a Cu-O-Cu interaction, and presents a typical semiconductor behaviour.

The $LiCrTiO_4$ spinel presents a cubic symmetry with the Li^+ ions are located at the tetrahedral sites. In this compound, a conduction band can indeed be obtained form the mixing of d-orbitals of titanium with d-orbitals of chromium; consequently is a good electric conductor. On the other hand, the Li^+ cations are occupying the tetrahedral positions and this fact favours a good ionic conductivity.

The Li_2TeO_4 spinel presents a tetragonal symmetry, then it is an ordered type with the Te and Li atoms occupying the octahedral sites and the Li atoms are occupying the tetrahedral positions. Tetragonal distortion in this spinel is attributed to the layer sequence of octahedral positions (Li and Te) because the strong charges difference. This compound can be considered as a Li^+ ion conductor, which presents lower conductivity than $LiCrTiO_4$ (2).

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LAICM3212P **105, Tue. 14**

SYNTHESYS, STRUCTURAL CHARACTERIZACION, MAGNETIC AND ELECTRIC BEHAVIOUR OF $Ti_{3(1-x)}Ni_xM_{2x}O_6$ (M= Sb, Nb) PHASES.

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Solid solution of composition $Ti_{3(1-x)}Ni_xM_{2x}O_6$ (M= Sb, Nb) have been prepared by solid state reaction between $Ni(CO_3)_2$, TiO_2, and Sb_2O_3 or Nb_2O_5(1).

These phases are isomorphous with the rutile (lower Sb content, which can by partially substituted by Nb) or trirutile structure (higher Sb content). The crystal structures were refined from x-ray powder diffraction data by Rietveld's method. The lattice parameters and the final reliability factors are in apreement with the proposed structural model.

The magnetic susceptibility of these solid solutions has been measured in the temperature range 4.2-300 K. From these results an antiferromagnetic ordering is deduced for the trirutile phases whereas a single paramagnetic behaviour is observed for the rutile ones. (2)

The electrical properties were studied and the obtained values for conductivity are in the range of clasical semiconductors. The conductivity increase with the Nb content in these oxides.

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SYNTHESIS AND CHARACTERIZATION OF CHROMIUMSILICATE WITH MFI STRUCTURE

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A fractional factorial design was applied to the synthesis of chromiumsilicalites. The study was performed using two different levels for the concentrations of Cr^{+3}, BO_3^{-3} , F^- , H^+, TPA^+Br^- and crystallization times. The solids obtained presented colors varying from light to dark green, and some of them are even bluish. In a first stage the goodness of the syntheses was evaluated by the degree of pentasil ring formation using the absorption ratio of the bands observed in 550cm^{-1} and 450cm^{-1} in the infrared spectrum. The results showed a very accentuated influence of the TPA^+Br^- concentration. The increase in Cr^{+3} concentration and higher pH values seem to favor MFI structure formation, while the addition of BO_3^{-3} showed opposite effect. The better formed chromiumsilicalites were characterized by the following physical techniques: Powder X-Ray Diffraction, Scanning Electron Microscopy, Electron Spin Resonance, X-Ray Fluorescence, Magic Angle Spinning Nuclear Magnetic Resonance and Photoacoustic Spectroscopy. The powder X-ray diffratograms were typical of MFI-structure in the orthorhombic form. Scanning electron micrographs showed the presence of single elongated euhedral crystals that have a range of dimensions from batch to batch, and of spherulitic agglomerates, besides, in some cases, amorphous or non-zeolitic materials. The electron spin resonance spectra profile changes with the concentration of water showing that its presence or absence causes serious disturbances in the Cr^{+3} coordination sphere, regardless of the site that this ion occupies within the silicate.

LAICM3223P **107, Tue. 14**

The Immm-R_2BaCoO_5 Oxides (R= Rare Earth): Structural Stability and Magnetic Properties.

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New R_2BaCoO_5 oxides (R=Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm) have been prepared and the X-Ray difraction data reveal that they crystallize in the Nd_2BaNiO_5- type (S.G. Immm) [1], which main structural feature is the presence of one-dimensional arrangement of vertex-sharing flattened $[CoO_6]$ octahedra. Nevertheless, for the compounds where R= Tb, Dy, Ho, Er, Tm, Yb, Lu and Y; the Sm_2BaCuO_5- type (S.G. Pnma) [2] is adopted by these oxides, and presents, as main structural characteristic, the existence of isolated distorted $[CoO_5]$ square pyramids. From these results, the existence of dimorphism has been shown for R= Tb-Tm.

A comparative study of the influence of the rare earth size on the structural parameters is presented for this family of compounds. The relative stability of these oxides is discussed from the variation of the so-called Global Instability Index (GII) calculated using the Bond Valence Method estimating the agreement between bond valences sums and formal valence states, showing a systematic variation. The GII values around 0.2 v.u. are indicatives of the high stress present in this structure.

The magnetic properties of these oxides have been studied from magnetic susceptibility measurements and one-dimensional antiferromagnetic order in the Co^{2+} sublattice is presented around the room temperature, while three-dimensional antiferromagnetic interactions in both the Co^{2+} and R^{+3} sublattices have been observed at lower temperatures (T_{Neel} < 40 K) in this family of oxides. This behavior is explained considering the crystal structure of these compounds and the electronic states of the Co^{2+} and R^{+3} cations.

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SYNTHESIS, STRUCTURE AND GAS SENSIVITY PROPERTIES OF CuO-SnO$_2$ SYSTEM

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Tin oxide is a semiconductor used for gas sensors since it's very sensitive to the surrounding atmosphere. Dispersed metallic particles as Pd or Pt on the grain surface are generally used to increase the sensitivity (1).

Microparticles were synthesized by pyrolysis of an aerosol produced by ultrahigh-frequency spraying of a solution in a tubular furnace. Tin (II) chloride and copper (II) chloride were dissolved in aqueous solution with oxalic acid and ammonia till a transparent solution is reached.

The powders were obtained by using solutions with 10%, 50% and 70% of copper at 400°, 800° and 900° C as pyrolysis temperature.

The X-ray diffraction (XRD) study shows, in all cases, two structural types that corrrespond to cassiterite and tenorite. The proportion of SnO$_2$ and CuO has been determined by XRD and scanning electron microscopy (SEM). From X-ray diffraction measurements the crystal size has been estimated. The crystallite size increases as the synthesis and annealing temperature increase.

SEM shows that powders are formed by hollow spherical particles in which a homogeneous distribution of SnO$_2$ and CuO has been observed by energy dispersive spectroscopy (EDS).

Electrical meassurements were achieved on ceramic materials as a function of the temperature and surrounding atmosphere (CO and ethanol). A progressive evolution of electrical response is observed increasing copper amount. By performing impedance spectroscopy it is possible to provide evidence for p-n junctions between CuO (p) and SnO$_2$ (n) grains.

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LAICM3236P **109, Tue. 14**

ENTHALPIES OF FORMATION OF BUCKMINSTERFULLERENE (C_{60}) AND OF THE PARENT IONS C_{60}^{+}, C_{60}^{2+} AND C_{60}^{-}

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The standard enthalpy of formation of buckminsterfullerene (C_{60}) in the crystalline state has been determined as 2507.1±17.4 kJ mol^{-1} by using a micro combustion calorimeter. Statistical mechanics calculations of the heat capacity of gaseous C_{60} as a function of the temperature, along with a critical survey of the literature data for the enthalpy of sublimation, the heat capacity in the crystalline state, the first and second ionization energies and the electron affinity of C_{60}, enabled the derivation of the enthalpy of formation of gaseous C_{60}, and the enthalpies of formation of the ions C_{60}^{+}, C_{60}^{2+} and C_{60}^{-}

LAICM3247P **110, Tue. 14**

V^{4+} - TiO_2 RUTILE SOLID SOLUTIONS AT HIGH TEMPERATURE

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In this study V^{4+} -TiO_2 rutile solid solutions have been synthesized in V_2O_5 - TiO_2, Al_2O_3 - V_2O_5 - TiO_2 and Cr_2O_3 - V_2O_5 - TiO_2 systems from ceramic method. Characterization of these solid solutions was carried by X-ray diffraction, vanadium analysis, CIELAB parameter measurements, UV-V and IR spectroscopy.

Effect of anatase-rutile TiO_2 transition accompained by the formation of solid solutions of V^{4+} in TiO_2 rutile on catalytic properties has been studied by several authors (1). On heating any of anatase with V_2O_5 some oxygen is evolved, and some authors (2) suggest that this is due to the partial or complete reduction of V^{5+} to V^{4+}. The quantity of V_2O_5 capable of being reduced is about 8% by weight. Simultaneously with this reduction, the polymorphic transformation of anatase into rutile takes place.This is an order-disorder transition involving changes in secondary coordination. In both structures the Ti^{4+} ions are octahedrally coordinated to oxide ions, but anatase has three short oxide-oxide distances while rutile has only two. At 700 °C the V^{4+} ions are present in solid solution in the rutile lattice.

In this study, samples were prepared from TiO_2 (anatase), NH_4VO_3, Al_2O_3 and Cr_2O_3.The appropiate amounts of the starting materials were mixed and homogeneized in acetone in a planetary ball mill for 20 min. Residual acetone was removed by evaporation. The dried mixtures were put into refractory crucibles and fired at temperatures between 600 and 1400 °C for various soaking times. The resulting materials were examined with a powder diffractometer using CuK_α radiation and Ni filter to study the development of the crystalline phases. Rutile unit cell parameter measurements were carried by a least squares program.The variation of these parameters with the composition of samples indicates the formation of desired solid solutions in all the studied systems. The stability of the obtained V^{4+} -TiO_2 rutile solid solutions at high temperature was checked in the above mentioned systems. Interatomic distances in rutile structure was determinated by Rietveld method. Samples were washed with 0.3 M HNO_3 and the vanadium analysis in the samples was obtained. CIELAB colour parameter measurements were used to differenciate the samples in terms of colour. UV-V spectroscopy (diffuse reflectance) allows the vanadium site in these rutile solid solutions to be studied. Infrared spectroscopy was employed to study the structural evolution of these solid solutions.

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LAICM3248P **111, Tue. 14**

TEOS HYDROLYSIS RATE IN DMSO

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Hydrolysis of tetraethyl orthosilicate (TEOS), has been widely studied by several authors (1). TEOS is hydrolizable under either acid or basic conditions, usually in the presence of an "inert" diluent such as ethanol. In principle, the reaction sequence can be separated into a hydrolysis stage followed by a condensation one, which will produce the idealized network gel. Subsequently, the gel structure can be heated to higher temperatures to produce a dense glass.
On the other hand, our research group are interested in obtaining new SiO_2 - MS (M= Zn, Cd) gels pointed to optical glass (2). In this order, it would be interesting to get information about the hydrolysis rate of TEOS in several "non-clasical" solvents in this synthesis to enhance the sulfur amount in gels and to avoid the problematic process of formation "in situ" of sulfides. In this sense the dimethilsulfoxide (DMSO), as high dipolar and boiling temperature solvent, would allow to a more efficiency formation of SiO_2 network and metallic sulfide stabilization into the gel structure. The experimental conditions like temperature, acid and basic catalyst nature and time of complete hydrolysis of TEOS-DMSO system has been determined by infrared (IR) and nuclear magnetic resonance (^{1}H NMR).

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LAICM3252P **112, Tue. 1**

CRYSTAL GROWTH , STRUCTURE AND THERMAL DECOMPOSITION OF $KLn(CrO_4)_2$ (Ln = Y , Dy-Lu).

