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ABSTRACTS

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**WEDNESDAY— Poster Session
and Microsymposia**

BROADBEACH, QUEENSLAND, AUSTRALIA

2-7 JULY, 1989

WEDNESDAY

POSTER SESSION

AND

MICROSYMPOSIA

STUDIES OF COORDINATION COMPOUND PRECURSORS TO THE CUPRATE SUPERCONDUCTORS

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The cuprate superconductors, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$ have been prepared using polymeric metal complexes derived from the interaction of citric acid, or other polycarboxalate ligands, ethylene-glycol, and various metal salts. Pyrolysis of films of these precursor complexes on zirconia and alumina substrates in air at 800-950°C followed by oxygen annealing yields the corresponding oxide films. Alternatively, pyrolysis of the polymeric precursor in bulk form in oxygen to 1000°C yields fine, homogeneous powders of these oxides. FTIR, ^1H and ^{13}C NMR, and VPO studies of these precursors, as well as XRD, FTIR, pyrolysis G.C., SEM/TEM, electrical and magnetic property measurements on the pyrolysis products have been carried out which provide information regarding the probable structure of the precursor and the course of its conversion to the final oxide phase(s).

METAL ORGANIC CHEMICAL VAPOR DEPOSITION OF SUPERCONDUCTING FILMS FROM VOLATILE METAL CHELATES

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Recently, several research groups have made high quality thin films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor using metal organic chemical vapor deposition (MOCVD) with volatile metal β -diketonate complexes. For example, Watanabe, et al. [1] have prepared the best thin film superconductor yet made with a critical current density of $190,000 \text{ A/cm}^2$ at 10 Tesla and an onset temperature of 89 K using this technique. Using mass spectrometry, nuclear magnetic resonance spectrometry and thermogravimetric analysis, we have studied the metal complexes that we are using in MOCVD of superconducting thin films [2]. One difficulty in making these films is that the barium chelates are less volatile and thermally stable than the other precursors. Mass spectral studies have shown that these barium complexes may exist as oligomers. Various experiments indicate that the presence of these oligomeric ions in the mass spectra is not just the result of reactions in the mass spectrometer source. We have also investigated how mixtures of chelates interact to form mixed metal and mixed ligand species. In addition to studying the metal organic precursors for MOCVD, we are investigating the chemistry that occurs during the MOCVD process itself. For example, adding excess ligand to the oligomeric bis(2,2,6,6-tetramethyl-3,5-heptanedionato)barium(II) complex during volatilization reduces the amount of thermal decomposition and produces better superconducting films [2]. The dissociation of the chelates once they are transported to the target substrate is facilitated by hydrolysis and by the addition of oxidants.

1. K. Watanabe, H. Yamane, H. Kurosawa, T. Hirai, N. Kobayashi, H. Iwasake, K. Noto, and Y. Muto, submitted to Appl. Phys. Lett., 1988, and references cited therein.
2. P.H. Dickinson, A. Sanjurjo, T.H. Geballe, D. Hildenbrand, G. Craig, M. Zisk, J. Collman, S.S. Banning and R.E. Sievers, J. Appl. Phys., 1989, accepted for publication.

SUITABILITY OF METAL β -DIKETONATES AS MO-CVD PRECURSORS FOR
HIGH Tc SUPERCONDUCTORS

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Thin films of high Tc superconducting oxides, e.g. $\text{YBa}_2\text{Cu}_3\text{O}_7$ or Bi-Sr-Ca-Cu-oxides can be deposited on suitable substrates (e.g. SrTiO_3) by metal-organic chemical vapour deposition (MO-CVD), as recently reported in the literature. Metal β -diketonates are generally applied as precursors in the MO-CVD process. However, for optimal process conditions and film properties a number of variables require further optimisation. This includes the selection of appropriate precursors with sufficient volatility and thermal stability at a required work temperature of $\pm 200^\circ\text{C}$.

Evaporation of Ca,Sr,Ba- β -diketonates appears to be much more difficult than evaporation of the more volatile corresponding yttrium and copper compounds. Actually, upon prolonged heating $\geq 200^\circ\text{C}$, a temperature required for sufficient mass transport, a gradual decomposition of the Ca,Sr,Ba- β -diketonates to virtually non-volatile products is observed. This phenomenon is prohibitive for a further development of a practical MO-CVD process for high Tc superconducting oxides.

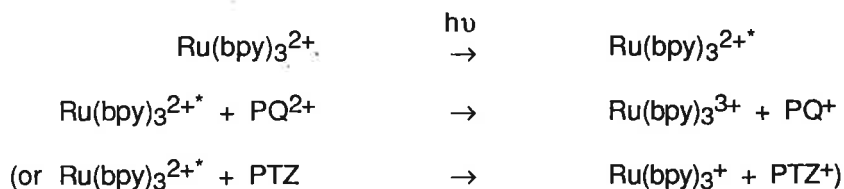
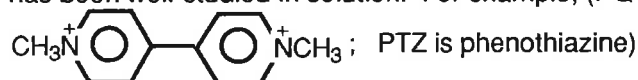
At TNO, investigations into the development of pathways to a higher volatility and a constant mass transport of alkaline earth metal MO-CVD precursors are currently undertaken. First results demonstrate that a substantial increase in mass transport of Ca,Sr,Ba- β -diketonates in the vapour phase can be achieved by co-evaporation of these compounds with specific donor ligands.

At present, optimal conditions for a constant mass transport are being investigated. The progress in this TNO programme will be reported at the meeting.

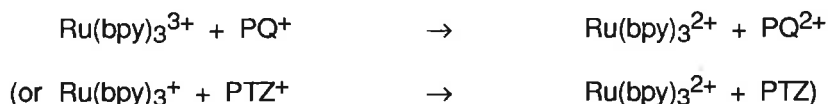
TRILAYER POLYMERIC FILMS FOR PHOTOCURRENT GENERATION

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The conversion of light energy to redox energy by the optical excitation of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy is 2,2'-bipyridine) followed by oxidative or reductive electron transfer quenching has been well-studied in solution. For example, (PQ^{2+} is paraquat,

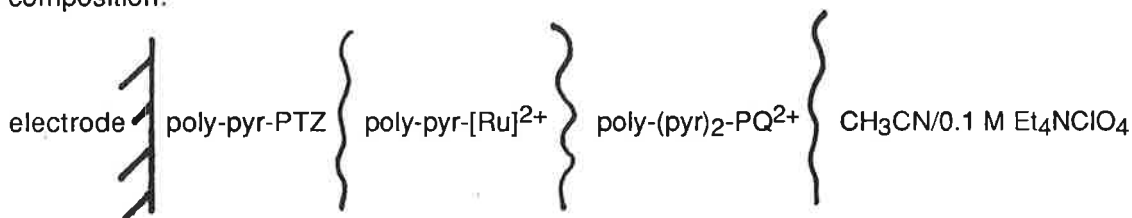


In the absence of designed following events however, the redox energy is stored only transiently because of recombination by back electron transfer.



In an attempt to solve the recombination problem and to generate photocurrents in the solid state we have been assembling chromophore/quencher systems in thin polymeric films on electrodes. Our goal is to achieve separation of photoproduced oxidative and reductive equivalents in spatially distinct areas of the films.

Sequential electropolymerisation of pyrrole derivatives of PTZ (pyr-PTZ), $\text{Ru}(\text{bpy})_3^{2+}$ (pyr- $[\text{Ru}]^{2+}$) and PQ^{2+} ((pyr)₂- PQ^{2+}) gives rise to electrodes modified with trilayer films of composition:



Irradiation of films at 436 nm produces a cathodic photocurrent which may be attributed to reduction of photoproduced poly-pyr-PTZ⁺. However, no evidence has been found for delivery of photoproduced reductive equivalents as poly-(pyr)₂-PQ⁺ to the film/solution interface. Participation of the conducting polypyrrole backbone of the films in the electron transfer pathway may account for this observation.

MS4

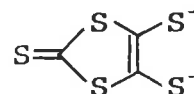
STRUCTURE AND PROPERTIES OF ELECTRICALLY CONDUCTING $[V(C_3S_5)_3]^-$ ANION SALTS

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Cubic tris(dmit)metallate anion complexes[dmit; 4,5-dimercapto-1,3-dithiole-2-thionate (**A**)] are expected to behave as new electrical conductors upon oxidation through multi-dimensional dmit-dmit interactions in the solid state. This paper reports preparation, spectroscopic and electrical properties of $[V(dmit)_3]^{2-}$ anion salts and their oxidized analogs.

**A**

Reactions of $[NBu^N_4]_2[V(dmit)_3]$ (**1**) [1] with an excess amount of $[FeCp_2][PF_6]$ (Cp; cyclopentadienyl) in MeCN gave black microcrystals of $[FeCp_2][V(dmit)_3]$ (**2**). Reactions of **1** with $[Fe(MeCp)_2][PF_6]$, $Fe(ClO_4)_3 \cdot 9H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, and $(TTF)_3(BF_4)_2$ (TTF; tetrathiafulvalene) in MeCN gave $[Fe(MeCp)_2][V(dmit)_3]$ (**3**), $Fe[V(dmit)_3] \cdot 3H_2O$ (**4**), $Co[V(dmit)_3] \cdot 3H_2O$ (**5**) and $[TTF]_2[V(dmit)_3]$ (**6**), respectively.

A cyclic voltammogram of **1** measured in MeCN has shown a reversible redox wave at $E_{1/2} = +0.15$ V vs. SCE corresponding to the $[V(dmit)_3]^{2-}/[V(dmit)_3]^-$ process. Thus, **1** can be easily oxidized by $[FeCp_2]^+$, $[Fe(MeCp)_2]^+$, Fe^{3+} , Co^{2+} , and TTF^+ to afford stable salts **2-6**.

Binding energies of V 2p electrons determined from XPS are summarized in Table. The energies of **2-5** are rather close to that of **1**, indicating that essentially the dmit ligand-centered oxidation occurs. On the other hand, **6** shows an appreciably small binding energy compared with those of other salts, which suggests a charge transfer from TTF^+/TTF^0 moieties to the $[V(dmit)_3]^-$ anion moieties through an S-S interaction.

Although **1** has a small electrical conductivity, **2-6** show raised conductivities (see Table). This may be due to extended molecular interaction of the oxidized tris(dmit)vanadium anions through S-S contacts, as is apparent from the crystal structure of $[NMP]_2[V(dmit)_3]$ (NMP; N-methylphenazinium) [1].

Table. Binding energies of vanadium 2p electrons, electrical conductivities (σ) for compacted pellets and activation energies (E_a) of the tris(dmit)vanadium anion salts

Salt	Binding energy V 2p _{1/2} /eV	$\sigma_{25^\circ C}$ /S cm ⁻¹	E_a /eV
1	523.4	4.5×10^{-10}	0.62
2	523.4	1.2×10^{-5}	0.58
3	523.8	2.5×10^{-6}	0.57
4	523.9	6.9×10^{-5}	0.11
5	524.0	1.0×10^{-4}	0.24
6	522.3	1.0×10^{-2}	0.15

1. G. Matsubayashi, K. Akiba, and T. Tanaka, *Inorg. Chem.*, **1988**, 27, 4744.

CONTROL OF THE SPIN-STATE OF PSEUDO-TETRAHEDRAL DIIMINO-DITHIOLATO NICKEL(II) COMPLEXES THROUGH LIGAND DESIGN

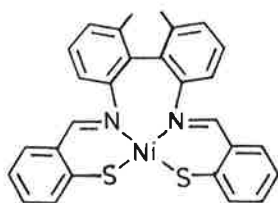
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In general, four-coordinate nickel(II) complexes can exist as either tetrahedral high-spin or square planar low-spin species depending on the strength of the ligand field and the steric requirements of the ligand(s).