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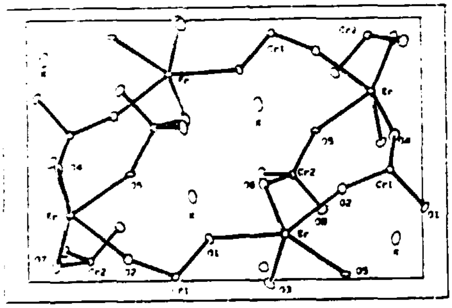
Within the study that we are carring out in the system $KLn(CrO_4)_2$ (1-2) , we have sinthesized the third and last isostructural series for the smaller lanthanide cations (Ln = Y , Dy-Lu).

These new compounds have been obtained using the same two differen routes that we used in the previous series : hydrothermal procedure and ceramic method.



The structure have been determined from a single crystal of $KEr(CrO_4)_2$.All these compounds crystallize in the monoclinic system S.G.$P2_1/n$ and Z=4.

In this threedimensional structure the Er polyhedra share vertex and edges with tetrahedra of Cr_1 and Cr_2 , respectively , in such a way that the structure have tunnels along <u>a</u> , where are located the K atoms.

Each K atoms is coordinated to 7 oxygen atoms and the average distance is greater than the expected one for this kind of bonds.As a consequence it is foreseeable ionic conductivity due to the movility of the potassium cations as have been observed.

The crystallographic parameters found for the family decrease progressively due to the lanthanide contracction.

We also have studied the thermal decomposition of these compounds by T.G., D.T.G. and D.T.A., showing that them remains stable until 560-600ºC and afterwards decompose in only one step giving the corresponding chromites ($LnCrO_3$) , Cr_2O_3 and potassium chromates.

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LAICM3253P **113, Tue. 14**

SYNTHESIS OF PILLARED CLAYS DERIVED FROM MONTMORILLONITE BY USING CRTA.

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3. CTM du CNRS.- Marseille.- France

Pillared Clays are materials derived from phyllosilicates (2:1) in which, by means of ionic exchange processes, voluminous cations are inserted acting as pillars and conferring rigidity to the structure of the host silicate.

We have synthesized these materials by using CRTA* with the polyoxycation $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ as pillaring agent that by thermal treatment is transformed into the corresponding aggregate oxide. CRTA is the ideal technique from the preparative point of view, due to the homogeneity of the final products and to the reproducibility, leading to an accurate control of the texture of the obatined materials.

Experiments in CR-EGA were performed by using a residual water vapour pressure of $6\cdot10^{-3}$ mbar, cutting off and on the experiment at different temperatures in order to monitoring the process by X-ray powder diffraction. Results showed that the basal d-spacing is mantained up to 500°C and disappears at 800°C, indicating a collapse of the structure.

Textural characterization of the pillared clays was performed by N_2 adsorption.

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SYNTHESIS OF TERNARY AND QUATERNARY OXIDES WITH A PEROVSKITE STRUCTURE

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The structural flexibility of the perovskite framework, ABO_3, has the ability to stabilize a large number of ternary and quaternary oxides. Results of an attempt to replace A cations (Ca,Sr,Ba) and B cations (Ti,Sn,Zr) simultaneously on the perovskite system are presented. Structural characterization by X-ray diffraction were performed over various compositions along the perovskite series and different phases were identified. No significative replacement of Zr vs. Sn or Ti takes place, using the usual reaction sintering process. Effects of the synthesis conditions on the formation of perovskite solid solutions were tried to improve the understanding of the role played by different structural sites.

LAICM3268P **115, Tue. 14**

LOW TEMPERATURE PREPARATION OF MANGANESE COBALTITE SPINELS $Mn_xCo_{3-x}O_4$, $0 \leq x \leq 1$.

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The synthesis of spinel-type cobaltites with high surface area has attracted the attention of many solid state chemists because of their tecnological interest. A synthetic route of low-temperature preparation of manganese cobaltite spinels $Mn_xCo_{3-x}O_4$ in the composition range $0 \leq x \leq 1$, has been investigated. Gels formed by precipitating mixed Co^{2+} and Mn^{2+} chloride solutions with n-butylamine leads to the formation at 200°C, of the spinel-type oxide as a single phase in fine particulate form. Cell parameter values and mean crystallite size determined by the Rietveld method, are shown in Table I.

TABLE I

	80°C		200°C		
x	Phases	a(Å)*	Phase	a(Å)	size(nm)
0.0	β-$Co(OH)_2$ + $CoOOH.nH_2O$		S	8.083(2)	8
0.2	S+β-$Co(OH)_2$	8.120(1)	S	8.096(1)	35
0.4	S+β-$Co(OH)_2$	8.167(3)	S	8.145(3)	24
0.6	S+β-$Co(OH)_2$	8.184(3)	S	8.146(2)	24
0.8	S+$Co_8O_6Cl_4 \cdot 7H_2O$	8.198(6)	S	8.195(5)	24
1.0	S	8.202(5)	S	8.215(4)	11

S refers to cubic spinel-type phase

*cell parameter of the cubic spinel-type phase

The application of this procedure permits the formation of the spinel phase $MnCo_2O_4$ with specific surface area of 34 and 44 m^2/g at 80° and 200°C respectively, being these higher than the reported in the literature.

LAICM3273P

116, Tue. 14

INCLUSION OF A LITHIUM-AMINE ION IN A NEW MATRIX: THIOUREA-CHLORIDE

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The inclusion of lithium in thiourea matrix may be of great interest for modeling of biological systems as well as for studying from a pharmacological point of view the transport and bio-availability of this element. Further, the high mobility of the host cationic species expected for this kind of host-guest complexes may be useful for developing new fast ionic conducting materials[1].

Recently, we have informed that the crystallization of thiourea in the presence of saturated amines as dicyclohexylamine, N-methylcyclohexylamine and quinuclidine bears to inclusion compounds which are in some extend similar to the classical inclusion of hydrocarbons in the same matrix[2].

The reaction of thiourea with quinuclidine and lithium chloride in ethanol/acetone mixture leads to the formation of the inclusion compound $(thiourea)_2\cdot(quinuclidine)_2\cdot Li^+Cl^-$. Complete structure determination of the product was performed and shows a channel structure formed by monodimensional, non-intersecting chains of thiourea molecules linked by chloride ions. This first ternary lithium-amine-thiourea supercomplex may be described as the inclusion of a lithium quinuclidine cationic complex in the van der Waals holes of a thiourea-chloride matriz. The thiourea channels accommodate the complex species $[Li(quinuclidine)_2]^+$ in a stacked form.

Acknowledgments: Research financed by following Grants: FONDECYT 90-1120 and 91-0847; DTI, Universidad de Chile Q3287, Fundación Andes C-10810/2.

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DESIGN AND SYNTHESIS OF SOLID SOLUTIONS $SrTi_{1-x}Ru_xO_3$ PEROVSKITES

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We report on the solid state synthesis of ceramics $SrTi_{1-x}Ru_xO_3$ in all the Ru concentration range. The accurate composition of the different compounds was determined by plasma emission spectrophotometry. Crystallographic data show that compounds with x=0.10, 0.33, 0.40, 0.50 and 0.80 are single phase materials and there is no evidence of superstructure implying a random distribution of Ti and Ru in perovskite b sites. It was found that a small tilting of the RuO_6 octahedra leads to an O-orthorhombic deformation particularly manifested for x>0.50. Energy dispersive x-ray analysis (EDAX) from different size areas indicate an uniform distribution of Ru and Ti. Observations done with scanning electron microscopy show a main grain size in the 1-3μ range. On the other hand, four probe resistivity measurements show that the metallic conduction of $SrRuO_3$ appears to be maintained down to x=0.50; a fact that also is reflected in preliminary infrared transmission spectra for the internal modes vibrational region that show features becoming increasingly screened by free carriers as titanium is replaced by ruthenium. It also corroborates a metal-insulator phase transition in the same range as suggested by low temperature transport measurements between x=0.40 and x=0.50.

PREPARATION AND CHARACTERIZATION OF IRON(III) OXIDE HIGHLY DISPERSED OVER SYNTHETIC HYDROTALCITE

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A new inorganic material was prepared reacting $Fe_3(CO)_{12}$ with hydrotalcite,in THF, at 25°C. After 30 minutes stirring a red air sensitive solid is obtained and characterized by infrared as being the $HFe_3(CO)_{11}^-$ anion supported on the hydrotalcite matrix. In contact with oxygen the material becomes light yellow - the ν_{CO} infrared bands disappear from the IR spectrum - due to decomposition of the organometallic intermediate. This yellow solid exhibits a single doublet in the Mössbauer spectrum, the isomer shift value being concordant with the reported one for α-Fe_2O_3. The absence of the superparamagnetic sextet, common in bulky α-Fe_2O_3 samples, indicates that the iron oxide is highly dispersed over the hydrotalcite matrix. The X-ray difratogram of the yellow material in identical to that obtained for pure hydrotalcite indicating that the iron oxide is bound to the surface of the matrix.The ^{27}Al-MAS-NMR spectrum shows no change in the octahedral symmetry of aluminum sites, in line with the previous observations.

LAICM3298P **119, Tue. 14**

A HREM STUDY OF THE LnBa$_2$FeO$_z$ SYSTEM.

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The different anionic coordinations that can be adopted by copper atoms in the RE-Ba-Cu-O system (RE = Rare Earth) have led to several oxygen-deficient perovskites. After the discovery of $YBa_2Cu_3O_7$, the 1:2:3, RE:Ba:B (B = transition metal) ratio has been the most widely studied. If iron were substituted by copper maintaining the cationic ratio 1:2:3, the differences in stability at the metallic sites should lead to other results in the RE-Ba-Fe-O system. Accordingly, we have undertaken a study on the accommodation of compositional variations in $LnBa_2Fe_3O_z$ (Ln = Nd, Sm, Eu, Gd, Dy and Ho).

The microstructural characterization of these materials allows us to propose the existence of two members of a new homologous series of general formula $Ln_{1/3}Ba_{2/3}FeO_{3-(1/(2n+1))}$. The n = 1 term is constituted by $Dy(Ho)_{1/3}Ba_{2/3}FeO_{2.67}$ and the n = 2 term is $Nd_{1/3}Ba_{2/3}FeO_{2.80}$, which can be described as formed by the different alternance of $[FeO_5]$ square pyramids and $[FeO_6]$ octahedra along the c-axis leading to a tetragonal symetry (P4mm). The same study developed for Ln = Sm and Eu reveals a more complex microstructure, exhibiting a short-range order situation

Finally, when Ln = Gd two new members of the previous family, n = 7/6 and n = 7/5, are obtained as a function of the thermal treatment. A modulated structure approach to $LnBa_2Fe_3O_z$ over the description of these phases is discussed.

ELECTROCHEMICAL LITHIUM INSERTION IN REDUCED TUNGSTEN OXIDES

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Among the compounds having a ReO_3 related type-structure, both monoclinic WO_3 and MoO_3, have been obtained by low temperature routes. These oxides have shown the capability of playing a "host" role in intercalation reactions yielding bronzes such as Na_xWO_3 or Li_xMoO_3.

Although a lot of attention has been paid to these compounds little work has been done on the intercalation chemistry of the corresponding reduced oxides. The removal of some oxygens from the ReO_3 type structure produces CS phases in the tunsgten case. Besides, lithium intercalation in some of these phases such as $W_{19}O_{55}$ using n-butyl lithium was shown to occur up to 9 lithium per formula [1]. Due to the high reductive strength of n-butyl lithium the existence of intermediate lithium compounds was probably not detected.

We have investigated the formation of $Li_xW_{19}O_{55}$, $0<x<9$, by means of electrochemical methods. These allow a fine control of the stoichometry and hence the study of the possible lithium ordering into the tunnelled structure of the reduced oxides.

The voltage-composition curves so far obtained have shown the presence of several voltage drops and plateaus indicating the existence of different phases $Li_xW_{19}O_{55}$ in the range $0<x<9$. Since for $Li_9W_{19}O_{55}$ the structure of the reduced oxide appears to be kept, the formation of the new phases are thought to be due to different lithium ordering. A structural study of these new bronzes will also be presented.

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LAICM3318P **121, Tue. 14**

NEW IRIDIUM PEROVSKITE-LIKE MIXED OXIDES: Ba_2LnIrO_6 (Ln = Pr, Eu, Lu)

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The ideal perovskite structure (a_0=4A) is modified when the octahedral B sites are occupied by different cations ($A_2BB'O_6$). When the differences between the radii and the charges of B cations are quite large, long-range ordering occurs giving rise to a superstructure and the unit-cell parameters are related to a_0 ($a - a_0$). In our case the A sites are occupied by Ba cations (which ionic radius is similar to the oxygen one) and the cubic symmetry is maintained.

The materials Ba_2LnIrO_6 (Ln=Pr, Eu, Lu) were obtained by solid state reactions between $BaCO_3$, IrO_2 and the respective lanthanide oxides (Pr_4O_{11}, Eu_2O_3, Lu_2O_3) at 1373 K in several steps.

The products were characterized by X-ray diffractionand the parameters, refined by the AFFMA program, are listed in the table:

Compound	a (Å)
Ba_2PrIrO_6	8.3939(5)
Ba_2EuIrO_6	8.4348(5)
Ba_2LuIrO_6	8.2938(5)

The crystal structure of Ba_2PrIrO_6 was refined by a Rietveld analysis of powder X-ray diffraction data. The cubic space group is *Fm3m*. Magnetic susceptibility measurements are interpreted on the basis of the presence of Ln and Ir cations on the *B* sites. Electrical measurements show that the compounds are good semiconductors.

LAICM3319P **122, Tue. 14**

A NOVEL EXAMPLE OF A-CATIONS ORDERING IN THE PEROVSKITES (MLa)(MgTe)O_6 FOR M = Na Y K.

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It is well known that in $A_2(BB')O_6$ and $AA'(BB')O_6$ perovskites an ordered distribution of two types of B and B' ions along (111) planes is most probable when a large differences in both their charges and ionic radii exists (1). However, an ordered arrangement of A and A' ions on twelve coordinated site in $(AA')B_2O_6$ perovskites is found in a very limited number of compounds (2).

The compound (MLa)(MgTe)O_6, M = Na and K, show an X-ray powder pattern characteristic of the perovskite structure. The cell-edges are approximately $\sqrt{2}a_o$ for the *a*- and *b*- axis and $2a_o$ for the *c*-axis and β close to 90°, where a_o is the parameter of the ideal cubic perovskite. In the both compounds, a cation ordering of Na^+ and La^{3+} ions is therefore considered to occur along alternated c-planes. Thus a superstructure model based on cation ordering is proposed as shown in figure 1. In order to confirm the proposed superstructure a study by neutron diffraction has been carried out.

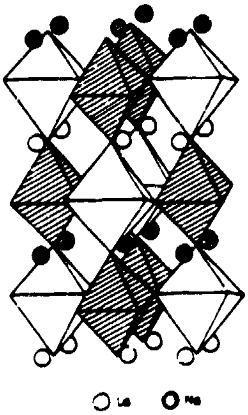

Figure 1.- Structural model of NaLaMgTeO_6

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LAICM3332P **123, Tue. 14**

MANGANESE-CONTAINING HYDROTALCITES.

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Hydrotalcite-like compounds are Layered Double Hydroxides (LHDs) with the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}]^{x+}A^{z-}_{x/z}.nH_{2}O$, where the trivalent cations partially substitute for divalent ones in the brucite like layers; the resulting net positive charge is cancelled by counteranions associated to variable amounts of water between the layers. The properties and applications of some LDHs and their decomposition products have been recently reviewed (1).

In the present work, new LDHS containing Ni-Mn and Mg-Mn have been synthesized at room temperature and constante pH. During precipitation Mn(II) ions undergo partial oxidation to Mn(III), given rise to the LDH structure, that was confirmed by X-ray powder diffraction. The interlayer spacing corresponding to the presence of carbonate as the counteranion (d_{003}= 7.8-7.9), also confirmed by FT-IR spectroscopy. DTA profiles recorded in air and in N_2 for the Mg-Mn sample were very similar, with two endothermic effects at 190 (dehydration) and 350°C(dehydroxylation and decarboxylation), their position coinciding with TG weight losses. For the Ni-Mn sample, these peaks were recorded at 195 and 300°C, with two additional peaks at 580 (exo) and 800°C (endo) when the analysis was carried out in air. Calcination at increasing temperatures gives rise to formation of divalent cation with the rock-salt structure, and to the corresponding spinels.

The differences between the thermal stability of both compounds are discussed on the basis of the different chemical properties of the constituting cations.

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LAICM3334P **124, Tue. 14**

SYNTHESIS OF TiO_2 BY PYROLYSIS OF AN AEROSOL

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TiO_2 is one of the best catalyst in the photocatalytic action for waste water treatment, the photocatalytic efficiency depending widely with its structural type, crystallinity and particle size[1]. More recently, and due to its semiconductor behaviour, TiO_2 is being used for gas sensor[2], since its near-surface region conductivity is very sensitive to the atmosphere. For most of these applications, it is of particular importance to synthesize a material showing very high specific surface, which is strongly dependent on the preparation method and ulterior annealing treatment.

For these reasons, we have prepared titanium oxide microparticles by pyrolysis at 700°C of an aerosol generated by ultra high-frequency spraying of a 0.05M titanium citrate solution, obtained by reaction of $TiO_2.nH_2O$ freshly prepared by hydrolysis of $TiCl_4$ with citric acid 0.02M. The material so obtained was subjected to different annealing treatments in order to study the influence of the temperature and time treatment on the amorphous-anatase-rutile transition.

The characterization by means of X-ray, TG-DTA, IR and SEM will be reported. Such a study indicates the presence of TiO_2 hollow spherical particles (1-2 µm), anatase or rutile being isolated as a function of the thermal treatment.

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LAICM3335P **125, Tue. 14**

DETERMINATION OF THE CARBON IMPURITIES IN THE 2212 Bi-SUPERCONDUCTOR.

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Many different methods have been used to prepare superconductor materials. One of the usefull methods for the synthesis of bulk superconductor oxides is the Pechini method (1). However, some carbon remains between the grains of the product, due to the thermal decomposition of citrates and ethyleneglycol. Obviously, this should influence on the electrical and magnetic properties of the materials obtained. Flükiger et al (2) reported that high J_c values depends dramatically on the carbon content.
However, the amount of carbon impurities has not been well evaluated. For this reason, we have prepared the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor material using the Pechini process (1), controlling different aspects related to the carbon content of the final product: (i) initial synthesis conditions; (ii) influence of the atmosphere (O_2, air and N_2) during the resin decomposition, after 450 °C; (iii) influence of the sintering time of the 2212 phase on the magnetic properties. We have performed the thermogravimetric study of the thermal decomposition of the initial resin under O_2, air and N_2 respectively. In all cases, carbon elemental analysis was performed. Morphological characteristics (by scanning electron microscopy) and magnetic properties (by susceptibility measurements) were studied.

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2.- R.Flukiger, A.Jeremie, B.Hensel, E.Seibt, J.Q.Xu and Y.Yamada, Adv. Cryogenic Eng. 38, 1073 (1992)

LAICM3336P **101, Thu. 16**

COMPLEX SUPERSTRUCTURES IN THE $Pr_{2-x}Sr_xCuO_{4-\delta}$ SYSTEM

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Three sructural types, T, T' and T*, related to the K_2NiF_4 structure have been reported for R_2CuO_4 materials (R=rare earth) which are dependent of the R anionic radium (1).

The rare earth cuprates R_2CuO_4 (R=Pr, Nd and Sm) are parent compounds of the electron-doped superconductors $R_{2-x}Ce_xCuO_{4-\delta}$ showing the so-called T' structures.

The T structure in $La_{2-x}Sr_xCuO_{4-\delta}$ can be stable for a wide composition range ($0 \leq x \leq 1.34$) but mixture of the T-type phase and Sr_2CuO_3 is obtained for $x>1.34$. The stabilization of the T structure occurs in $Pr_{2-x}Sr_xCuO_{4-\delta}$ and $Nd_{2-x}Sr_xCuO_{4-\delta}$ for x=1 and x=1.4, respectively (2).

On the other hand, a T'-T*-T-Sr_2CuO_3 phase transition seems to be observed in the $Pr_{2-x}Sr_xCuO_{4-\delta}$ system ($0 \leq x \leq 2$) with increasing Sr substitution. In order to understand the accommodation of compositional variations in this system, samples have been prepared with accurate control of both x and δ.

The microstructural characterization by electron diffraction and microscopy shows that non-stoichometry is accommodated by means of the formation of .complex superstructures related to T and T'structural types. Structural models as a function of the oxygen content will be discussed.

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HOW MANY POLYTYPES CAN EXIST IN THE $BaMnO_3$ SYSTEM ?

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AMO_3 perovskites can be usually described from the AO_3 stacking layers, M cations occupying octahedral sites. If all AO_3 layers are cubically stacked a cubic **3C** perovskite is obtained. When the stacking is hexagonal, the $BaNiO_3$ (**2H**) structural-type is obtained. Between both **3C** and **2H**-types, the existence of an almost infinite number of intermediate types can be imaged by intergrowing hexagonal and cubic layers. However, only a few number of them have been described up to now, generically named hexagonal perovskites.

In this way, powder X-ray diffraction studies by Negas and Roth (1) have shown that $BaMnO_3$ adopts a **2H** type structure. According to these authors, besides this one, a series of anion deficient $BaMnO_{3-y}$ phases exists, including different hexagonal types as **8H**, **6H**, **10H** and **4H** and one rhombohedral **15R** type.

However, in a microstructural study of some of these materials, as **15R** and **6H**-types, we have shown the existence of disorder as a result of the disordered intergrowth of phases with different alternance of AO_3 layers. We show in this paper, a HREM study of the $BaMnO_{3-y}$ system which evidences the existence of new polytypes. Particular attention will be devoted to two possible new types: **21R** and **8H'**.

1. T. Negas and S. Roth, J. Solid State Chem., 3, 323 (1971).

COMPOSITIONAL VARIATIONS AND STRUCTURAL TRANSITIONS IN $Nd_{2-x}Sr_xNiO_{4+\delta}$

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$Nd_2NiO_{4+\delta}$ shows the K_2NiF_4-structural type, the space group being dependent on the oxygen stoichiometry (1). The partial substitution of Nd by Sr in air synthesized samples of the $Nd_{2-x}Sr_xNiO_{4+\delta}$ system is accompanied by an orthorhombic (Fmmm)-tetragonal (I4/mmm) structural transition for x=0.2 (2). Since structural transitions seem to be dependent of both x and δ, we have undertaken a study of this system by accurate control of the oxygen content.

$Nd_{2-x}Sr_xNiO_{4+\delta}$ ($0\leq x\leq 1$) prepared at 1400°C in air shows a high Ni^{3+} percentage. Such materials were reduced under controlled atmosphere at different conditions leading to two different series as a function of δ:

a) when the average oxidation state of Ni is 2+, (R_x^{II} samples) orthorhombic Bmab materials were obtained for ($0\leq x\leq 0.4$).

b) when both Ni^{2+} and Ni^{+} are present ($R_x^{I,II}$ samples), a B112/n space group is obtained for x=0.2, and Immm for $0.2\leq x\leq 0.6$. A comparative study of both oxidated and reduced samples will be reported.

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LAICM3339P **104, Thu. 16**

ED AND HREM STUDY OF THE $LaNiO_{3-y}$ SYSTEM

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A microstructural study of the $LaNiO_{3-y}$ perovskite-related system has been performed. Samples were obtained by reducing the stoichiometric $LaNiO_3$ material, where y has been accurately controlled by means of a high sensitivity thermogravimetric technique.