In our work on the preparation of pseudo-tetrahedral copper(II) complexes with sterically constrained tetradentate N_2S_2 ligands we have found that the corresponding nickel(II) complexes exist in spin equilibrium in solution, and that minor variations in the ligand cause a shift in this equilibrium as well as different spin-states in the solid phase.

The four new nickel(II) complexes 1-4 were prepared and characterized magnetically and spectroscopically.



1



- | | |
|--|---|
| R: CH ₃ , R': CH ₃ | 2 |
| R: H, R': ph | 3 |
| R: H, R': CH ₃ | 4 |

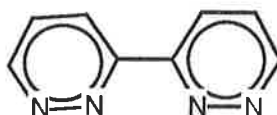
The complexes 1-3 were structurally characterized by single crystal X-ray diffraction. Complex 1 is low-spin nearly square planar, 2 is high-spin of roughly tetrahedral geometry, 3 is low-spin with a severely distorted square planar structure, whereas 4 is high-spin. The possible causes for this variation in spin-state and geometry are discussed.

ELECTRONIC PROPERTIES OF THE IRON(II) AND COBALT(II) COMPLEXES OF THE STRONG FIELD DI-IMINE 3,3'-BIPYRIDAZINE.

D. Onggo and H.A. Goodwin

School of Chemistry, University of New South Wales, Kensington, N.S.W., 2033.

3,3'-Bipyridazine (L) provides the di-imine moiety found in 2,2'-bipyridine and



(L)

other strong field bidentate chelate groups but its structure possesses important differences. Thus the 6 and 6'-positions in bipyridine are occupied by -CH- groups whereas the corresponding positions in L are taken up by a single atom, nitrogen. The hydrogen atoms in the 6 and 6'-positions of bipyridine introduce strong steric barriers to tetragonal coordination of two ligand molecules [1] but also have an important stereochemical effect in *tris*(ligand) octahedral complexes [2]. Previous studies of L are limited but the recent results of Ernst and Kaim [3], which indicate the enhanced π -acceptor character of L, are very significant.

Coordination of L with iron(II) yields the deep red *low-spin* $[\text{Fe L}_3]^{2+}$ species. This species is formed in all attempts to prepare *bis*(ligand)dihalo species and also when L interacts with iron(III) chloride. In the latter instance the mixed iron(II)/iron(III) species $[\text{Fe L}_3][\text{Fe Cl}_4]_2$ is formed. The *bis*(ligand)dithiocyanato iron(II) complex is also *low-spin* and this is indicative of the high field strength of L. Spectral data for $[\text{Ni L}_3]^{2+}$ confirm the greater field strength of L, compared to that of bipyridine.

Salts of $[\text{Co L}_3]^{2+}$ have strongly temperature-dependent magnetic moments which are associated with a temperature-induced doublet/quartet spin transition, and again this is in contrast to the simple *high-spin* nature of the corresponding bipyridine complex.

Electronic and Mössbauer spectroscopic data, together with magnetic and structural information will be presented.

1. E.D. McKenzie, *Coord. Chem. Rev.*, **1971**, 6, 187.
2. H.A. Goodwin, D.L. Kepert, J.M. Patrick, B.W. Skelton, and A.H. White, *Aust. J. Chem.*, **1984**, 37, 1817.
3. S. Ernst and W. Kaim, *J. Am. Chem. Soc.*, **1986**, 108, 3578.

Magnetic properties of triangular tri-nuclear
coordination compounds

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& T.Yamaguchi⁺ Y.Sasaki⁺ and T.Ito⁺

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Magnetic properties of the tri-nuclear coordination compounds of 4d transition metals with a central-O are very attractive. Some of those compounds are already known their electronic structure. Magnetic susceptibilities of $[\text{Ru}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{py})_3]\text{ClO}_4$ (1), $[\text{Ru}_2\text{RhO}(\text{CH}_3\text{CO}_2)_6(\text{py})_3]\text{ClO}_4$ (2) and $[\text{Rh}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{py})_3]\text{ClO}_4$ (3) have been measured at temperatures 2~300K. $[\text{Ru}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{py})_3]$ salt was investigated by J.A.Baumann et al(1978), but new measurements would elucidate some electronic properties. μ_{eff} obtained from the magnetic susceptibility was about $3.9\mu_B$ at 300K and about $1.5\mu_B$ at 2K, that is, (1) had total effective spin of $S=3/2$ at room temperature and continuously decreased to effective $S=1/2$ at 2K. Ru^{3+} ions in (1) are low spin states of t_{2g}^5 , its magnetic moment has an orbital moment and should have a temperature dependence as shown by Kotani(1949). Bringing the effective magnetic moment concerned temperature dependence with assumed $S=1/2$, $g=2$, and $\lambda=-750\text{ cm}^{-1}$ into the susceptibility of Kambe model(1950), a moderate fit has been obtained on $J=-14\text{ kK}$. The temperature independent paramagnetic susceptibility χ_{TIP} of (1) is $3.45 \times 10^{-3}\text{ cm}^3$, if the spins would be localized. Samples (2) and (3) showed almost temperature independent paramagnetic susceptibilities which increased at low temperature region. The temperature independent parts of (2) and (3) were considered as their χ_{TIP} , comparing them, much decreased χ_{TIP} of Ru^{3+} ion than that mentioned above was found, which showed (2) was in the MO state. χ_{TIP} of (3) consists with that calculated from the spectroscopic data by T.Glowiak et al(1977), which is also smaller than that of localized ions. An excess paramagnetic susceptibility of (1) seen at the lowest temperature region was considered due to the orbital paramagnetism suggested by B.S. Tsukerblat et al(1973). The increase of the susceptibility of (2) below 60K too, might be due to the orbital paramagnetism.

MAGNETIC EXCHANGE PATHS IN HETEROBINUCLEAR COMPLEXES CONTAINING A μ -OXO-BIS(μ -ACETATO)DIMETAL CORE.

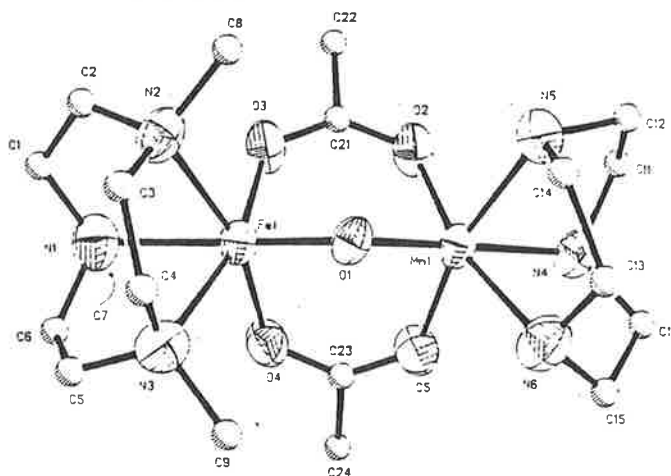
K. Wieghardt^a, U. Bossek^a, R. Hotzelmann^a, J. Bonvoisin^b, J. J. Girerd^b, U. Flörke^c, H.-J. Haupt^c, D. Weatherburn^d

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We have synthesized and characterized by X-ray crystallography a series of heterobinuclear complexes containing the μ -oxo-bis(μ -acetato)dimetal core with two different transition metals as well as their homobinuclear counterparts. Hydrolysis of LM^1Cl_3 and $L'M^2Cl_3$ complexes in aqueous solution containing ammonium acetate affords these complexes in good yields. From susceptibility measurements intramolecular ferromagnetic or antiferromagnetic spin exchange coupling has been observed depending solely on the d^n electronic configuration of M^1 and M^2 ,

M^1	M^2	J, cm^{-1}
Fe(III)	Fe(III)	- 120
Mn(III)	Mn(III)	+ 18
Fe(III)	Mn(III)	- 145
Fe(III)	Cr(III)	- 137
Mn(III)	Cr(III)	+ 2
Cr(III)	V(III)	+ 18



$$H = -2JS_1 \cdot S_2$$

L = 1,4,7-triazacyclononane

L' = N,N',N''-trimethyl-1,4,7-triazacyclononane

A detailed analysis of the interacting magnetic magnetic orbitals revealed that the d_z^2 - d_{xz} -orbital interaction is the dominant magnetic path propagating strong antiferromagnetic exchange coupling when the d_z^2 at one metal site and d_{xz} -orbital at the other metal site are occupied by one electron, respectively; depletion of one or both electrons from these orbitals leads to ferromagnetic coupling.

W10

MS5

IRON MINERALIZATION PROCESSES IN FERRITINS

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In ferritin, iron mineralization occurs within the confined space provided by a spherical protein with a hollow centre of 8nm diameter. The maximum capacity so provided is about 4000 Fe Atoms and about 10,000 oxygens. Ferrihydrite, the iron-core mineral of ferritin, is a hydrous ferric oxide. Knowledge of the three-dimensional structure of apoferritin provides us with details of the inner surface on which mineralization occurs. Hence we have a good model system for studying this process. It is complicated, however, by the presence in most ferritins of two subunits of different amino acid sequence (5% identity, known as H and L) including different residues on their internal surfaces. Mineralization also involves redox processes. Fe(II) presented to apoferritin is bound, oxidized and hydrolysed to give Fe(III) clusters in which Fe atoms are bridged by O or OH. These clusters can also bind Fe (II).

We have studied iron mineralization in ferritin by: UV/visible spectroscopy, Mossbauer spectroscopy (in collaboration with E R Bauminger and I Nowik), electron microscopy (in collaboration with S Mann and V Wade), and X-ray analysis of crystals of both iron-free apoferritin and molecules containing small amounts of iron. In these studies we have used horse spleen apoferritin (assembled predominantly from L-type subunits), recombinant rat liver ferritin containing only L chain (in collaboration with C D Thomas and W V Shaw), recombinant human H chain apoferritin, including recombinants bearing specific sequence changes (in collaboration with G Cesareni and A Luzzago) and bacterioferritin (in collaboration with S Mann, J M Williams and G D Watt). Results will be presented and discussed.

We thank the Wellcome Trust, the Science and Engineering Research Council and the Commission of European Communities (contract no. BAP-0253-UK) for financial support.

MS5

FORMATION OF MIXED VALENCE Fe(II)-Fe(III) DIMERS DURING THE OXIDATIVE DEPOSITION OF IRON IN HORSE SPLEEN FERRITIN

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The mechanism of iron deposition in ferritin is poorly understood. We have undertaken a study of ferritin to identify the complexes that lead to the formation of the FeOOH core. In previous work we observed an unusual EPR signal with $g=1.87$ when both Fe(III) and Fe(II) were present in apoferritin preparations to which small amounts of iron had been added back [1]. The low g factor (<2.0) and the pronounced temperature dependence of the EPR signal was consistent with the formation of a mixed valence dimeric Fe(III)-Fe(II) species. A resonance was also observed at $g'=4.3$ due to a mononuclear Fe(III) complex with the protein. The present study was undertaken to further characterize the putative mixed valence complex and its relationship to the observed mononuclear complex.