Electron diffraction (ED) results show that ordering of oxygen vacancies leads to the formation of new superstructures of a homologous series of general formula $La_nNi_nO_{3n-1}$ when y=0.5 and 0.25, i.e., for n=2 and 4, respectively. Structural models of such phases can be described as formed by ordered intergrowths of (n-1) octahedral layers alternating with one layer in which Ni^{2+} adopts square-planar coordination. A high resolution electron microscopy (HREM) and image simulation study confirms this structural model.

Compositional variations for y=0.20 and y=0.33 are accommodated by means of disordered intergrowths of octahedral and square planar layers.

LAICM3340P **105, Thu. 16**

CHAINS IN TWO NEW FLUOROMANGANATES: HYDROGEN BOND FRAMEWORK.

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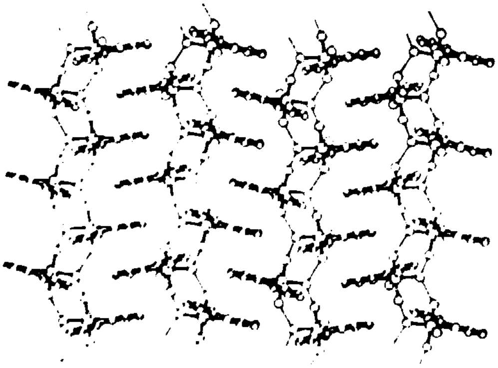
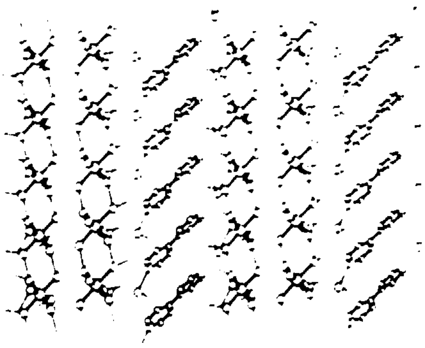
Two new fluoromanganates (III) with 2,2'dipyridyl and 4,4'dipyridyl, not described in the literature, have been obtained by mixing hydrofluoric acid solutions of Mn (III) and the corresponding organic base. They were characterizated by chemistry analyses, I.R. spectroscopy and single crystal X-Ray diffraction.

Compound I $[MnF_4L1]H$, where L1=2,2'dipyridyl, has a monoclinic cell ($P2_1/n$): a=19.737(4);b=7.490(2);c=9.031(3) Å;β=95.22°(3);Z=4. The ligand is bonded to Mn, via its two nitrogen atoms. The structure shows chains running parallel to b axes of elongated octahedra connected each other by a double hydrogen bonding.



Compound I



Compound II

Compound II: $L2[MnF_4(H_2O)_2]_2 \cdot 2H_2O$, with L2=4,4'dipyridyl diprotonated, has a monoclinic cell ($P2_1$): a=5.164(2);b= 18.519(4);c=9.863(2)Å;β=99.07°(0.03);Z=2. The ligand acts as countercation with charge +2.

As can be deduced of both figures a very rich intermolecular hydrogen bond framework is present and it will be discussed.

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LAYERED TIN-TITANIUM PHOSPHATES

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In the last years, the lamellar phosphates of tetravalent metals have been the subject of several investigations as a consequence of their interesting properties in fields such as ion exchange, catalysis, ionic conductivity, etc.. Two structural types have been mainly studied: α- and γ-forms. Despite the chemical composition of both varieties is similar [$M(HPO_4)_2 \cdot nH_2O$], they are very different since the α-form is a bis(hydrogenphosphate) monohydrate and the γ-form is dihydrogenphosphate orthophosphate dihydrate.

Although many lamellar phosphates with α-structure [α-$M(HPO_4)_2 \cdot H_2O$ (M=Ti,Zr,Hf,Sn,Pb)] are known, only the synthesis of the γ-$M(H_2PO_4)(PO_4) \cdot 2H_2O$ (M=Ti,Zr) has been described. The synthesis of both varieties is easy for the titanium phosphates. By addition of diluted H_3PO_4 to an aqueous solution of $TiCl_4$, a gel of titanium phosphate is obtained with a molar ratio P/Ti lower than 2 which at reflux in concentrated H_3PO_4 gives rise to a microcrystalline material with a molar ratio P/Ti of 2. When the concentration of H_3PO_4 is 10 M, the α-compound is obtained. When it is 17 M the variety obtained is the γ.

The synthesis method of α-tin phosphate is similar to that of the α-titanium phosphate. γ-Tin phosphate has not been synthesized yet. This paper reports the synthesis of tin-titanium phosphates in similar conditions to those used in the synthesis of γ-titanium phosphate. The new materials are characterized by chemical, textural and thermal analysis, X-ray diffraction, i.r. spectroscopy and electron microscopy.

Our tin-titanium phosphates are solid solutions showing an isomorphic substitution of tin by titanium in the α-tin phosphate lattice and tin substitution in the γ-titanium phosphate lattice. In both cases, the solubility is partial. The coexistence of both saturated phases is observed in samples of composition between the solubility limits. Lattice parameters scarcely vary during the isomorphic substitution. The intercalation compounds of mixed tin titanium phosphates with n-butylamine were synthesized being their interlayer distances a function of the Ti/Sn ratio.

α-Tin phosphate and γ-titanium phosphate are materials with low specific surface. The porosity of the tin-titanium phosphates is higher so that is more suitable to be used as catalyst and catalyst support.

INTERCALATION OF α,ω-ALKYLDIAMINES IN LAYERED γ-TITANIUM PHOSPHATE FROM AQUEOUS SOLUTIONS

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Introduction

Intercalation of dibasic organic molecules in an acid layered solid transforms the compound in a framework material that may show a potentially accessible porosity. In the last years, many papers on the properties of layered phosphates of tetravalent metals in intercalation procedures have been published. This paper reports a study of the acid basic topotactic solid state reaction between alkyldiamine solutions (H_2N-$[CH_2]_n$-NH_2, n=2-9) and the γ-titanium phosphate, γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$, to obtain γ-$Ti(H_2PO_4)(PO_4)\cdot xR(NH_2)_2\cdot mH_2O$ compounds.

Experimental

The intercalation process was carried out with the batch technique. Two series of compounds were synthesized by dispersing, at 25°C, 0.4g of γ-TiP in 40 ml of standardized diamine solutions, with variable concentrations. The materials were obtained using reaction times of 5 hours for the first series, and 48 hours for the second one. All the samples were dried at 50°C and then their XRD patterns were obtained. The intercalation compounds were also characterized by measuring the diamine content by elementary analysis (C,H,N) and weigth loss measurements. Thermal analysis (TG and DSC) and the pH variations occurring during the intercalation process were also determined.

Results and discussion

The free area of each POH group in γ-titanium phosphate (16.4 $Å^2$) is lower than the size of the cross section of the amine (18.6 $Å^2$) so that steric hindrance should be encountered for the simultaneous interaction of amine with two adjacent active centers. The intercalation of one mole of amine per mole of γ-titanium phosphate is geometrically impossible. The compounds with higher organic content have the formula γ-$Ti(H_2PO_4)(PO_4)\cdot 0.7R(NH_2)_2\cdot H_2O$. Their basal spacings increase linearly with the number of carbon atoms in the alkylchain. In the equilibrium, the amines are located in the interlayer spacings as a monolayer. The -NH_2 groups of each amine interact with hydrogen ions of two different layers. The alkylchain is located in a *trans-trans* configuration and the N-C bond is approximately perpendicular to the phosphate layer. The crystalline phases obtained under non-equilibrium conditions (short reaction times) show interlayer distances smaller than those found in the thermodynamically stable compounds, which indicates a higher inclination of the alkylchain and more stretched configurations (it is even possible the existence of diamine molecules bonded to the layer through only one amino group). The thermal stability and textural properties of the intercalation compounds are analyzed.

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DSC AND XRD STUDY OF THE SYSTEM $(NH_4)_2SO_4$-$(NH_4)_2BeF_4$.

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Compounds of the general formula A_2BX_4 have drawn much interest in recent years because of their ferroelastic/ferroelectric behaviour and their structural phase transitions, sometimes, incommensurate phase transitions.

Ammonium sulfate, $(NH_4)_2SO_4$ [AS] undergoes a ferroelectric transition at 223K. Both paraelectric and ferroelectric phases are othorhombic, the symmetry changes from the space group Pnam in the paraelectric phase to $Pna2_1$ in the ferroelectric phase. Ammonium tetrafluoroberilate, $(NH_4)_2BeF_4$ [ABF] undergoes two succesive phase transitions at T_i= 183K and T_C= 177K. The crystal symmetry of the paraelectric phase above T_i is orthorhombic Pnam, the ferroelectric phase below T_C is also orthorhombic but $Pn2_1a$, and the intermediate phase is undetermined, with the incommensurate modulation along the *a* axis.[1].

In recent papers the system $(NH_4)_2(SO_4)_{1-x}(BeF_4)_x$ $(1>x>0)$ [ASBF] has been studied. The phases rich in sulfate show a behaviour very similar with the AS. The phases rich in tetrafluoroberilate show a behaviour related with the ABF. Another intermediate domain exists which is not well characterized[2]. For this reason we have studied the behaviour of the solid solution ASBF using DSC and XRD powder at variable temperature in order to delimit the different domains.

We can conclude: 1) there are solid solutions for all values of *x*, 2) the two ferroelectric phases $Pn2_1a$ and $Pna2_1$ have a limited range of existence, 3) the intermediate incommensurate phase is different than the other two phases and it has a finite range of composition.

	$(NH_4)_2SO_4$		$(NH_4)_2BeF_4$	
T(K)	298	183	298	143
a(A)	7.782	7.837	7.651	15.131
b(A)	10.636	10.610	10.457	10.501
c(A)	5.993	5.967	5.932	5.925
	Pnam	$Pna2_1$	Pnam	$Pn2_1a$

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LAICM3352P **109, Thu. 16**

PHASE CHEMISTRY AND MICROSTRUCTURE OF ZONE REFINED SUPERCONDUCTING COMPOSITE WIRES

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Practical devices based on High Temperature Superconducting Ceramics (HTSC) imply, for many of the envisaged applications, their use in the form of metal/ and alloy/ superconductor oxide composites. In order to prevent the structural weaknesses inherent to HTSC materials, as well as to increase their chemical stability and improve their electrical and thermal contact characteristics, it is necessary to develop and increase our understanding of the above mentioned composites.

The Powder-in-Tube (PIT) method, one of the most successful ways of obtaining superconducting composite wires, has been used in this study to prepare these composites with varying configurations. These included using $Bi_2Sr_2Ca_2Cu_3O_{10}$ (BSCCO) and $YBa_2Cu_3O_7$ (YBCO), as the core ceramic superconducting matrix, combined with different metal and alloy sheaths. The superconducting BSCCO and YBCO powders used to fill the starting metal tubes were prepared using a polymer matrix synthesis route which yields uniform, platelet-like grains of the desired HTSC stoichiometry. Long wires were obtained by drawing the starting filled tubes through progressively reducing diameter dies. These wires were then zone refined in order to establish an adequate level of texture and electrical connectivity between the superconductor grains.

Phase chemistry and microstructure of the starting HTSC powders and the resulting wires have been studied using powder X-ray diffraction, electronic (SEM with EDX) and optical microscopy. The physical properties of these products have been studied using magnetic a.c. susceptibility, magnetisation and transport critical current measurements.

The zone refining method applied to the drawn wires yields, in many cases, superconducting composites with textured grains.

COMPOUND AND SOLID SOLUTION FORMATION IN THE SYSTEM $Li_2O-Nb_2O_5-MgO$

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The title system contains a number of well-characterized binary compounds, of this, $LiNbO_3$ is an important material with applications in optoelectronics including light modulation microwave filters, frequency doublets. It is also useful for optical information processing.

The properties of $LiNbO_3$ may be modified by incorporating different cations into the structure. The effect of Mg doping has also been investigated: Mg doped samples of $LiNbO_3$ hold promise as substrates for optical wave guide fabrication.

On the other hand, Li_3NbO_4 has rock salt related structure and form ordered-disordered polymorphs. The disordered polymorph have the face centered cubic structure of NaCl in which the cations are distributed at random over the octahedral sites in a cubic close packed array of oxygens. The disordered polymorph is prepared as metastable phase at relatively low temperature.

Hence, order-disorder phenomena commonly occur and have been studied in detail in the systems Li_2TiO_3-MgO and $Li_2TiO_3-Li_3NbO_4$.

In this work a systematic study of compound and solid solution formation in the system $Li_2O-Nb_2O_5-MgO$ has been made. Three solid solution series based on $LiNbO_3$, Li_3NbO_4 and MgO have been founded. Two new phases of approximate formulae: "$Li_5Nb_3MgO_{11}$" and "$Li_6MgNb_2O_9$" have been prepared. The last one presents the cation ordering transition. Indexed x-ray powder data and cell parameters of both phases are reported.

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INFUENCE OF STOICHIOMETRY AND CHEMICAL COMPOSITION ON THE MAGNETIC RELAXATION IN FERRIMAGNETIC SPINELS

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Ferrimagnetic oxides, the so called ferrites, form a broad class of magnetic materials with important technical applications. Among these materials, soft ferrites presenting spinel structure and MFe_2O_4 type chemical composition ($M=Ni, Mn, Co, Zn, Ti...$) have an outstanding place. Their quality and possible range of applications are mainly evaluated by means of the measurement of three basic parameters: initial permeability and magnetic losses and relaxation. All these parameters are strongly dependent on the chemical composition, stoichiometry and microstructure of the materials

In this work we present the study of magnetic relaxation in two spinels, magnetite and Ni-ferrites, in the temperature interval $200<T(K)<600$. In magnetite, two relaxation peaks occur in this temperature range. They are designated as peak III ($250<T(K)<350$) and peak I ($400<T(K)<500$). Although there is a general agreement amongst various authors as to the interpretation of peak III, there is still a controversy as to the nature of the higher temperature relaxation peak. In this context[1] we have recently proposed an interpretation of peak III and peak I as being, respectively, due to the reorientation and diffusion respectively of the same kind of defect, the octahedrally coordinated vacancy.

For Ni-ferrites in this temperature range we observe three well defined relaxation peaks. These are designated as peak III ($250< T(K)< 350$), peak II ($350<T(K)<400$) and peak I ($450<T(K)<600$). Peak III is the peak discussed before for magnetite. A closer look at peak I has revealed that it is made up by two relaxation processes we have attributed to a Ni-Ni pair reorientation and a bulk diffusion process with participation of both Ni and Fe ions. The origin of peak II is more controversial. The original idea was that peak II was due to the reorientation of the Ni ion, but its presence in Ba ferrites[2], where we can assume that the Ba ion because of its large size remains immobile, leads us to the conclusion that peak II is due to a modification of the movement of Fe ions due to the presence of Ni.

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF $NH_4NiPO_4.6H_2O$, ISOMORPHOUS TO THE STRUVITE MINERAL

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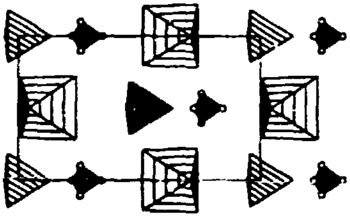
Ammonium phosphates with transition elements show a large variety of structural phases that make them an interesting domain to study the relationships between structural features and physico-chemical properties.

Single crystals of $NH_4NiPO_4.6H_2O$ suitable for X-ray study were obtained from water solutions of $NiCl_2.6H_2O$ and H_3PO_4 by addition of NH_4OH with pH control. This compound cristallizes in the orthorhombic space group $Pmn2_1$, with cell constants a=6.9133(3), b=6.0972(2), c=11.1581(5)Å and Z=2.

The structure of $NH_4NiPO_4.6H_2O$ was solved using the heavy atom method (Patterson, SHELX86). The obtained bond distances and angles show no major differences with respect to the values reported for isomorphous Struvite by Ferraris et al. [(1986) Acta Cryst., B42, 253].



Crystal structure of $NH_4NiPO_4.6H_2O$

The difference Fourier map gave the positions of all hydrogen atoms. The final refinement led to convergence at R = 0.027 and wR = 0.028. The structure consists on $Ni(H_2O)_6$ octahedra, PO_4 tetrahedra and ammonium groups, which hold together by hydrogen bonds. The water molecules donate some of the shortest hydrogen bonds ever found in crystalline hydrates, whereas ammonium group exhibits a polyfurcated system of weak bonds.

The thermal decomposition study of the title compound presents two different steps. The first one corresponds to the initial dehydration (6 water molecules) and deammoniation, and the second one is associated with PO_4 condensation to give the corresponding pyrophosphate.

Infrared spectrum of this compound shows two bands corresponding to the phosphate anion at 570 and 1020 cm^{-1}, which show no splitting due to the high local symmetry of the undistorted PO_4 ions.

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WP_2O_7: A NEW TUNGSTEN (IV) PHOSPHATE WITH A TUNNEL STRUCTURE

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The physical properties of the W-P-O compounds are determined by the great ability of the tungsten to form mixed valency phases. Really, most of the studied materials correspond to the four families of phosphate tungsten bronzes. However, electronic localization is expected when the $|WO_6|$ octahedra are embedded in an insulating matrix.

The synthesis of the WP_2O_7 compound was performed from a mixture of WO_3 and $(NH_4)_2HPO_4$, with a molar ratio of 1:5, heated at 600°C for 4 h. The crystal structure was determined from the X-ray powder diffraction pattern, using the Rietveld method and taking the coordinates of the MoP_2O_7 compound as starting point. It crystallizes in the Pa3 space group with four formula weights in a cell measuring a=7.9360(1) Å (R=0.042).

The structure can be described as a three dimensional framework built up from $|WO_6|$ octahedra sharing their corners with $|P_2O_7|$ groups. These polyhedra originate mixed layers characterized by the presence of pentagonal windows limited by two octahedra and three tetrahedra. The layers are staggered in a such way that the pentagonal windows delimit intersecting zig-zag tunnels.

The temperature dependence of the magnetic susceptibility is characteristic of compounds with localized electrons, in good agreement with the electrical conductivity measurements ($\sigma<10^{-8}\ \Omega^{-1}cm^{-1}$ a 250 K). The susceptibility follows a Curie-Weiss law with $C_m=0.31\ cm^3K/mol\text{-}W$ and $\theta=-4.2$ K. The strong reduction observed for the Curie-constant is mainly due to the influence of the spin-orbit coupling ($\lambda=1050\ cm^{-1}$ for the free-ion). The negative temperature intercept is due to, both, the zero-field splitting and the existence of antiferromagnetic interactions. Taking into account the structural features of this compound, the exchange pathway must necessary involves the phosphate groups.

Therefore, even if the structural features and composition induce to consider the WP_2O_7 as the first member (m=1) of the Diphosphate Tungsten Bronzes with Pentagonal Tunnels (DPTBp, $(P_2O_4)_2(WO_3)_{2m}$), the observed properties indicate that electronic delocalization is not present.

CRYSTALLOGRAPHIC, SPECTROSCOPIC AND MAGNETIC STUDIES OF THE (Mg, M)$_3$(AsO$_4$)$_2$·8H$_2$O [M= Co, Ni] SOLID SOLUTIONS.

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The phosphate and arsenate minerals offer a considerable number of structures which can give rise to original physico-chemical properties. Complex and original magnetic behaviours have been observed related to the nature of the metallic ions and the structural features. The existence of many possible exchange pathways in these compounds makes it difficult to understand their magnetic behaviour.

In this way, we have prepared $Mg_{3-x}M_x(AsO_4)_2 \cdot 8H_2O$ [M= Co, Ni; x= 0, 1, 1.5, 2, 3] compounds, which crystallize in the monoclinic system, with space group I2/m. The crystal ordering consists of octahedral dimers $[M_2O_6(H_2O)_4]$, and $[MO_2(H_2O)_4]$ insular octahedra, linked by $[XO_4]$ tetrahedra into sheets parallel to (010) plane, held together by hydrogen bonding between adjacent single and double octahedra. They form solid solutions over the whole composition range.

Increasing the amount of magnesium in these phases yields a progressive increase of the unit-cell volume, which is due to the weakening of hydrogen bonding as indicated by spectroscopic measurements.

Magnetic studies reveal the existence of 3D antiferromagnetic ordering in non substituted compounds, which disappears when Mg(II) ions are introduced into the structures. However, prevalent magnetic interactions in octahedral dimers are ferromagnetic ones. This fact is better observed in the nickel solid solutions and is in accord with the strong preference of Mg(II) ions for the dimeric sites, fundamentally owing to the ionicity of such sites.

LAICM3420P **115, Thu. 16**

Structures and Electrical Properties of the complexes $\mathrm{Ni(II)(CTH)(TCNQ)_2}$ and $\mathrm{Ni(II)(CTH)(TCNQ)_3}$.

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Tetracyanoquinodimethane, TCNQ, salts have been a classical subject of study in the field of low-dimensional molecular conductors. They may be classified as simple or complex salts according to the degree of ionicity that can be either integer or fractional, respectively. The crystal structure and physical properties of both kind of compounds are closely correlated to the extent of the charge transfer.

Our main interest in this subject is based on the possibility to obtain an effective magnetic coupling between localized (i.e. magnetic) and delocalized (i.e. conducting) electrons involving an indirect exchange mechanism. Our strategy implies the use of macrocyclic metal complexes as spin carriers, with vacant coordination sites combinated to π-radical anions capable, not only to coordinate to the metal ion, but even to stack among them to render a conducting columnar array which contains the free carriers.

In the present comunication we show the structures and the electrical properties of the complexes $\mathrm{Ni(CTH)(TCNQ)_2}$ and $\mathrm{Ni(CTH)(TCNQ)_3}$.

Table I. Conductivity Data for $\mathrm{Ni(CTH)(TCNQ)_2}$ and $\mathrm{Ni(CTH)(TCNQ)_3}$ complexes.

Compound	E_g/eV	σ_0/Scm^{-1}	σ_{298}/Scm^{-1}
$\mathrm{Ni(CTH)(TCNQ)}^2$	0.99	$1.06 \cdot 10^{-3}$	$4.62 \cdot 10^{-12}$
$\mathrm{Ni(CTH)(TCNQ)}^3$	0.60	$4.87 \cdot 10^{-3}$	$1.60 \cdot 10^{-3}$

LAICM3435P

116, Thu. 16

PREPARATION AND STUDY OF PEROVSKITES
Ba$_{1-x}$La$_x$NbO$_3$ (x = 0, 0.1).