Solutions of iron(III)-apoferritin at a ratio of 0.25 Fe(III)/subunit, added as Fe(II) followed by oxidation with O_2 , displayed only the $g'=4.3$ signal. To correlate the EPR intensity of this signal with the signal due to the mixed valence complex, varying amounts of Fe(II) (0.5 - 5.0 Fe(II)/subunit) were then added anaerobically to the above solution and the EPR spectrum recorded at 10 K. The $g'=4.3$ signal progressively lost intensity while the $g'=1.87$ signal grew in intensity with each addition of Fe(II) to the sample. However, spin quantitation of the two signals showed that the loss in intensity of the $g'=4.3$ signal does not quantitatively account for the gain in intensity of the $g'=1.87$ signal. Thus other sources of iron(III) in the protein such as EPR silent Fe(III) dimeric and oligomeric species appear to also contribute Fe(III) to the formation of the Fe(III)-Fe(II) mixed valence dimer.

The location of the mixed valence complex within the protein shell is of particular interest. Accordingly the influence of various competing metal ions on its formation was examined. The addition of Cd(II), Tb(III), Zn(II), and UO₂(VI) to Fe(III)-apoferritin prior to the addition of 5 Fe(II) per subunit caused reduction in the mixed valence EPR signal by 62%, 91%, 52%, and 100%, respectively. Since UO₂(VI) is known to bind uniquely at the interface of subunit dimers on the interior of the protein shell [2], this result suggests that the mixed valence dimer is formed there as well. The other metal ions are known to bind at the subunit dimer interface but also in the hydrophilic channels [2].

The temperature dependence of the intensity of the $g'=1.87$ signal was investigated in the range 10 - 45 K. Deviation from Curie Law behavior was observed. Curve fitting of the intensity to a model for an exchange coupled dimer described by the Hamiltonian $H=-2JS_1S_2$ suggests a value for J near -5 cm⁻¹, indicative of weak antiferromagnetic exchange coupling to give an $S=1/2$ ground state.

1. N.D. Chasteen, B.C. Antanaitis, and P. Aisen, J. Biol. Chem., 1985, 260, 2926.
2. P.M. Harris, A. Treffry and T.H. Lilley, J. Inorg. Biochem., 1986, 27, 287 and references therein.

FE(II) AND THE PROTEIN COAT OF HORSE SPLEEN FERRITIN.

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The ferritins are a family of proteins found in plants, animals, and microorganisms, that provide a reservoir for iron-proteins for DNA synthesis, respiration, activation, photosynthesis, and nitrogen fixation (1); certain types of ferritin are also involved with recycling iron from old cells or detoxifying excess iron. All members of the ferritin family share common features of structure, a hollow, multi-polypeptide (n=24) protein coat which surrounds a core of polynuclear hydrous ferric oxide; the core may vary in number of iron atoms (up to 4500), amount of phosphate, order, and hydration. Experimentally, bulk iron in the core is taken up or released as Fe(II); small amounts (10-15%) of Fe(III) can be removed by chelation and small clusters of Fe(III) can be bound to the protein coat. Other metal ions (ca. 10/molecule) may also be bound by the protein coat.

To study the effect of various ferritin protein coats on iron core formation we began by investigating the incorporation and oxidation of Fe(II) by the protein coats from the ferritin of horse spleen at pH=7, where Fe(II) without the protein precipitates; horse spleen ferritin is a useful model because it is simple (>90% identity among polypeptide subunits) and well characterized. X-ray absorption spectroscopy (XAS) was used initially, to monitor the conversion of Fe(II) to Fe(III) when 480 Fe(II) were added per protein molecule (2). The XAS results show that Fe(II) persists for up to 16-24 hours, although the Fe(II) rapidly becomes inaccessible to chelators. For example, 15 minutes after mixing, only 52% of the Fe(II) was accessible to 1,10-phenanthroline but 90-95% of the added iron was Fe(II) by XAS or chelator-accessible after denaturing the protein coat; bubbling in air had no effect on the oxidation state, suggesting that dioxygen is not limiting. Mössbauer spectroscopy of Fe(II) oxidation confirmed the XAS studies. Preliminary data show that lowering the Fe/protein ratio to 120 or 240/molecule reduces the time required for oxidation to 3-4 or 12 hours, respectively, and that at an Fe/Zn of 2:1 (240 Fe/molecule) no oxidation had occurred even at 24 hours.

The results are compatible with a model in which Fe(II) is rapidly sequestered by the protein coat of ferritin and forms an intramolecular solid phase oxidized slowly at its surface near the inner surface of the protein. (Part support by NIH grant GM34675.)

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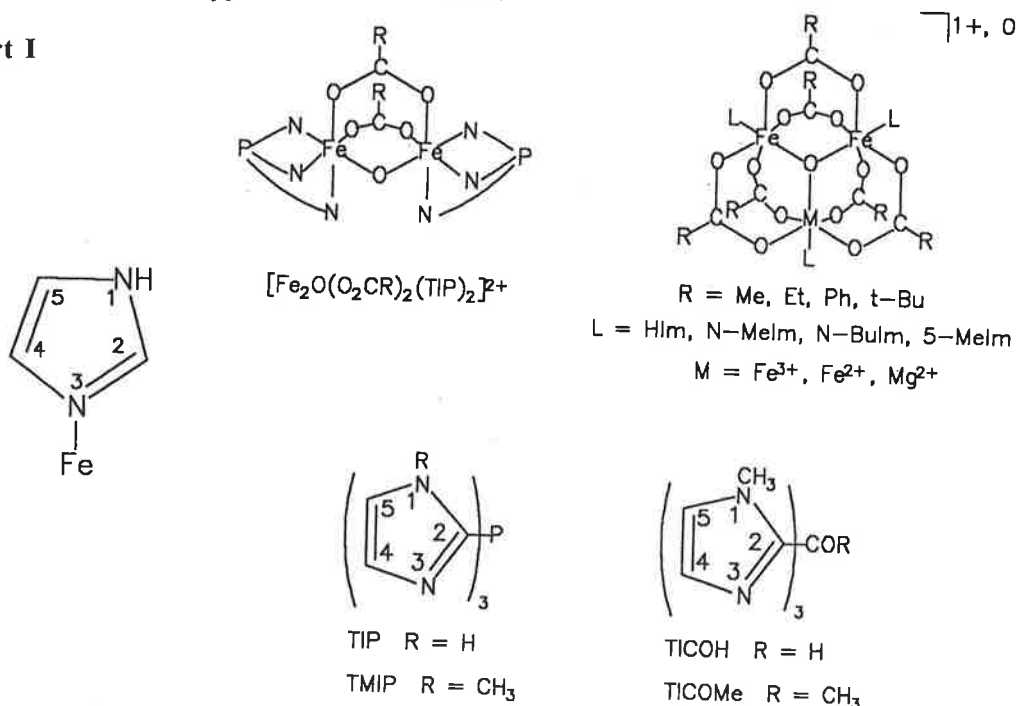
¹H NMR OF IMIDAZOLE LIGANDS IN PARAMAGNETIC FERRIC AND FERROUS COMPLEXES AND CLUSTERS. RELEVANCE TO NON-HEME PROTEINS.

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In order to provide an overview of the ¹H NMR behavior expected for imidazole ligands to paramagnetic non-heme iron, we have examined a set of ferric and ferrous imidazole complexes and a new set of binuclear and trinuclear clusters with the ligands and cluster types shown in Chart I.

Chart I



For octahedral high-spin ferrous hexakis-imidazole complexes, the isotropic shifts can serve as contact shift references. For these complexes, σ spin delocalization dominates, and the order of downfield isotropic shifts at 300 K is: $N(1)-H > 5-H > 4-H > 2-H > N-CH_3 \approx 5-CH_3$. For low-spin Fe(III) direct π spin delocalization leads to upfield contact contributions for imidazole ring protons and downfield contact contributions for ring methyls. Dipolar contributions can be either upfield or downfield, and, in the case of low-spin $[Fe(TICOH)_2]^{3+}$, these contributions were quantitatively separated. From this separation the orientation of the imidazole rings with respect to the principal magnetic axis was determined. For imidazole ligands in high-spin ferric complexes, σ spin delocalization leads to exclusively downfield isotropic shifts, usually in the order: $N(1)-H > 4-H > 5-H > 2-H > 5-CH_3 \approx N-CH_3$. The imidazole ligand 2-H and 4-H were observable only for the trinuclear "basic iron carboxylate" clusters, due to an unusually short $T_{1\rho}$. The results indicate that the histidyl ligand $\beta-CH_2$ should be observable well downfield of 10 ppm for magnetically uncoupled high-spin ferric sites, and upfield of 9 ppm for $-J \approx 30 \text{ cm}^{-1}$. The imidazole N-H (19.2 and 15.1 ppm) and acetate methyl (10.2 ppm) resonances of the diiron(III) complex, $[Fe_2O(O_2CMe)_2(TIP)_2]^{2+}$, together confirm the presence of a μ -oxo rather than μ -hydroxo bridge in oxy- and methemerythrin. The 4.1 ppm separation between the two N-H resonances of $[Fe_2O(O_2CMe)_2(TIP)_2]^{2+}$ reflects the μ -oxo trans effect. Constraints of the tridentate TIP ligand apparently result in a smaller μ -oxo trans effect than that in oxy- and methemerythrin. For the mixed-valent "basic iron carboxylate" clusters, valence delocalization allows the upfield dipolar contributions to the isotropic shifts to be understood in terms of distances and angles of the ligand protons with respect to magnetic axes of the cluster.

W14

MS5

GEMINATE REBINDING PROCESSES IN HEME AND HEME PROTEIN LIGATION REACTIONS.

Teddy G. Traylor, Douglas Magde, Douglas Taube, Jikun Luo, and Karen Jongeward

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Picosecond kinetic studies of the reactions occurring after subpicosecond flash photolyses of isocyanide, carbon monoxide, dioxygen, imidazole with hemes and heme proteins reveal recombination from contact pairs with rate constants on the order of $2-7 \times 10^{10} \text{ sec}^{-1}$. Changes in the amounts and rates of these processes with variations in proximal and distal steric effects, electronic effects, and viscosity and polarity of solvents reveal the details of heme protein binding mechanisms and provide some interesting results relevant to the general nature of cage processes with uncharged species. Mechanistic conclusion based upon these results will be discussed.

MS5

THE EFFECT OF HINDERED AXIAL LIGAND ROTATION ON THE NMR, EPR AND ELECTROCHEMICAL PROPERTIES OF A SERIES OF MONO-ORTHO-SUBSTITUTED DIALKYLAMIDO-TETRAPHENYLPORPHINATOIRON(III) BIS-IMIDAZOLE OR -PYRIDINE COMPLEXES.

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Axial ligand orientation has been suggested to play an important role in adjusting the spectroscopic and redox properties of some heme proteins. In an attempt to evaluate the importance of the orientation effect, a series of mono-ortho-substituted dialkylamidotetraphenylporphinatoiron(III) complexes have been synthesized, where the dialkylamide is derived from dimethyl- or diethylamine, pyrrolidine, piperidine, hexamethyleneimine, or 3-azabicyclo[3.2.2]nonane. NMR spectroscopic studies of the free base porphyrins as compared to the respective benzamides showed clearly that the alkyl groups lay very close to the porphyrin ring and they were severely limited in their internal motions by its presence. Detailed nmr investigations as a function of temperature of the low-spin Fe(III) complexes of this series of mono-ortho-substituted TPP derivatives showed very unique pyrrole proton splitting patterns: Up to eight pyrrole-H resonances were observed at low temperatures, followed by a coalescence to two peaks at intermediate temperatures and splitting out to three or four peaks at higher temperatures in the case of the smallest alkyl groups. (The definition of low, intermediate and higher temperature differs for each dialkylamide complex, allowing the relative sizes of the substituents to be assigned.) The bis-N-methylimidazole complexes gave the largest spread of pyrrole-H resonances at a given temperature, followed by the bis complexes of imidazole and 5-methylimidazole in decreasing spread. The complexes of 4-dimethylaminopyridine and 2-methylimidazole both gave very small spreads of the pyrrole proton resonances. Despite the individual differences, the types of patterns and their temperature dependences were remarkably similar. The nmr results can be explained by realizing that the effect of unsymmetrical substitution alone is to split the pyrrole-H resonance of low-spin Fe(III) TPP derivatives into four peaks. Superimposing upon this the effect of a non-rotating planar axial ligand explains the existence of eight pyrrole-H resonances at low temperatures. EPR spectra of the bis-N-methylimidazole complexes of all of the dialkylamido TPPFe(III) complexes were identical, indicating that all complexes are able to achieve the same axial ligand orientations at 100° K. The Fe(III)/(II) reduction potentials of the complexes with the largest and smallest amide substituents were within experimental error of each other at ambient temperature. This result unfortunately does not contribute either positively or negatively to the hypothesis that axial ligand plane orientation should affect reduction potentials because of potential kinetic effects.

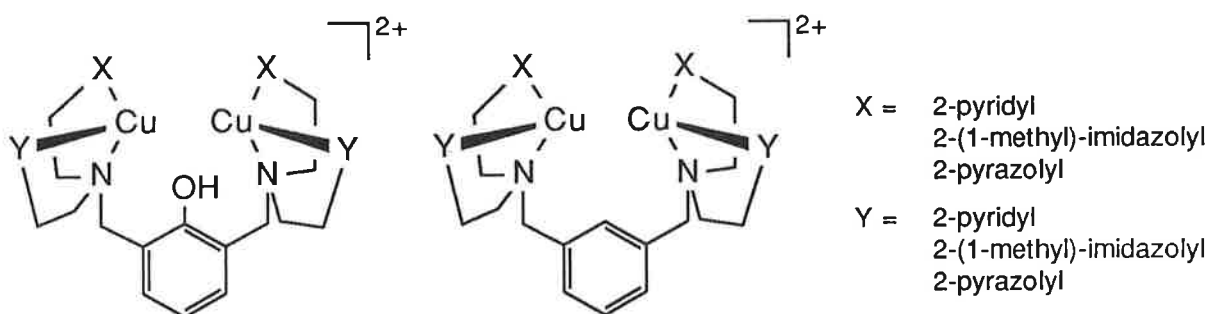
SYNTHETIC MODELS FOR THE ACTIVE SITE OF HEMOCYANIN

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The hemocyanins (Hc) are highly aggregated molecules that contain a binuclear-copper active site which functions for many species of marine organisms to bind molecular oxygen for respiration [1]. A crystal structure of deoxyHc shows that each copper(I) ion is coordinated by three imidazole groups from histidine residues [2]; and a variety of spectroscopic studies have further defined the active site structures in several forms of the protein, including oxyHc [3].

The purpose of modeling studies is to confirm the proposed structures for the active site in hemocyanin and to understand the intrinsic properties of the copper-dioxygen interaction [4,5]. Thus, most studies have focused on the synthesis of binuclear copper(I) complexes and those in which the copper(I) ions are coordinated by nitrogen heterocycles. The best studied species are those having pyridine or pyrazole donors; but the synthesis of imidazole-ligated complexes has become increasingly more important. We and others [5] have synthesized binuclear complexes that have six nitrogen donors comprising a combination of imidazole, pyrazole, pyridine, and amino-group ligands:



We report the reactivity of these complexes, and their mononuclear analogs, toward dioxygen. Depending on the nature of the donors, we observe no reaction, reversible binding (at low temperature), hydroxylation of the aromatic ring, or formation of hydroperoxide species. The reasons for the different types of reactivity will be discussed as well as the relationship of these results to understanding the structure and reactivity of hemocyanin.

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THE IRON-ACTIVATED ALCOHOL DEHYDROGENASE FROM ZYMOMONAS MOBILIS AND OTHER METAL-ADH DERIVATIVES

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The title enzyme contains ferrous iron in its native, active form. Inclusion of Co^{2+} in the isolation buffer leads to about 90% substitution of Fe^{II} for Co^{II} providing a preparation which is more stable and also active. Treatment of the Co^{II} enzyme with 1,10-phenanthroline leads to apo-enzyme (<3 atom % total metal content), which can be completely reactivated upon addition of a single equivalent of Fe^{2+} or Co^{2+} . Zn^{2+} is ineffective under the same conditions. Apparent metal dissociation constants, K_M , were determined for the bivalent metal ions of the first transition series. That for Co^{II} was defined using nitrilotriacetic acid as metal buffer while the remainder were determined by competition of two metal ions for the apo-enzyme. Complementary experiments in which the total concentration of, firstly, one metal ion and then the other was kept constant were employed to maximise precision. The K_M values increase slowly with atomic number and do not follow the classic Irving-Williams series:-

M:	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Fe^{III}
$\text{p}K_M$:	7.4	7.5	7.8	8.4	8.5	9.0	5.8

The tight binding allows generation of well-defined metallated enzyme species from apo-enzyme and M^{2+} .

The spectroscopic and magnetic properties of the active Fe^{II} and Co^{II} forms of the title enzyme are presented as well as those of the inactive Mn^{II} , Ni^{II} and Cu^{II} forms. Magnetic susceptibility, ESR, Mössbauer and electronic spectral data all point to the presence of high spin six-coordinate sites influenced by a ligand field close to octahedral. The electronic spectra of M^{II} -ADH ($\text{M} = \text{Co}, \text{Ni}$) are closely related to those exhibited by the MN_4O_2 sites in crystalline $\text{M}(\text{his})_2\cdot\text{H}_2\text{O}$. At least three and most probably four nitrogen ligands are observed directly via hyperfine structure in the ESR spectrum of Cu^{II} -ADH. Taken as a whole, the results strongly support the presence of a high spin, six-coordinate ferrous site in the native enzyme. The three or four nitrogen ligands present would appear to be histidine residues while the other ligands are most likely to be supplied by H_2O , aspartate, glutamate or, less likely, tyrosinate.

NMR EXAMINATION OF THE 8FE-8S FERREDOXIN FROM *CLOSTRIDIUM PASTEURIANUM*.

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The title protein functions as an electron transfer agent and features two $\text{Fe}_4\text{S}_4(\text{cys})_4$ centres in a 55 amino acid sequence of molar mass 6200 Da. Its proton NMR properties are being studied at 400 MHz.

In the oxidised form, antiferromagnetic interactions [1] within each $[\text{Fe}_4\text{S}_4]^{2+}$ centre cause the cysteinyl $\beta\text{-CH}_2$ proton resonances to be broadened and contact-shifted to lower field. Fifteen of the possible sixteen resonances have now been observed directly in the range 5.3–7.5 ppm. They fall into two distinct groups (5.3–10.5; 11.2–17.5 ppm) and every $\beta\text{-CH}_2$ group apparently contributes one resonance to each group.

Detailed results will be presented, including two-dimensional studies to determine the molecular structure in solution.

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INVESTIGATION OF IRON (III) COORDINATION IN FERREASCIDIN:
A DOPA PROTEIN FROM A STOLIDOBRANCH ASCIDIAN.

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The chemical constituents of the blood cells of the Ascidiacea, benthic marine invertebrates of the phylum Chordata, have been investigated since early this century to help explain their remarkable ability to accumulate selectively a particular transition metal. Species within the stolidobranch suborder of ascidians have been found to concentrate iron.

Recently a rather unusual protein called ferreascidin was isolated from the morula cells of the stolidobranch, Pyura stolonifera [1]. Ferreascidin is a glycoprotein (MW 10 000 Da) and is the most aromatic protein yet characterised, with 67% aromatic amino acids including 42% tyrosine and 17% 3,4-dihydroxyphenylalanine (DOPA). The catecholate grouping of the DOPA residues gives the protein a strong iron binding capacity. It removes two Fe^{3+} ions per protein molecule from bis(nitrilotriaceto) iron (III) at pH 7.0 as determined by spectrophotometric titrations. At pH 5.0 - 7.0 the FaFe_2 spectrum has a band a with a λ_{max} at 570 nm which is the exact position where a maximum occurs in the visible spectrum of bis(catecholato) iron (III). Under more alkaline conditions FaFe_2 exhibits a λ_{max} at 540 nm. This bathochromic shift probably reflects deprotonation and coordination of histidyl imidazoles at the metal sites. Signals in the EPR spectra of FaFe and FaFe_2 at $g = 4.24$ are characteristic of high spin ferric ion in a non-axial environment. From the Mössbauer spectrum of FaFe_2 we can infer that the two Fe's are very close. The evidence for the mode of iron (III) coordination in ferreascidin will be presented.

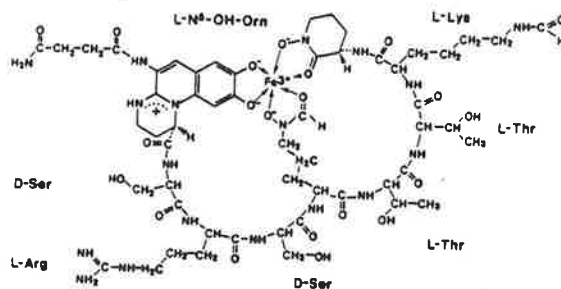
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PYOVERDINS, A NEW CLASS OF SIDEROPHORES: STRUCTURE AND PHYSICOCHEMICAL PROPERTIES.

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The structure of the siderophores originating from several strains of *Pseudomonas* and *Azotobacter vinelandii* has been elucidated using essentially FAB Mass Spectrometry and NMR techniques [1-3]. These compounds, called pyoverdins and azotobactin, consist of a peptide, composed of 6 to 10 hydrophilic amino acids, which is bound via its N-terminus to a chromophore derived from 2,3-diamino-6,7-hydroxyquinoline. A given strain produces several pyoverdins having the same peptide chain with minor structural differences on the chromophore. However the peptide chain generally varies from strain to strain. In presence of Fe(III), all these siderophores yield very stable octahedral complexes with a 1:1 stoichiometry by means of three bidentate chelating groups which are a catechol group (on the chromophore), a hydroxamate group (at the end of the peptide chain) and an α -hydroxy acid moiety or a second hydroxamate group (in the middle of the peptide chain).



Structure of Pyoverdine Pa A.

The protonation constants of the free ligands, the binding constants of their iron(III) complexes as well as the spectra of the different species in solution were obtained combining spectrophotometry (250-650 nm) and potentiometry[4]. The stability constant relative to the equilibrium $L^4 + Fe(III) \rightleftharpoons LFe^-$ for pyoverdine Pa A was found to be $\log K_1 = 30.8 \pm 0.9$. In this respect pyoverdine Pa A is closer to ferrichromes than to enterobactin. At physiological pH, a neutral species $LHFe$ was observed, with a constant of $\log K_2 = 43 \pm 1$ ($L^4 + H^+ + Fe(III) \rightleftharpoons LHFe$).