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Many of the transition metal oxides with electronic configuration d^1 that adopt perovskite structure, e.g. LaTiO$_3$, present interesting electrical and magnetic properties. Besides, materials with d^1 electronic configuration are of particular interest to test whether the superconducting properties of single-hole divalent Cu (d^9) oxides are electron-hole symmetric or not. These reasons have impelled us to study some d^1 systems, for which a very few structural, electrical and magnetic data have been described. This is probably due to the difficulties found in their synthesis. This is the case of the system BaNbO$_3$ that contains Nb(IV). The obvius procedure of synthesis from BaO and NbO$_2$, in vacuum, leads invariably to the obtention of Ba$_5$Nb$_4$O$_{15}$ with Nb(V). We have managed to obtain BaNbO$_3$ from mixtures of Ba$_5$Nb$_4$O$_{15}$ and metallic Nb with ratio Ba/Nb=1.4. Its X-ray diffractogram corresponds to a cubic perovskite with a=4Å. The ratio Ba/Nb in the starting mixtures could suggest the existence of vacancies of Ba in the structure , similar to those of the bronzes described for Sr$_{1-x}$NbO$_3$(1). In our case, the analysis of profiles of the diagram allows us to confirm the absence of such vacancies on the Ba sites. The compound, reddish in colour, shows metallic behaviour between 4K and room temperature. At present, we are studying the system Ba$_{1-x}$La$_x$NbO$_3$. The stabilization of Nb^{3+} in the structure seems to be possible only for values of $x < 0.2$, for which perovskite phases without impurities have been obtained.

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PREPARATION AT HIGH OXYGEN PRESSURES AND STUDY OF $Ln_{1-x}A_xNiO_3$ (A = Ca, Sr; Ln = La, Nd, Sm, Eu).

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The study of the $LnNiO_3$ perovskites (Ln:Lanthanides) has a special interest due to the metallic behaviour shown for the (Ln=La) member and metal-insulator transitions described for the oxides with Ln=Pr, Nd, Sm, Eu (1). This behaviour, unusual in oxides of transition metals, is directely associated to the presence of Ni(III), whose stabilization requires special synthesis conditions.

In this work, we have tried the partial substitution of the lanthanide for an alkaline-earth, in order to study the influence on the electric and magnetic properties of the hole-doping of the nickel d-bands in these compounds.

The samples $Ln_{1-x}A_xNiO_3$ have been prepared by slow decomposition of a metal citrate solution. The precursor powders were heated at 900-1000ºC and 200 bars of oxygen.

A study by x-ray diffraction shows an increase of the rhombohedral distorsion for Ln=La or orthorhombic distorsion for Ln=Nd, Sm, Eu, when the Ca^{2+} and Sr^{2+} ions are introduced into the lattice. The thermal behaviour in a H_2/N_2 flow confirms the existence of nickel (III-IV). A preliminary study of the electric properties for $Nd_{0.9}Sr_{0.1}NiO_3$ suggests that the doping leads to the disappearance of the metal-insulator transition; it exhibits metallic behaviour between 1.5K and room temperature (similar to $LaNiO_3$).

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SYNTHESIS OF CYCLOTRIPHOSPHAZENES AND PHOSPHAZENE HIGH POLYMERS WITH FUNCTIONALIZED PHENOLS.

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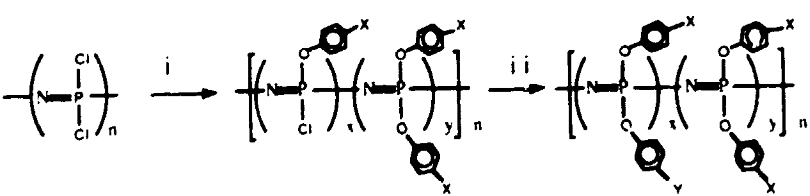
The hexaclorocyclotriphosphazene $[N_3P_3Cl_6]$ (**1**) reacts directly with the para-substiuted phenols $HO\text{-}C_6H_4\text{-}X$ (X=Bu^t, Br, CN, OMe) and K_2CO_3 in refluxing acetone to give the corresponding hexasubstituted aryloxyphosphazenes $[N_3P_3(O\text{-}C_6H_4\text{-}X)_6]$ (**2a-2d**). In the case of the CN and Br derivatives the reactions requiered only 1 hour to be completed and the yields are of the order of 90%, while in the other cases 200 to 300 hours are neccessary, and the yiled were lower (ca.50%). However, as shown early by Allcock [1], the reactions are much faster in the presence of Bu^t_4NBr, lasting only a few minutes for the Br and CN derivatives, and ca. 20 hours in the other cases.

Monitoring the reactions by ^{31}P NMR revealed that the sustitution of Cl by the phenoxide occurs predominantly by a non-geminal mechanism, and that all possible isomeric forms of the di, tri and tetra substituted products can be observed.

This method, but using thf as solvent, was extended to the synthesis of polyphosphazene high polymers of general formulae $\{[NP(O\text{-}C_6H_5\text{-}X)_2]_x\text{-}[NP(O\text{-}C_6H_5\text{-}Y)(O\text{-}C_6H_5\text{-}X)]_y\}_n$ (X=H or Bu^t, Y=Br or CN) (**3a-3d**), starting from $[NPCl2]_n$, (see scheme 1), that was obtained by the thermal polymerization of $[N_3P_3Cl_6]$ (**1**) in solution[2].

The new polymers, with less than 1% Cl content, had high molecular weights, as measured by GPC and low glass transition temperatures, as measured be DSC.



i. $HOC_6H_4X/\ K_2CO_3$/thf
ii. $HOC_6H_4Y\ /\ K_2CO_3$/ thf

Scheme 1

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1. Austin, P. E.; Riding, G.H.; Allcock, H.R. *Macromolecules* **1983**, *16*, 719

2. Mujundar, A. N.; Young, S. G.; Merker, R. L.; Magill, J. H. *Macromolecules* **1990**, *23*, 14

LAICM3451P **119, Thu. 16**

COMPOUNDS OF FIRST ROW TRANSITION METALS WITH POLYFUNCTIONAL LIGANDS. PREPARATION AND CHARACTERIZATION OF TWO NEW COPPER CYANURATES WITH DISTINCT HYDROGEN BONDING PATTERNS

Larry R. Falvello, Isabel Pascual, and Milagros Tomás.
Departamento de Química Inorganica; Instituto de Ciencias de Materiales de Aragón; Universidad de Zaragoza-C.S.I.C 50009
Zaragoza, Spain

During the course of a more extensive study on the modulation of intra-molecular structures by inter-molecular forces in the crystalline state, we have prepared two systems in which new complexes of copper are bridged by extensive patterns of hydrogen bonds. The implications of these and related structures for the formation of molecular solid solutions are discussed.

Crystals of $[Cu(NH_3)_2(C_3H_2N_3O_3)_2]\cdot[Cu(NH_3)_4](C_3H_2N_3O_3)_2$, **1**, were produced by slow cooling of a concentrated aqueous solution of the product in the presence of an excess of ammonia. Diffraction data were taken, via single-crystal methods, from a crystalline twin, which was resolved. The crystals are triclinic, space group $P\bar{1}$, with a=7.143(1), b=8.683(2), c=11.603(2) Å, α =102.12(3), β=101.24(3), γ=106.22(3)° V=650.5(3) Å^3 and Z =2. Independent refinements of the structure were conducted using both the twinned-crystal diffraction data and x-ray powder diffraction data. Two different complexes of copper are present in the cell, and the entire structure is stabilized by an extensive net of hydrogen bonds.

The complex $[Cu(H_2O)_2(C_3H_2N_3O_3)_2]\cdot Na(C_3H_2N_3O_3)(H_2O)_2$, **2**, crystallizes via slow diffusion of isopropanol into the aqueous phase in the triclinic system, space group $P\bar{1}$, with a=6.776(1), b=10.462(2), c=10.463(3), α =62.86(3), β= 71.79(3), γ=83.78(3)° V=626.5(3) Å^3 and Z = 2. The crystal structure presents a rich net of hydrogen bonding interactions.

The structures of complexes **1** and **2** are presented in detail, with emphasis on the hydrogen bonding patterns. The implications of the latter for the formation of molecular solid solutions by these systems are discussed, and reference is made to related new cyanurate compounds of other first-row transition metals, which we have recently characterized.

LAICM3465P **120, Thu. 16**

ON THE REDUCTION OF $PrBa_2Cu_3O_{7\pm\delta}$

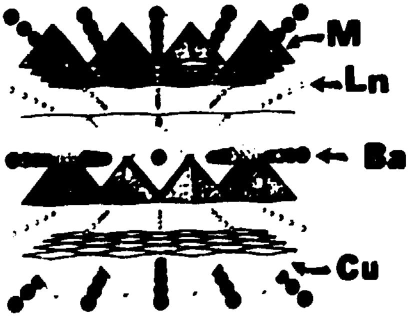
M. A. Alario-Franco, U. Amador, I. Garrote, E. Morán,
R. Sáez-Puche, C. Torrón* and A. Várez.
Departamento de Química. Inorgánica. Fac. C. Químicas.
Universidad Complutense . 28040 Madrid (Spain) and
* LAFIMAS. Facultad de Fisica. Universidad de
Santiago de Compostela. 15706 (Spain).

This praseodymium-barium-copper oxide, member of the $LnBa_2Cu_3O_7$ family (123) (Ln = lanthanide) is not superconductor. Some authors have reported this fact as being due to a too high oxidation state of the praseodymium ions. Thus, it appears attractive trying to reduce them. We have performed it by three different means: long treatments under vacuum in the presence of an oxygen getter (zirconium metal), reduction with n-butyl lithium and finally, reduction with H_2 under mild conditions. A common feature in all the reduced samples is the presence of extended defects perpendicular to the c axis, which in the case of the lithium reduction can be unambiguously interpreted as intergrowths of copper richer phases (either the 124 or the 247) in the 123 matrix. Magnetic susceptibility measurements indicate a trivalent oxidation state for praseodymium taking into account crystal field effects and none of the reduced samples show superconductivity.

SYNTHESIS AND STRUCTURE OF NOVEL CUPRATES IN THE Ba-Ln-M-Cu-O SYSTEMS (LN:Y, La; M:Ni, Co).

M.J.Ruiz, E. Morán.
Dpto. Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid

New compounds of formula $LnBaCuMO_{5+\delta}$ (Ln=Y,La;M=Co,Ni) have been synthesized. Their structure determined by powder X Ray diffraction (XRD), Rietveld analysis, can be described as formed by double layers of corner-sharing [$Cu-O_5$] and [$M-O_5$] pyramids perpendicular to the c axis. Nevertheless and in spite of having (Cu-O) planes none of these materials is superconductor. Besides XRD, EDS analysis, and magnetic susceptibility measurements have been used to characterize them.



NEW SPINEL FERRITES OBTAINED BY IONIC EXCHANGE

M.C.Blesa[1], E.Morán[1], U.Amador[1], N.Menéndez[2], J.D.Tornero[2].
1.Dpto.de Química Inorgánica, Facultad de C.Químicas, Universidad Complutense, 28040-Madrid.
2.Dpto.de Química Física Aplicada.Facultad de Ciencias, Universidad Autónoma.Cantoblanco 28049-Madrid.

Ferrites with spinel structure can be obtained by ionic exchange performed in molten salts on α-$NaFeO_2$. In order to perform it, molten salts containing small enough divalent cations, such as Ni or Mg, have been used, the alkali metal being easyly exchanged through a topotactic mechanism. (1). In this communication we have extended the method to some other cations (Co and Zn) and have used chlorides instead nitrates as reaction media; the advantage of it is to avoid hydrolysis problems -arising from the water that most of the divalent nitrates contain-, thus getting purer samples, although higher temperatures have to be used. By these means, very pure and well crystallized spinel ferrites have been prepared at remarkable relatively low temperatures (500 C) which structure has been determined by powder X-Ray diffraction methods (Rietveld analysis). Mössbauer spectra and magnetization measurements are being performed in order to get more information about cationic distributions and will be presented and discussed.

LAICM3490P **123, Thu. 16**

HYDROTERMIC SYNTHESIS OF M (PO) (OH) (M= Ca, Mg, Co).

R. Gonzales Santos, J. Guerra-López García, A. Gómez.

Lab. Biomaterials, National Center for Cientific Research, P.O. Box 6880 Havana City, Cuba.