The redox potential values were determined by cyclic voltammetry and found to be -0.490 V/NHE for pyoverdine Pa A/ iron complexes, suggesting that iron can be released to the cells by a reductive process.

Preliminary results performed on azotobactin indicate that the nature of the third bidentate chelating group induces important changes in the physicochemical properties of this latter compared to pyoverdine Pa A.

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FLUORESCENCE MEASUREMENT OF DISSOCIATION CONSTANTS FOR A SERIES OF METAL IONS TO OVOTRANSFERRIN AND ITS HALF-MOLECULES IN THE PRESENCE OF VARIOUS SYNERGISTIC ANIONS. R.C. Woodworth* and L.S. Ulundu, Department of Biochemistry, University of Vermont, Burlington, Vermont, USA 05405

Binding studies of a series of diamagnetic and potential paramagnetic shift/broadening metal ions was undertaken to determine the K'_d s and the rates of binding and release to ovotransferrin (OTF) and its half-molecules. These data will be useful in determining whether a given metal ion is in fast or slow exchange with the protein on the NMR time scale. The metal ions studied were the diamagnetic Ga(III), La(III), Lu(III), and the paramagnetic Co(II), Mn(II), Tb(III), Gd(III), Yb(III) and Pr(III). Binding was tested to OTF and its separate half-molecules with carbonate, oxalate and malonate as synergistic anions. The protein was in 25 mM PIPES buffer, pH 7.4. The technique involved saturating the protein with Tb(III), which is barely fluorescent in the hexaaquo form, but highly fluorescent when complexed to OTF. The Tb-protein was then titrated with competing metal ion until a new fluorescence plateau was reached and the titration curves were analyzed by a computer routine to extract K'_d s (S. Krishnaswamy, personal communication). When corrected for the hydrolysis constants of the several metals at pH 7.4 or the appropriate chelation constants to the synergistic anions, the K'_d s yielded K^*_d s in good agreement with those previously reported in the literature. In the case of OTF the constants for the two binding sites differed by ca. three orders of magnitude, rather than the one to two orders of magnitude found for hTF. This was the case whether the binding sites were connected in OTF or separated into the half-molecules. Substitution of malonate for carbonate decreased the K'_d s by an order of magnitude, and oxalate by another two orders of magnitude. The lanthanides with large radii, La(III) and Pr(III) bind only to the C-terminal site.

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BIOLOGICAL MINERALIZATION OF IRON: STRUCTURAL ORGANIZATION AND BIOSYNTHESIS IN MOLLUSCAN TEETH

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Comparatively recently it has been recognised that the bioinorganic chemistry of iron includes solid phases and associated solid state chemistry [1]. Biological examples of iron-containing solid phases, or biominerals, are now known to occur in a wide range of organisms, ranging from unicellular bacteria to mammals. The comparatively well-characterised examples of iron biominerals include magnetite (Fe_3O_4), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), ferrihydrites (generally, $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) and hydrous iron(III) phosphates.

The biological mineralizing systems for iron that have been studied most extensively are the magnetotactic bacteria, the small particle deposits in ferritin and hemosiderin and the teeth of certain marine molluscs (chitons and limpets).

This latter system is comparatively complicated in that the teeth are constructed from a complex composite material containing several types of iron biomineral together with other non-iron-containing mineral deposits.

We have studied biomineralization in the teeth of chitons and limpets for some time and the poster will present an overview and recent data [1-3]. In general, these studies are directed to understand the following:

1. The principles of structural organisation or microarchitecture within the mineralized tissue. This basic structure is composed, in general, of the several mineral components together with organic components such as proteins and polysaccharides often referred to as the organic matrix.
2. The principles of the biosynthesis of the minerals from their precursors and of the interconversions among the several biomineral phases present. The chemical and biochemical factors involved in the control of the growth of the biominerals are of particular interest.
3. Together with such studies of the biological material *per se*, related studies *in vitro* can be developed to apply the insights from the biominerals to the design of composite materials that are of interest to materials science and emerging technologies.

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INTERACTION OF FE(III) AND CU(II) IONS WITH HEN PHOSVITIN

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Hen phosvitin, 35000 M.W., is one of the most phosphorylated protein known to day, containing about 10% phosphorous as phosphoserins. This protein, whose X-ray structure has not yet been obtained, has a great tendency to bind large amounts of divalent and trivalent metal ions like Fe(III), Co(II), Cu(II), Zn(II) etc.[1] Although its physiological role is still unknown, it has been proposed that phosvitin can be involved in metal transport in particular of iron and copper. For this reason we have investigated, mainly through CD, EPR and EXAFS spectroscopies, the binding properties of the protein toward these two ions with the aim of characterizing the nature of the groups involved in the coordination and the geometry of the adducts.

In the case of Fe(III) a sample containing a Fe to protein 10:1 molar ratio at pH 7.2, was investigated through EXAFS spectroscopy which showed that the main binding sites of iron are provided by the oxygen atoms of serine bound phosphate groups at 1.93(2) Å from the metal. The average number of bound phosphate is 4.4(9) per iron atom, hexacoordination being achieved upon binding of other possible donors from protein or solvent water molecules.

Copper(II) seems to give rise to a more complex pattern as tetragonal N_2O_2 , N_3O , and N_4 chromophores have been revealed in the range of pH 6.5-10.5 and with metal to protein molar ratios ranging from 1:1 to 24:1. Furthermore histidines appear to be the main side chain residues involved in coordination at least until the metal to protein ratio does not exceed 10:1. Amide nitrogens are also present in the chromophores, whereas the involvement of phosphate groups, if any, appears to be minor. In conclusion phosvitin in dependence of the nature of the metal, pH and molar ratios appears to be able to provide different donors and stereochemistries.

GEMINATE REBINDING PROCESSES IN HEME AND HEME PROTEIN LIGATION REACTIONS.

Teddy G. Traylor, Douglas Magde, Douglas Taube, Jikun Luo, and Karen Jongeward

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Picosecond kinetic studies of the reactions occurring after subpicosecond flash photolyses of isocyanide, carbon monoxide, dioxygen, imidazole with hemes and heme proteins reveal recombination from contact pairs with rate constants on the order of $2-7 \times 10^{10} \text{ sec}^{-1}$. Changes in the amounts and rates of these processes with variations in proximal and distal steric effects, electronic effects, and viscosity and polarity of solvents reveal the details of heme protein binding mechanisms and provide some interesting results relevant to the general nature of cage processes with uncharged species. Mechanistic conclusion based upon these results will be discussed.

EFFECT OF CARBONYL HYDRATES ON RATES OF HEMIN-CATALYZED EPOXIDATION BY
HYDROGEN PEROXIDE.

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92110

In 80-20 acetonitrile-water at 25 °C, no epoxidation of 1,4-diphenylbutadiene occurs in the presence of tetra-2,6-dichlorophenylporphinate iron(III) chloride and up to 10^{-2} M hydrogen peroxide. Addition of carbonyl hydrates such as formalin, chloral hydrate, and hexafluoroacetone hydrate in concentrations 0.01 M to 0.6 M leads to epoxidation of rates which increase with the concentrations of the carbonyl hydrates. This makes possible the efficient use of hydrogen peroxide, either as added oxidant or produced *in situ* by dioxygen reduction, in epoxidation reactions.

The Formation of Reduced Glutathione-Fe(II) Complex and Its Reaction with Oxygen Molecule

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The universal distributions of glutathione and iron ion in living cells bring a number of investigations in vitro. Some of them include the oxygen uptake and/or consumption of glutathione-iron complex [1,2,]. These system are necessary to use the large excess reduced glutathione to iron. We found the complex formation for molar ratio just 1:1 reduced glutathione and Fe(II) ion. This complex reacts reversibly with air oxygen about ten times with cyclical colour changes from colourless to red. At last, this complex decomposes and yellow precipitate occurs. In the case of oxidized glutathione ligand, the red complex was not formed. The 1:1 glutathione-Fe(II) complex is silent to ESR and electronic absorptions measurements. The red coloured glutathione-Fe(II)-O₂ system after shaking in air showed an ESR ($g=4.2$ at 77K)² and electronic absorptions at 345 and 490 nm, respectively. The half-life of red complex is 80 sec. ESR parameter indicates the high spin Fe(III)-glutathione complex.

The spin trapping method was used to detect the radical species generating from the glutathione-Fe(II) and O₂. The ESR parameters of PBN adduct were $A_N=15.9$ and $A_H=3.3$ G., which indicated the trap of ethanol radical (the solvent of PBN). The oxygen anion radical generated produces the new ethanol radical based on a chain reaction. These facts propose the unique biological activities of oxygen anion radical generated by glutathione-Fe(II) complex, in contrast to the dismutation of superoxide radical by the glutathione ligand only.

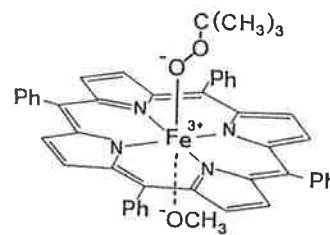
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Direct Evidence of Heme-t-butylperoxide Adduct Formation Demonstrated by Simultaneous ESR and Optical Measurements

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A possible model of hemeprotein-peroxide complex has been obtained by mixing chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) (Fe(III)TPPCl) with t-butylhydroperoxide (BHPO) in the presence of alkaline reagents. The ESR and optical absorption spectra were simultaneously measured for the frozen solution at 77 K. The observed optical spectra showed Soret-, α - and β - bands absorption maxima at 420, 543 and 571 nm. The ESR spectra show that this iron complex takes low-spin ferric state with anomalously small g-anisotropy ($g_1=1.96$, $g_2=2.15$ and $g_3=2.30$). It has been shown from thaw-and-freeze ESR measurements that this complex is very unstable above 5°C and readily decomposes to the non-heme iron type species such as open chain poly-pyrrol complexes. Based on the ESR spectrometric titration carried out by changing the mixing molar ratio of BHPO and NaOCH₃, the coordination structure of the intermediate complex is concluded to be a six-coordinated Fe(III)TPP(⁻OCH₃)(⁻OOC(CH₃)₃) complex. The present complex would be the first example for low-spin six coordinate ferric alkylperoxide complex.



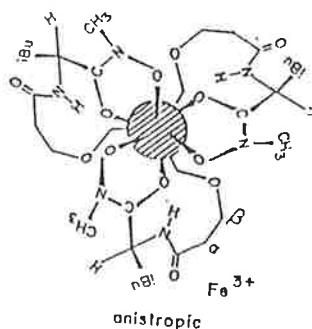
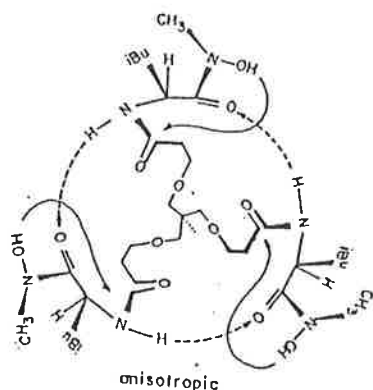
**Peroxide
complex**

K. Tajima, J. Jinno, K. Ishizu, H. Sakurai and H. Ohya-Nishiguchi, Inorg. Chem. (1989) in press

PROTON DRIVEN CARRIERS FOR TRANSITION METAL IONS

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Two families of synthetic binders for transition and related metal ions are introduced which exhibit selective ion binding and transport properties. These binders are based on tripode- and dipode-like molecules that form octahedral and tetrahedral ion binding cavities respectively. Incorporation of a network of inter-strand H-Bonds is shown to shape the conformations of these molecules to an ion binding configuration prior to binding and to thereby impart high binding selectivity. The use of hydroxamate groups as ion binding sites provides for facile proton driven transport, since these groups form electrically neutral complexes that are readily unloaded under acidic conditions.



Octahedrally binding hydroxamates prepared according to this design are shown to selectively extract and transport Fe³⁺ from a mixture of Fe³⁺ and Cu²⁺, thanks to their defined, H-bonded configuration in the free state, while tetrahedrally binding hydroxamates to selectively extract tetrahedrally coordinating Cu²⁺ from a mixture of six divalent metal ions.

The detailed conformations and ion binding configurations of these molecules will be described in relations to their H-bonding network, and their potential application as metal extractants, metal ion scavengers and biomedical markers indicated.

MODEL COMPOUNDS OF COPPER PROTEINS CONTAINING TYPE 11 AND TYPE 111 COPPER ATOMS.

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Three types of copper atoms can occur in copper proteins. They are called types 1, 11 and 111. Multicopper oxidases such as Laccase and Ceruloplasmin contain each of these three types of copper.

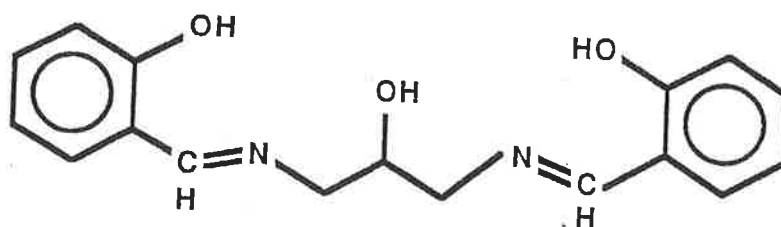
We have synthesised a series of multicopper complexes of the type:



where:

XSAL = a substituted salicylaldehyde.

L = 6-aminoindazole, β -alanine, 4-aminobutyric acid and 4-aminobenzoic acid.



SALDPLH₃

These complexes each contain two type 111 and one type 11 sites.

The structure of one of the complexes containing the 6-aminoindazole bridge will be described in this poster.

The visible and infrared spectra, the magnetochemistry and electrochemistry of these complexes will also be described in this poster.

DIOXYGEN AND SUPEROXIDE REACTIONS WITH A TETRANUCLEAR COPPER(I) COMPLEX.

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Ethylenethiourea (ettu) forms a ligand bridged complex with Cu(I), $\text{Cu}_4(\text{ettu})_9^{4+}$, in which the ethylenethiourea is involved in four types of coordinate covalent bonds with tetracoordinate Cu(I): four ettu ligands are terminally bound to Cu(I) via a S atom lone pair of electrons; four ettu ligands bridge two Cu(I) atoms each via S atom lone electron pair donation to Cu(I) and C=S pi-electron cloud donation to an adjacent Cu(I) atom; the ninth ettu ligand forms a "cap" to the eight-membered (Cu-S) ring linking all four Cu(I) atoms by two three-center two-electron bonds formed by donation of the two S atom lone electron pairs [1]. This tetranuclear Cu(I) complex has been observed to undergo a range of related reactions with O_2 and O_2^- which serve to mimic similar interactions between Cu(I) and O_2 in biological systems. These include a reversible interaction with O_2 (O_2 carrier activity), catalytic O_2^- dismutation (superoxide dismutase, SOD, activity), and catalysis of O_2 oxidation of organic substrates (oxygenase activity).

In water and alcohol solvents the complex reacts reversibly with O_2 over several oxygenation/deoxygenation cycles at room temperature to produce a metastable species with a broad absorption maximum at 553 nm. The complex is also an effective catalytic O_2^- scavenger by means of a dismutation reaction. The production of O_2^- by xanthine/xanthine oxidase was monitored by following the rate of ferri-cytochrome c reduction by O_2^- spectrophotometrically. A 5×10^{-6} M solution of the tetranuclear Cu(I) complex is capable of reducing the rate of the ferri/ferro-cytochrome c reduction by 50%. This represents a significant level of SOD type activity. For comparison purposes, at similar conditions a 5×10^{-8} M solution of bovine superoxide dismutase will effect a 50% inhibition of the ferri/ferro-cytochrome c reduction reaction. Solutions of $\text{Cu}_4(\text{ettu})_9^{4+}$ are capable of catalytically inserting O_2 across the C=C of 2,3-dimethylindole to produce the corresponding ketoamide. This reaction has been shown to proceed via the formation of a hydroperoxide intermediate. Solutions of $\text{Cu}_4(\text{ettu})_9^{4+}$ have also been shown to catalyze the oxidation of 2,6-di-*tert*-butylphenol by O_2 to produce the corresponding quinone and diphenoquinone. We suggest that all of these reactions proceed with the direct and reversible interaction of a Cu(I) center with O_2 .

1. A. L. Crumbliss, L. J. Gestaut, R. Rickard and A. T. McPhail, *J. Chem. Soc. Chem. Commun.*, 545 (1974).

Binding of Copper(II)
to the
Cyclic Octapeptide, Patellamide D.

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Department of Chemistry, University of Queensland,
St. Lucia, 4067, Queensland, Australia.

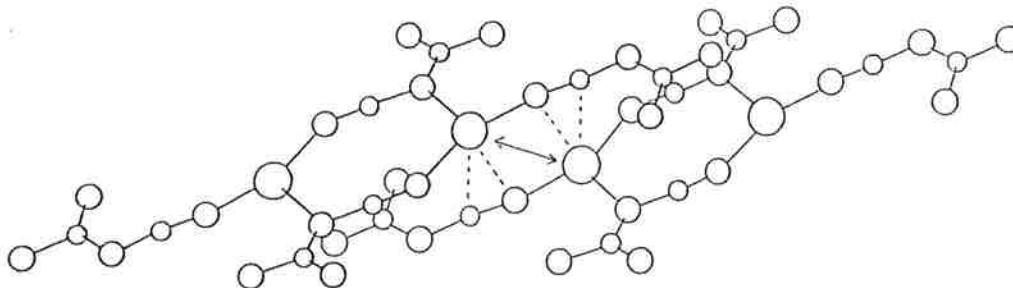
Patellamide D, a cyclic octapeptide from the ascidian *Lissoclinum patella* with two oxazoline and two thiazole rings, has the 24-azacrown-8 macrocyclic structure. It forms a mononuclear copper(II) complex in methanol and acetonitrile with one peptide amide deprotonated, and a binuclear copper(II) complex with two peptide amides deprotonated. In methanol a third deprotonation occurs and this has been interpreted as solvent deprotonation to form a bridge between the two copper(II) ions. The electronic absorption, circular dichroism and electron spin resonance spectra will be reported as a function of added base. The two copper(II) ions interact ferromagnetically. A copper(II) - zinc(II) complex has also been formed and its spectroscopic data will also be reported. A comparison of the linewidth parameters ($\sigma g/g$ and σA) for this complex and the mononuclear copper(II) complex indicates that the copper(II) site in the latter complex is more flexible.

UNSATURATED COPPER(I) CENTRES CRYSTALLISED FROM AQUEOUS SOLUTION.

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Nottingham. NG7 2RD. U.K.

Unsaturated copper(I) centres are important in the biomimetic modelling of copper containing enzymes, particularly in the elucidation of the mechanism of reversible dioxygen binding in haemocyanins, the deoxy form of which contains two copper(I) centres ca. 3.8 Å apart [1]. However the synthesis of suitable models is complicated by the fact that unsaturated copper(I) species are often converted either by polymerisation to the saturated four co-ordinate analogues or by reaction to the more moisture stable copper(II) derivatives. Hence, the synthesis of unsaturated copper(I) centres usually involves co-ordination by geometrically constrained, tridentate ligands prepared in anhydrous conditions. We report the synthesis and structural analysis of four crystalline copper(I) 1-cyanoguanidine (cng) complexes, which are notable inasmuch as they contain unsaturated copper(I) centres and are crystallised from halide rich aqueous solutions. The remarkable tendency of cng to stabilise planar three co-ordinate geometries has allowed a study of the interactions of these centres within their crystal lattices.



The structures are characterised by cng bridging two copper atoms, either as isolated dimers or polymeric chains. Furthermore a trend in co-ordination environments has appeared on changing the relative amounts of cng to copper; copper(I) co-ordinated by cng exists in trigonal planar, trigonal pyramidal and distorted tetrahedral environments. One complex (figure) contains an inter dimer bridged binuclear copper(I) centre with a copper-copper distance of 3.6 Å.

- [1] W P J Gaykema, W G L Hol, J M Vereijken, N M Soeter, H J Bak and J J Beintema. Nature **1984**, 309, 23

STUDIES ON CARBONIC ANHYDRASE: THE KINETICS OF ZINC REMOVAL BY 8-HYDROXY- QUINOLINE-5-SULFONIC ACID

C. Geiser and H. Elias

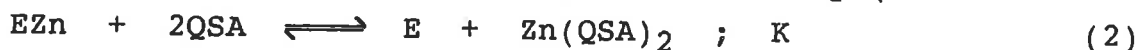
*Anorganische Chemie III, Technische Hochschule Darmstadt,
6100 Darmstadt, Federal Republic of Germany*

The spectrophotometric study of the kinetics of zinc removal and zinc incorporation for the zinc enzyme Bovine Carbonic Anhydrase II = EZn according to (1) (charges omitted) requires



a ligand L, the absorption of which changes upon complexation. The ligand 8-hydroxyquinoline-5-sulfonic acid = QSA meets this requirement.

Reaction (2) was studied spectrophotometrically (and also



by monitoring the enzyme activity) at pH=6,1 (25°C, I = 0,1M NaClO₄). Under pseudo-first order conditions ([EZn] << [QSA]) the absorbance/time data describing the formation of Zn(QSA)₂ can be fitted to the sum of two exponentials:

$$A = \Delta_1 \cdot \exp[-k_{\text{obs}}(1) \cdot t] + \Delta_2 \cdot \exp[-k_{\text{obs}}(2) \cdot t] + \Delta_3 \quad (3)$$

$$(\Delta_2 : \Delta_1 \approx 15 : 1)$$

It is found:

- 1) The half life $t_{1/2}(1)$ and $t_{1/2}(2)$ (corresponding to $k_{\text{obs}}(1)$ and $k_{\text{obs}}(2)$) is of the order of 2h and 20h, respectively.
- 2) The ligand QSA equilibrates with EZn in the sense that even for a 500-fold molar excess of QSA the removal of zinc according to (2) is only 80 %.
- 3) The equilibrium constant K for (2) is found to be 0.24 M⁻¹. This value leads to $K_{\text{EZn}} = 1.15 \times 10^{-11}$ M for (4) (charges omitted), which is in good agreement with earlier findings [1].



- 4) The size of $k_{\text{obs}}(2)$ depends linearly on [QSA] according to: $k_{\text{obs}} = k_0 + k \cdot [\text{QSA}]$.
- 5) Both $k_{\text{obs}}(1)$ and $k_{\text{obs}}(2)$ decrease with increasing ionic strength.

The mechanistic implications of these kinetic findings are discussed.

-
1. S. Lindskog and P.O. Nyman, Biochim. Biophys. Acta, **1964**, 65, 462.