Apatites form a large family of isomorphous compounds. From this family the calcium hidroxyapatite (Ca-Hap) has been the most studied ones; it is the main constituent of mineral biological tissue (eg, bone and enamel). The "biological" apatites are similar but not identical with synthetic hydroxyapatites in composition and structural properties. More important than this similarity observed, it is the study of "impurity" ions present in biological apatites, which are the principal responsible for these differences. The aim of this work is to study the effects over the structure of Ca-Hap produced by Mg and Co ions, when they are obtained by hydrotermic synthesis from its respective metalic carbonates in ammoniacal solution.

The results of IR spectroscopy and powder X-Ray Difraction showed the substitution of M by NH ion in the crystal lattice in dependence of conditions of reactions.

LAICM3491P **124, Thu. 16**

EFFECTS OF PHYSICAL-CHEMICAL PROPERTIES OVER THE BEHAVIOR "IN VIVO" OF TWO BIOMATERIALS DERIVED FROM SEA CORALS.

R. Gonzales Santos; J. Guerra-López García; M.C. Melo; O. Pereda.

Lab. Biomaterial, National Center for Scientific Research, P.O. Box 6880. Havana City, Cuba.

The Ca-phosphate systems and in particular the apatites have been researched very extensively in the last years as biomaterials for reconstruction of osseous tissue by its great structural and chemical similitude with bone calcified tissue. At present it is known the influence of chemistry composition and structure of these compounds over their bioactive property (osteoconduction, reabsortion, osteointegration, etc.). In this work, two biomaterials obtained from sea corals of different chemical composition and physical-chemical properties (Osteocoral and Hap-porous 200) have been compared according to their behaviour in clinical use.

CHARACTERIZATION OF THE ANHYDROUS CU-SR AND CU-CA FORMATES

P.K.de Perazzo,G.Leyva,G.Polla,H.Lanza,M.R.de Benyacar
División Física del Sólido. Depto. de Física
Comisión Nacional de Energía Atómica
Av. del Libertador 8250. Buenos Aires (1429). Argentina.

Anhydrous copper-strontium and copper-calcium formates have been used to obtain double oxides as precursors in the high temperature superconductor synthesis.
The aim of this communication is to correlate the thermal behavior of these double formates with the corresponding alkaline-terreous formate.
The existence of some polymorphic species of the anhydrous calcium formate and anhydrous strontium formate between 20 and 300 °C, the importance of the presence of water vapor on the phase transition and the effect of different oxides on the decomposition temperature is discussed.
Differential scanning calorimetry, X-ray diffraction, thermogravimetric analysis and optical microscopy on heating stage were used to study the thermal behavior of the anhydrous Cu-Ca and Cu-Sr formates in the range of 20 to 1000°C.

References:
R.F.Baggio, M.A.R. de Benyacar, P.K. de Perazzo, G.Polla. J.Solid State Chem. 56, 298-303, (1985).
B.F.Mentzen, C.Comel. J.Solid State Chem. 9, 214-223, (1974).
C.Comel, B.F.Mentzen. J.Solid State Chem. 9, 210-213, (1974).

LAICM3503P **126, Thu. 16**

CRYSTALLINE STRUCTURE OF Cu-Sr AND Cu-Ca FORMATE.Cu-Ca FORMATE SUPERSTRUCTURE ANALYSIS

A.G.Leyva, G.Polla, P.K.de Perazzo and F.Parisi
Comisión Nacional de Energía Atómica
Avda. del Libertador 8250
Buenos Aires (1429) Argentina

Cu-Sr and Cu-Ca formates have been synthesized and used as precursors of binary oxides and these to obtain high Tc superconductors.

The crystal structure of both compounds ($CuSr(HCOO)_4$ and $CuCa_2(HCOO)_6$) were undertaken to correlate their structural features.

The Cu-Sr formate structure was solved and refined in the $P2_1/c$ space group. It converged to an anisotropic R value of 0.042.

The diffraction pattern of the Ca compound showed a sub-group of intense reflexions that were used to solve the basic structure with a=22.291 b=8.799 c=6.374 Å, β=101.04° and refined in the C2/c space group to a final R value of 0.033. Including the sub-group of weak reflexions, a super-structure with a super-cell seven times bigger and C2 space symmetry was obtained.

Cu atom in both structures is required to be in the crystallographic two fold axis and is surrounded by 6 oxygens of the formic ions forming an elongated octahedra; neighbor octahedra share an edge and forms a chain parallel to c. Both structures stabilize with different Cu:alkaline-terreous ratio and the Sr ion is surrounded by 8, while Ca ion by (7+1) oxygen atoms.

The Ca-Cu formate super-structure was treated as a modulation of the basic-structure and refined in the [illegible] space group showing as the main feature the modulation of the distance between Ca and the eighth oxygen atom, thus showing that the Ca coordination sphere ranges from 7 to 8 atoms.

References:
P.M.de Wolff, T.Janssen, A.Janner. Acta Cryst.(1981). A37, 625-636.
T.Watanabe, M.Matsui. Acta Cryst.(1978), B34, 2731-2736.

AUTHOR INDEX

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All correspondence concerning registration to:

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Deadlines
Deadline Abstracts: May 15, 1993
(see page 10)
Deadline Advance Registration and payments: May 15, 1993
(see pages 16-18)
Deadline for guaranteed Accommodation: June 30, 1993
(see page 19)

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Grupo Especializado de Química del Estado Sólido de la R.S.E.Q.

Scientific Programme

Plenary Lectures (one hour)

The microstructure of some superconducting oxides
by M. Alario (Madrid, SPAIN)

Solid-gas reactions of molecular organometallic compounds
by C. Bianchini (Firenze, ITALY)

Oxygen content in superconductors and related materials
by A. Carneiro (San Carlos de Bariloche, ARGENTINA)

Cationic manganese porphyrins as artificial endonucleases and potential anti-HIV molecules
by B. Meunier (Toulouse, FRANCE)

Homo and heterometallic cubane-type iron-sulphur clusters: Structure and reactivity in relation to Biology and Chemistry
by J. Moura (Lisboa, PORTUGAL)

Coordination and reactivity of thiophenes on transition metal centres. Molecular analogues of surface species and reactions relevant to hydrodesulphurisation
by R. Sánchez-Delgado (Caracas, VENEZUELA)

Some new chemistry of transition metal organoimido compounds
by Sir G. Wilkinson (London, ENGLAND)

Session Lectures (40 min. plus 5 min. of discussion)

1 COORDINATION AND BIOINORGANIC CHEMISTRY

Photochemical molecular devices based on transition metal complexes
by V. Balzani (Bologna, ITALY)

Neutral divalent transition-metal complexes with thioether-imidazole-containing ligands as models for metalloproteins
by R. Bastida (Santiago de Compostela, SPAIN)

EPR and voltammetric characterization of electrochemically generated Schiff base nickel(I) and nickel(II) complexes with catalytic properties
by B. de Castro (Porto, PORTUGAL)

Title to be announced
by J.A. Costamagna (Santiago, CHILE)

Polyimidazole complexes modelling the active site of mononuclear non heme iron proteins
by J.C. Chottard (Paris, FRANCE)

Metal complexes of some tetra-aza macrocyclic ligands containing pyridine
by R. Delgado (Lisboa, PORTUGAL)

Metals and nucleobases: Coordination chemistry and biological relevance
by B. Lippert (Dortmund, GERMANY)

Redox proteins in environmental biotechnology
by C. Luchinat (Bologna, ITALY)

Complexing properties of functionalized cyclodextrins
by E. Rizarelli (Catania, ITALY)

Study of the reactivity of some ruthenium (II) and (III) complexes containing triphenylphosphine and multidentate ligands
by L. Ruíz Azuara (Mexico D.F., MEXICO)

Metallodrugs: New chemistry of platinum anticancer complexes
by P.J. Sadler (London, ENGLAND)

Carboranes and macrocycles; an effective cooperation
by F. Teixidor (Barcelona, SPAIN)

Structural information from ^{119}*Sn Mössbauer spectroscopy*
by D. Tudela (Madrid, SPAIN)

Some optical properties of rare earth compounds
by G. Vicentini (São Paulo, BRAZIL)

High-valent iron-oxo porphyrin species: Generation and characterization of new models for peroxidase compound I
by R. Weiss (Strasbourg, FRANCE)

2 ORGANOMETALLIC CHEMISTRY AND CATALYSIS

Activation of terminal alkynes: new access to alkenyl- and polyenyl-carbene metal complexes
by H. le Bozec (Rennes, FRANCE)

Uranium complexes with oxygen, sulphur, nitrogen and phosphorus ligands. Influence of electronic factors on structure and reactivity
by M. Ephritikhine (Gif Sur Yvette, FRANCE)

Metallomesogens: How they are fished for, and cooking recipes
by P. Espinet (Valladolid, SPAIN)

Recent advances in the chemistry of perhalophenylplatinate(II) complexes
by J. Fornies (Zaragoza, SPAIN)

The new round world of fullerene chemistry and material science
by H. Kroto (Brighton, ENGLAND)

Organometallic chemistry of lanthanides and some implications in diolefine polymerization reactions
by G. Lugli (Novara, ITALY)

From ionic salts to early transition metal and actinide complexes: the energetics of metal-oxygen bonds in lithium, sodium, zirconium and uranium complexes
by J.A. Martinho Simoes (Oeiras, PORTUGAL)

New frontiers in bond activation by electron-rich metal complexes
by D. Milstein (Rehovot, ISRAEL)

Molecular dihydrogen complexes in homogeneous catalysis
by L. Oro (Zaragoza, SPAIN)

Reactivity of pentadienyl transition metal complexes towards neutral nucleophiles
by A. Paz-Sandoval (Mexico D.F., MEXICO)

Protonation and dehydrogenation of complexes with small unsaturated carbon or nitrogen ligands: A chemical and electrochemical approach
by A. Pombeiro (Lisboa, PORTUGAL)

Binuclear organometallic derivatives: Synthesis and reactivity
by V. Riera (Oviedo, SPAIN)

Metallocene chemistry of the group 8 elements
by E. Román (Santiago, CHILE)

Platinum catalysed oxidations with hydrogen peroxide
by G. Strukul (Venezia, ITALY)

Some of the chemistry of phosphido bridged iridium carbonyl clusters
by M. Vargas (Campinas, BRAZIL)

3 SOLID STATE CHEMISTRY AND INORGANIC MATERIALS

Sol-gel glasses and thin films
by R.M. Almeida (Lisboa, PORTUGAL)

Design and synthesis of new inorganic solids: applications to the tailoring of specific properties
by R.E. Carbonio (Córdoba, ARGENTINA)

Molecular sieves as selective catalysts
by A. Corma (Valencia, SPAIN)

Crystal chemistry in the nineties: Facts, features and perspectives
by Mª O. Figueiredo (Lisboa, PORTUGAL)

Phase formation and current transport in high T_c *superconducting oxides*
by R. Flükiger (Geneve, SWITZERLAND)

Design of new opto-microelectronic devices: III-V semiconductor heterostructures
by R. García Roja (Cadiz, SPAIN)

High nuclearity spin clusters - a new dimension in molecular magnetism
by D. Gatteschi (Firenze, ITALY)

Synthesis and crystal growth of superconducting compounds in C.N.E.A. laboratories
by A.G. Leyva (Buenos Aires, ARGENTINA)

Molecular design of advanced ceramics
by J. Livage (Paris, FRANCE)

Zeolite chemistry: catalytic applications
by A. Oviedo (Bogotá, COLOMBIA)

Applications of solid state neutron powder diffraction
by J. Pannetier (Grenoble, FRANCE)

Biomaterials, a substitute for hard tissues
by J.A. Planell (Barcelona, SPAIN)

Basic principles of biomineralization. Some particular cases
by M.A. Quijano (Bogotá, COLOMBIA)

Science, technology and applications of bioceramics: State of the art and future perspectives
by A. Ravaglioli (Faenza, ITALY)

Solid state chemistry of ceramic materials
by A.R. West (Aberdeen, ENGLAND)

Poster Sessions

Posters on any aspect of inorganic chemistry may be contributed by participants. They will be classified under the heading of one of the main topics of the conference, as follows:

1. Coordination and Bioinorganic Chemistry
2. Organometallic Chemistry and Catalysis
3. Solid State Chemistry and Inorganic Materials

The posters will be on display in three separate sessions. The space allocated will be approximately *1.00 m* (wide) x *1.20 m* (high).
Posters must be brought by the author and must not be mailed to the conference secretariat.