ELECTROCHEMICAL PROPERTIES OF MODIFIED ELECTRODE BY A COORDINATION POLYMER

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Department of Applied Chemistry, University of Tokushima,
Minami-josanjima Tokushima, JAPAN

A family of coordination polymer, copper(II)-N,N'-disubstituted dithiooxamides has interesting properties, for example all of them are more or less semiconductive attributed to their two-dimensional π -electron network composed of Cu, S, N and C atoms. These polymers can be prepared both as bulky precipitates in solution and as monomolecular films at an air-water interface. When the substituent R is HOC_2H_4- , the solid specimen of the copper coordination polymer $(\text{HOC}_2\text{H}_4)_2\text{dtoaCu}$ exhibits proton conductivity indicating the existence of proton network cooperating with the π -electron network.

Those knowledge led us to an attempt to modify electrodes by the polymers and to inquire the electrochemical behavior both in dark and under illumination.

The modification of the electrode(copper or copper plated glassy carbon) were carried out by cyclic application of potential in the cathodic range to the electrodes in the ligand-supporting electrolyte solution. The electrochemically well-estimated films were obtained on glassy carbon electrode rather than on copper electrode. The films, $(\text{CH}_3)_2\text{dtoaCu}$ and $(\text{HOC}_2\text{H}_4)_2\text{dtoaCu}$, were identified by IR spectra comparing with those of the bulk phase preparation. Optical-microscopic examinations of the modified films reveal the homogeneity and smoothness of the surface and the thickness of the depositions. Cyclic voltammograms of the modified electrodes show the redox reactions of the polymer films in between $-1.0 \sim 0$ V vs. SCE. A potential sweeping to -1.2 V vs. SCE results in the onset of the reduction current of $\text{H}^+ \rightarrow \text{H}^0$ at -1.1 V and the onset of new anodic oxidation current of $\text{H}^0 \rightarrow \text{H}^+$ at $-0.9 \sim -0.8$ V vs. SCE, which had been absent after the cathodic scanning up to -1.0 V vs. SCE. An intake mechanism of reduced hydrogen at -1.2 V into the films will be discussed in connection with the thickness of the film and the time-course of reduction at -1.2 V vs. SCE.

MS6

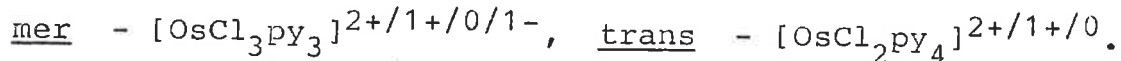
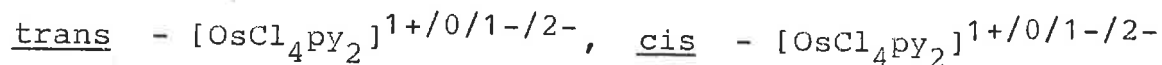
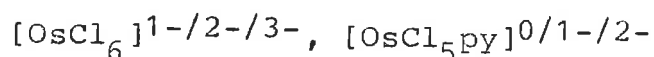
COORDINATION COMPLEXES OF OSMIUM - THEIR SYNTHESIS AND ELECTRONIC PROPERTIES

K.J. Taylor and L.J. Yellowlees

Department of Chemistry, University of Edinburgh, Scotland, U.K.

One fruitful method of probing the electronic structure of Transition Metal coordination complexes is to correctly assign absorption bands to particular electronic transitions in a uv-vis absorption spectrum. This is, of course, notoriously difficult but can be made much easier if the spectra of several similar complexes can be compared. For example the advent of variable temperature spectroelectrochemical cells has made the spectral analysis of complexes with differing electronic populations most successful[1].

In this poster we address ourselves to a comparative spectral and electrochemical study of the extended series $[\text{OsCl}_x \text{L}_{6-x}]^{n+}$ where for L = pyridine $x = 6, 5, 4, 3, 2$ and the oxidation state of the metal ranges from Os(II) to Os(V). The complexes are all prepared by redox-induced substitution reactions of $[\text{OsCl}_6]^{2-}$ in dichloromethane to which a stoichiometric amount of pyridine (py) is added. This method gives clean products and by the subtle alteration of temperature and/or electrogeneration potential the following species have been prepared :



1. A.E.D. McQueen, A.J. Blake, T.A. Stephenson, M. Schröder and L.J. Yellowlees, J. Chem. Soc., Chem. Commun., 1988, 1533.

AXIAL LIGATION AND SUBSTITUENT EFFECTS OF MANGANESE TETRAPHENYL PORPHYRINS – A SPECTROELECTROCHEMICAL APPROACH

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School of Chemistry, University of Sydney, N.S.W. 2006, Australia

The study of manganese porphyrins and proteins by various techniques remains a particularly active field of research with recent work continuing to focus on axial ligand effects [1,2], as well as such properties as the correlation between electronic configuration and molecular structure [3].

In this work we report the use of resonance Raman (RR) spectroscopy and microelectrode voltammetry to probe the axial ligand environment of manganese(III) tetraphenyl porphyrins and also to characterize the effects of phenyl-ring substituents on the metal centre.

The unusual indifference which manganese(III) porphyrins show towards axial ligation is well documented and it has been suggested that solution ionic strength may have some effect on the degree of this ligation [4]. A dependence of axial chloride ligand dissociation on the supporting electrolyte concentration was first observed as a change in relative intensity of axial ligand dependent modes in the RR spectrum of Mn(III)TPPCl [5] (See Fig. 1).

Verification of this interpretation was obtained by a study of the shifts in potential of the manganese(III/II) redox couple at various concentrations of supporting electrolyte. Using a 10 μm diameter, gold microdisc electrode, it was possible to measure half-wave potentials even at very low solution conductivities. When measured against the ferricenium/ferrocene redox couple, a clear dependence of the half-wave potential of the manganese(III/II) couple on solution ionic strength was observed (See Table 1). The magnitude and direction of the shifts are as would be expected for a ligand dissociation. Similar effects have been observed in the 4-methoxy and 4-chloro phenyl substituted manganese porphyrins. Importantly, conventional electrochemistry and chemical redox processes generally require solution ionic strengths in the region where ligand dissociation is already significant, i.e. $\sim 0.1\text{ M}$.

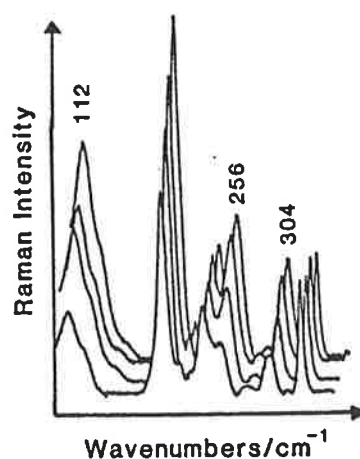
TABLE 1 Dependence of Mn(III/II) redox couple of MnTPPCl on [TBATFB].

[TBATFB] \dagger	$E_{1/2}/\text{mV}^*$
0.000266 M	-1027
0.001179 M	-975
0.01006 M	-906
0.1005 M	-813
0.5057 M	-759

\dagger TBATFB \equiv tetra(1-butyl)ammonium tetrafluoroborate

* Half-wave potentials are measured relative to the ferricenium/ferrocene redox couple.

FIG 1 Dependence of RR spectrum of MnTPPCl on [TBATFB]



- [1] M.M. Williamson and C.L. Hall, *Inorg. Chem.*, **1987**, *26*, 4155.
- [2] N. Parthasarathi and T.G. Spiro, *Inorg. Chem.*, **1987**, 2280.
- [3] N. Parthasarathi, C. Hansen, S. Yamaguchi and T.G. Spiro, *J. Am. Chem. Soc.*, **1987**, *109*, 3865.
- [4] S.L. Kelly and K.M. Kadish, *Inorg. Chem.*, **1982**, *21*, 3631.
- [5] R.S. Armstrong, G.J. Foran and P.A. Lay, *Proc. XI Int. Conf. Raman Spec.*, **1988**, 587, eds. R.J.H. Clark and D.A. Long

"PRESSURE-TESTING" MARCUS-HUSH THEORIES OF ELECTRON TRANSFER KINETICS

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The Marcus, Hush, and related theories imply that the effects of pressure (P) on adiabatic outer-sphere electron exchange rates (expressible as volumes of activation, ΔV^*) should be quantitatively predictable from the P dependences of such parameters as the refractive index n and static relative permittivity D of the solvent. In practice, $(\partial n / \partial P)_T$ is often unavailable and must be measured, or estimated from a modification of the Clausius-Mosotti relation, and there is no adequate theory of the P dependence of ionic strength effects beyond the Debye-Hückel range. Furthermore, theory predicts that the ΔV^* values will themselves be pressure dependent. Experimental tests of predictions are hindered by chemical difficulties (redox of solvents; solubility) and interpretation of results may be complicated by counter-ion effects (ion pairing, as with $\text{Bu}_4\text{N}^+/\text{Ru}(\text{hfac})_3^{0/-}$ in CHCl_3 , or catalysis, as with $\text{MnO}_4^{-/2-}$ in water) or uncertainty over the coordination number (as with $\text{Cu}(\text{dmp})_2^{2+/+}$). Nevertheless, Marcus-Hush-type two-sphere continuous-dielectric models account adequately for the observed P effects with relatively large reactants ($\text{Fe}(\text{H}_2\text{O})_6^{3+/2+}$ [1] and $\text{Fe}(\text{phen})_3^{3+/2+}$ in water, or $\text{Ru}(\text{hfac})_3^{0/-}$ in organic solvents). For $\text{Co}(\text{en})_3^{3+/2+}$ in water, anomalously strongly negative ΔV^* values [1] imply non-adiabaticity. In no case is there any evidence for solvent-dynamical effects, which would generate strongly positive contributions to ΔV^* in non-aqueous solvents (but not in water). Current work includes complementary studies of electrode reactions under pressure, e.g., of $\text{M}(\text{C}_5\text{H}_5)_2^{+/0}$ on Pt in CH_3CN ($\text{M} = \text{Fe}, \text{Co}$), by cyclic and a.c. voltammetry.

[1] D.R. Stranks, *Pure Appl. Chem.*, 1974, 38, 303; W.H. Jolley, unpublished work.

ELECTRON TRANSFER REACTIONS OF THE HEXACYANORUTHENATE(II)/(III) COUPLE IN AQUEOUS MEDIA.