Call for Papers

Participants are invited to submit papers on all aspects of inorganic chemistry with specific reference to the topics given above. The abstract should be prepared conscientiously in accordance with the Abstract Preparation Guidelines (page 11). Abstracts must be submitted in accordance with the Abstract Submission Procedure (page 12). Each registered participant may submit one and only one abstract. However, participants may figure as coauthors in abstracts submitted by others. All contributions should be sent to the Scientific Secretariat, in triplicate.

Notice of acceptance will be given before June 30, 1993.

Abstracts must be submitted in English.

The deadline for the submission of abstracts is May 15, 1993.

Abstract Preparation Guidelines

Only one page may be used, including text and figures. Instructions on the abstract format are given below. Abstracts should arrive unfolded. Poorly prepared or damaged abstracts may be rejected by the Scientific Committee.

Hardcopy submission

1. Use sheet paper size A4. Text may be no wider than *15 cm* and only *23 cm* long. The frame of *15x23 cm* must be in the centre of the form. Border lines may be drawn only with a light blue pencil.

2. Use a typewriter with a new ribbon or a laser printer to ensure good reproduction. DO NOT erase, use correction fluid if absolutely necessary.

3. Use 1.5 spaced lines with 10 characters per inch (25 mm).

4. Leave a space of *25 mm* before the first word of the title to allow for the abstract number. The title of the abstract must always be in capital letters, except where formulae require small letters. The authors' names and addresses must be in small letters except for initials. Underline the name of the author presenting the paper.

5. DO NOT indent paragraphs.

6. Diagrams should be drawn in black ink, lettered clearly, and mounted on the abstract page. High contrast photographs will be accepted, but quality reproduction is not guaranteed.

7. A maximum of two references to published work may be included at the end of the abstract, giving the full bibliographic reference (Author's names and initials, journal year, volume and page, using Chemical Abstracts abbreviations for journals). DO NOT refer to papers "submitted" or "to be published". DO NOT use footnotes.

Abstract Submission Procedure

Send the following items by 1st class mail to

Prof. Dr. A. Castiñeiras (LAICM Scientific Secretary)
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15706 SANTIAGO DE COMPOSTELA (SPAIN)

- abstract submission form (**Form A**, original and one copy)
- original abstract
- two copies of the abstract

Topics

The topics are designated by a number (see section on posters, page 9). Authors are requested to put the appropriate number for their contribution on the Abstract Submission form. The Scientific Committee may change the classification suggested by the author(s) if necessary.

Key Words

Authors are asked to supply at most four key words (max. 30 characters each) for indexing purposes. Key words referring to a specific aspect of the abstract are in general more helpful than words describing a very broad area of study.

Collected Abstracts

The book of abstracts (plenary lectures, session lectures and posters) will be available to registered participants (excluding accompanying persons) at the beginning of the meeting.

Social Programme (provisional)

Monday, September 13

9.00 h Opening Ceremony in the University Auditorium

20.00 h Reception offered by the Mayor of Santiago de Compostela

Tuesday, September 14

20.00 h Concert by the Grupo Universitario de Cámara of the University of Santiago de Compostela in the Salón Artesonado, Pazo de Fonseca.

21.30 h Reception offered by the Rector of the University of Santiago de Compostela.

Wednesday, September 15

11.30 h Conference Excursion, a full day trip to the *Costa da Morte* (incl. in full registration and accompanying persons fee).

Thursday, September 16

20.00 h Folk concert

22.00 h LAICM Conference Dinner

Friday, September 17

12.00 h Closing ceremony in the main lecture hall

Provisional Time Table

Registration of participants on Sunday, September 12, at the registration desk on the campus, from 17.00 h - 21.00 h.

Day Time	Monday Sept. 13	Tuesday Sept. 14	Wednesday Sept. 15	Thursday Sept. 16	Friday Sept. 17
9.00	Opening and Plen. Lect.	Plenary Lecture	Plenary Lectures	Plenary Lecture	Plenary Lecture
10.30	Coffee break	Coffee break		Coffee break	Coffee break
11.00	Session Lectures	Sesion Lectures	Conference excursion	Sesion Lectures	Plenary Lecture
13.15	Poster Session	Poster Session		Poster Session	Closing ceremony
14.00	Lunch	Lunch		Lunch	Lunch
16.30	Session Lectures	Session Lectures		Session Lectures	
18.00	Poster Session	Poster Session		Poster Session	
evening	Reception	Concert		Folk Concert Conference dinner	

Commercial Exhibition

During the symposium a commercial exhibition of chemicals, books and scientific and technological equipment related to chemistry is planned in the vicinity of the lecture halls. Opening hours of the exhibition will be approximately: Monday-Thursday, 10.00 - 19.00 h. Closed on Wednesday because of the programmed excursion.

General Information

The conference will be held on the *Campus Sur* of the University of Santiago de Compostela. Santiago de Compostela is one of the most charming european towns and the capital of the Autonomous Community of Galicia, N.W. Spain. The campus is situated near the city centre. The climate in September is generally warm (average daily maximum 25°C) and sometimes somewhat humid. Banking and shopping facilities are available within a few hundred metres of the campus. Swimming and other sports are catered for. All conference facilities, including the campus cafeteria and restaurants are a few minutes' walk from one another.

Language

The official language of the conference is English. There are no facilities for simultaneous translation. Posters may be presented in English, French, Portuguese, Italian or Spanish.

Address during the Conference

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Conference and Scientific Secretariat LAICM (for abstract submission and registration)

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Registration

Persons wishing to attend the conference must send a fully and legibly completed registration form (**Form B**) to the Conference Secretariat, **preferably before May 15, 1993** (advance registration).

Fees are in *pesetas* (Ptas.) 120 Ptas. = approx. 1.0 US $.

All active participants, including invited speakers, must submit a separate registration form (**Form B**). Copies of the registration form are acceptable. Registration, payments and hotel accommodation will be confirmed in the course of June/July 1993.

The various fees are:

	advance registration		**late registration**
	before May 15	after May 15 and before September 1, 1993	after September 1
Full registration	Ptas. 20,000.-	Ptas. 30,000.-	40,000.-
Accompanying persons	Ptas. 10,000.-	Ptas. 15,000.-	20,000.-

The fees for advance registration only apply to those registrations transacted completely before of May 15, 1993. All money due must be at the Organizing Committee's disposal before this date.

The full registration fee includes:

- admission to lecture halls
- admission to poster sessions
- admission to commercial exhibition
- concert on Tuesday, September 14
- conference excursion on Wednesday, September 15
- folk concert on Thursday, September 16
- all receptions
- a copy of the book of abstracts

The registration fee for accompanying persons includes:

- opening ceremony on Monday, September 13
- concert on Tuesday, September 14
- conference excursion on Wednesday, September 15
- folk concert on Thursday, September 16
- tour of the City (old town)
- all receptions
- closing ceremony on Friday, September 17

Accompanying persons do not participate in the scientific sections of the conference.

Young scientists

A limited amount of financial support is available for young scientists (maximum 27 years old) contributing with accepted papers. The grant covers registration and accommodation in student dormitories. Applicants must submit to the Conference Secretariat **before May 15, 1993**:

- the abstract (see page 11)
- a comprehensive Curriculum Vitae
- a letter of recommendation by the appropriate academic supervisor

All applicants will be notified before June 15, 1993

Successful applicants will receive their grants on registration at the registration desk.

In addition there will be a limited number of grants intended as a small contribution toward the cost of travel for Latin-American Researchers in special cases.

Payments

Payments are to be effected in *pesetas* (Ptas.).

The fees for registration and the accompanying persons should be paid in full by bank transfer into account number (C.C.C.) **2091.0300.4-3040124522** of the CAIXAGALICIA Bank, *Montero Rios 7, Santiago de Compostela, Spain*, stating your full name and address. Please make sure your remittance is marked "LAICM" and is free of transfer charges, at present approx. 1,000.- per international transfer. Partial payments are not accepted, registration takes effect as the complete amount due is received.

If payments are not free of transfer charges, the conference secretariat will deduct these charges from your hotel deposit or they will have to be paid upon registration. It is also possible to include cheques with your registration form. The cheques should be purchased in your own country in *pesetas*, drawn on a Spanish bank and made out to LAICM. Please make sure that your remittance states your full name and address and the purpose of your payment.

Payment by Credit Cards cannot be accepted.

Payments for early registration should be received before May 15, 1993.

Payments without full name and address will be returned to sender (if possible).

Cancellations

Cancellations must be sent in writing to the Conference Secretariat. For cancellations received before May 15, all fees, less 25% administrative costs will be reimbursed. For those received between May 15 and July 1, a cancellation charge of 50% will be applied. Cancellations received after July 1 will not be refunded.

Refunds will be processed after the meeting.

Hotel Accommodation

A block of rooms has been reserved in different hotels in and around Santiago de Compostela. 650 beds in College-Residence and university-residence are also avalilable. Hotel reservations should be received before **June 30, 1993**. After this date, accommodation cannot be guaranteed.

Please indicate your choice on the hotel reservation form **(Form C)**

Hotels/Category	**Type of Room**	**Prices in ptas. (per day)**
HOTEL REYES CATÓLICOS*****	Double/bath	29,210.-
	Double/bath-single use	22,540.-
HOTEL ARAGUANEY*****	Double/bath	28,290.-
	Double/bath-single use	21,620.-
HOTEL PEREGRINO****	Double/bath	18,974.-
	Double/bath-single use	14,416.-
HOTEL LOS TILOS**** *(4 Km from city center)*	Double/bath	15,900.-
	Double/bath-single use	11,925.-
HOTEL COMPOSTELA****	Double/bath	15,370.-
	Double/bath-single use	11,819.-
HOTEL GELMIREZ***	Double/bath	11,395.-
	Double/bath-single use	8,751.-
HOTEL APOSTOL SANTIAGO*** *(3 Km from city center)*	Double/bath	11,236.-
	Double/bath-single use	8,480.-
UNIVERSITY/RESIDENCES *(only accommodation, no breakfast is included)*	Double/bath-shower	4,982.-
	Single/bath-shower	3,180.-
COLLEGE/RESIDENCES *(only accommodation, no breakfast is included)*	Double/bath-shower	4,028.-
	Double/bath-shower single use	4,028.-

Transport

Santiago de Compostela can be reached by road, rail or air. For those travelling to Galicia by sea, Santiago de Compostela is within easy reacn of the ports of La Coruña (60 km) and Vigo (90 km).

Banking and Postal Facilities

Banks are generally open from 09.00 - 14.00 on weekdays and are closed on Saturdays and Sunday. A bank is located on the university campus.
The post office is open from 09.00 - 18.00 on weekdays.

Insurance

Participants are responsible for their own insurance arrangements. The organizers cannot accept any responsability for accidents, sickness, theft or damage to property, or for delays or any modification in the programme due to unforseeable circumstances.

Important dates

May 15, 1993	● Abstract submission deadline
May 15, 1993	● Deadline for advance registration and payments
June 30, 1993	● Deadline for guaranteed hotel bookings
July, 1993	● Confirmation of registration, payments and hotel booking

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