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In contrast to the considerable kinetic data concerning the electron exchange and electron transfer reactions of the $\text{Fe}(\text{CN})_6^{4-/3-}$ couple, relatively little attention has been paid to the corresponding reactions of the $\text{Ru}(\text{CN})_6^{4-/3-}$ couple.^{1,2} In connection with our investigations on the ligand substitution³ and electron transfer reactions of substituted pentacyanoruthenate(II) complexes, electrochemical and kinetic studies on the redox reactions of the $\text{Ru}(\text{CN})_6^{4-/3-}$ couple have been carried out. The reduction potential of the $\text{Ru}(\text{CN})_6^{3-}$ ion is about 0.5 V higher than the value for $\text{Fe}(\text{CN})_6^{3-}$, while the cyclic voltammograms exhibit similar electroprotic phenomena (Figure 1). The kinetics of the reductions of $\text{Ru}(\text{CN})_6^{3-}$ (prepared⁴ by the oxidation of $\text{Ru}(\text{CN})_6^{3-}$ with $\text{Ce}(\text{IV})$) using ascorbic acid and a series of 1,2- and 1,4-dihydroxybenzenes (H_2Q) were studied in aqueous perchlorate media. The observed pH/rate dependence is attributed to pathways involving H_2Q (k_1) and the anion HQ^- (k_2).

$$-d[\text{Ru}(\text{CN})_6]^{3-}/dt = (k_1 + k_2 K_a / [\text{H}^+]) [\text{Ru}(\text{CN})_6]^{3-} [\text{H}_2\text{Q}]$$

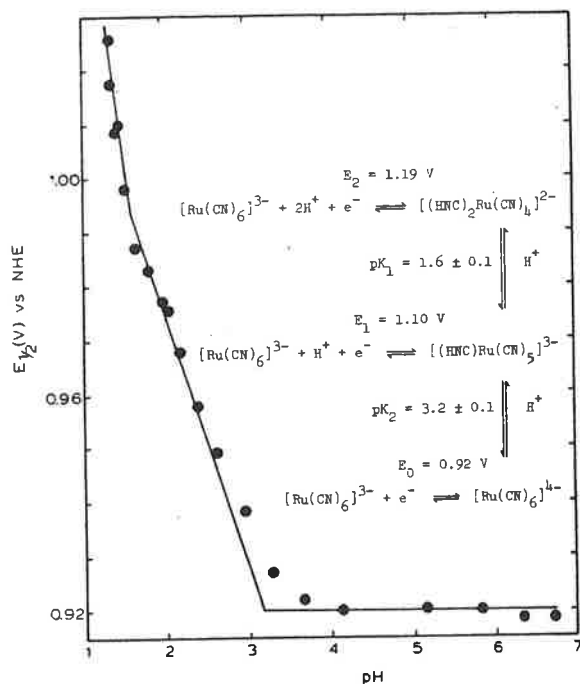


Figure 1. pH dependence of half-wave potentials for the $\text{Ru}(\text{CN})_6^{3-/4-}$ couple at 25.0°C ($I = 0.10 \text{ M}$).

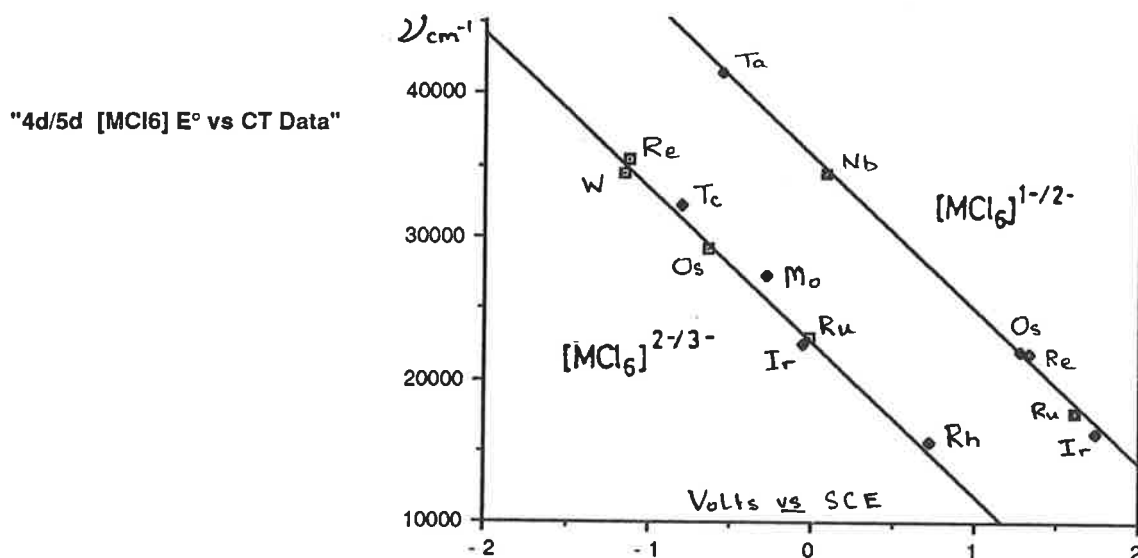
The kinetics of the reductions of $\text{Ru}(\text{CN})_6^{3-}$ with I^- , IrCl_6^{3-} , and NO_2^- and the oxidations of the $\text{Ru}(\text{CN})_6^{4-}$ ion by $\text{CoW}_{12}\text{O}_{40}^{5-}$ and IrCl_6^{3-} have also been studied as a function of H^+ and cation concentrations in aqueous perchlorate media. The self-exchange rate constant for the $\text{Ru}(\text{CN})_6^{4-/3-}$ couple has been estimated to be $10^{5.5 \pm 0.9} \text{ M}^{-1} \text{ s}^{-1}$ (25.0°C) by an application of the Marcus theory⁵ relationship to the cross-reaction data. Direct measurements of k_{11} , from ^{13}C NMR line-broadening studies are in progress. The k_{11} value will be compared with the exchange rate constants for other low-spin d^6/d^5 couples, such as $\text{Fe}(\text{CN})_6^{4-/3-}$, $\text{Ru}(\text{NH}_3)_6^{2+/3+}$, and $\text{Ru}(\text{H}_2\text{O})_6^{2+/3+}$, and discussed in terms of the inner-sphere and solvent reorganization barriers.⁶

- (1) K. W. Hicks and G. A. Chappelle, *Inorg. Chem.*, 1980, **19**, 1623.
- (2) K. Z. Ismail, M. S. Tunuli, and S. G. Weber, *Inorg. Chem.*, 1987, **26**, 1555.
- (3) J. M. A. Hoddenbagh and D. H. Macartney, *Inorg. Chem.*, 1986, **25**, 380, 2099.
- (4) F. M. Crean and K. Schug, *Inorg. Chem.*, 1984, **23**, 853.
- (5) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155.
- (6) B. S. Brunshwig, C. Creutz, D. H. Macartney, T.-K. Sham, and N. Sutin, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 113.

Comprehensive Reconstruction of Charge Transfer Spectra from Electrochemical Data: Hexa-chlorometallates and Tris-diketonates.

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If one takes the optimistic view (as we do) that both metal [1] and ligand [2] frontier orbitals can be mapped from systematic experimental electrode potential data, then testable predictions of the optical charge-transfer band energies for a given complex must follow. The present report is devoted to meeting this challenge.

A comprehensive study of the 4d- and 5d-hexahalometallates has shown that successive reversible E° values for the redox couples [MX₆]^{z/z-1} (z=0,-1,-2,-3) follow periodic patterns [1]. The Cl→M charge transfer band positions for 14 accessible [MCl₆]¹⁻ and [MCl₆]²⁻ complexes have been mapped against the respective newly surveyed V/IV and IV/III couples. Faithful linear progressions emerge (Fig), both with gradient 1.35 eV/V, and the Cl⁻ donor orbital energy is effectively raised by a consistent 12,500 cm⁻¹ (1.5 eV) between the M(V) and M(IV) plots.

In principle, the energy of any electronic charge-transfer transition can be related to the notional 'orbital electrode potentials' of donor and acceptor orbitals [3]. For example, in electron-volts, $h\nu_{MLCT} \sim E^\circ(M/M^-) - E^\circ(L^+/L)$

We take the familiar ruthenium tris-diketonates as a demanding test-case. Remarkably, the one set of appropriate empirically determined electrode potentials leads to self-consistent assignment of the uv/vis spectra (MLCT, LMCT, and Lπ-π* bands) of [RuIII(acac)₃], and of hitherto inaccessible [RuIV(acac)₃]⁺ and [RuII(acac)₃]⁻ as well. The electrogenerated spectra (50,000 - 5,000 cm⁻¹) of these and related complexes will be presented, and the implications of this deceptively simple approach to spectral analysis examined.

1. Heath, G.A.; Moock, K.A.; Sharp, D.W.A.; Yellowlees, L.J.; J.C.S., Chem. Comm. (1985) 1503
2. Coombe, V; Heath, G.A.; Yellowlees, L.J. & MacKenzie, A.; Inorg Chem. (1984) 23, 3428
3. Lever, A.B.P., "Inorganic Electronic Spectroscopy", 2nd Ed., Elsevier, NY (1984), Chap. 9

From MX_6 to ML_6 : Stepwise Redox-induced Ligand Substitutions, Linear Progressions in Electrode Potentials, & Complementary Trends in Charge Transfer Spectra

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Stepwise electrochemically induced ligand substitution in $[\text{RuX}_6]^{2-}$ to generate $[\text{RuX}_{6-n}(\text{PhCN})_n]^z$ ($\text{X}=\text{Cl}, \text{Br}$; $n=0$ to 4) has been achieved through careful control of experimental variables. Further reactions of $\text{RuX}_2(\text{PhCN})_4$ afforded the final two complexes of the series: $[\text{RuX}(\text{PhCN})_5]^+$ and $[\text{Ru}(\text{PhCN})_6]^{2+}$ ($n=5$ and 6).

Systematic characterization of each seven-membered series by voltammetric, electrosynthetic and spectroelectrochemical methods has revealed a strict linear dependence of the reversible redox couples (Ru IV/III & Ru III/II) on the extent of halide ligation. Successive substitutions of halide by nitrile induce consistent shifts in both the $E^\circ_{\text{Ru IV/III}}$ and $E^\circ_{\text{Ru III/II}}$: $+0.59 \text{ V/X}$ and $+0.62 \text{ V/X}$ respectively. Strikingly, this empirical relationship applies regardless of halide (Cl, Br) or nitrile ($\text{PhCN}, \text{MeCN}, p\text{-tolCN}$), and a corresponding dependence applies to the related series $[\text{OsBr}_{6-n}(\text{PhCN})_n]^z$ ($+0.59/\text{Br}$ in $E^\circ_{\text{Os IV/III}}$; $n=0$ to 3).[1]

Lever has speculated on the possible complementary nature of electrochemical and charge transfer data within appropriately chosen systems.[2] We find a pattern in the charge transfer spectra complementary to the E° data within each $[\text{MX}_{6-n}(\text{RCN})_n]^z$ series. Absorption energies relating to ligand-to-metal charge transfer (LMCT) at Ru III and metal-to-ligand charge transfer (MLCT) at Ru II vary linearly with halide ligation. The shift in the absorption bands at each substitution is naturally less than that observed for the E° values due to simultaneous orderly movements in the ligand frontier orbital energies.

A comprehensive study of the 4d- and 5d-hexahalometallates has shown that successive reversible E° values for the redox couples $[\text{MX}_6]^{z/z-1}$ ($z=0, -1, -2, -3$) follow periodic patterns which can be interpreted in terms of core-charge and inter-electronic correlation terms.[3][4] The linear relationship of E° values and halide ligation in $[\text{MX}_{6-n}(\text{RCN})_n]^z$ leads to the crucial corollary that the patterns observed for the highly symmetric $[\text{MX}_6]^z$ series must also exist across the periodic table for transition metal complexes of lower symmetry.

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 3. Heath, G.A.; Moock, K.A.; Sharp, D.W.A.; Yellowlees, L.J.; *J.C.S., Chem. Comm.* (1985) 1503
 4. Brownstein, S.; Heath, G.A.; Sengupta, A.; Sharp, D.W.A.; *J.C.S., Chem. Comm.* (1983) 669

THE ELECTRONIC PROPERTIES OF TRIPLY BRIDGED DIOSMIUM & DIRUTHENIUM COMPLEXES IN SUCCESSIVE OXIDATION STATES

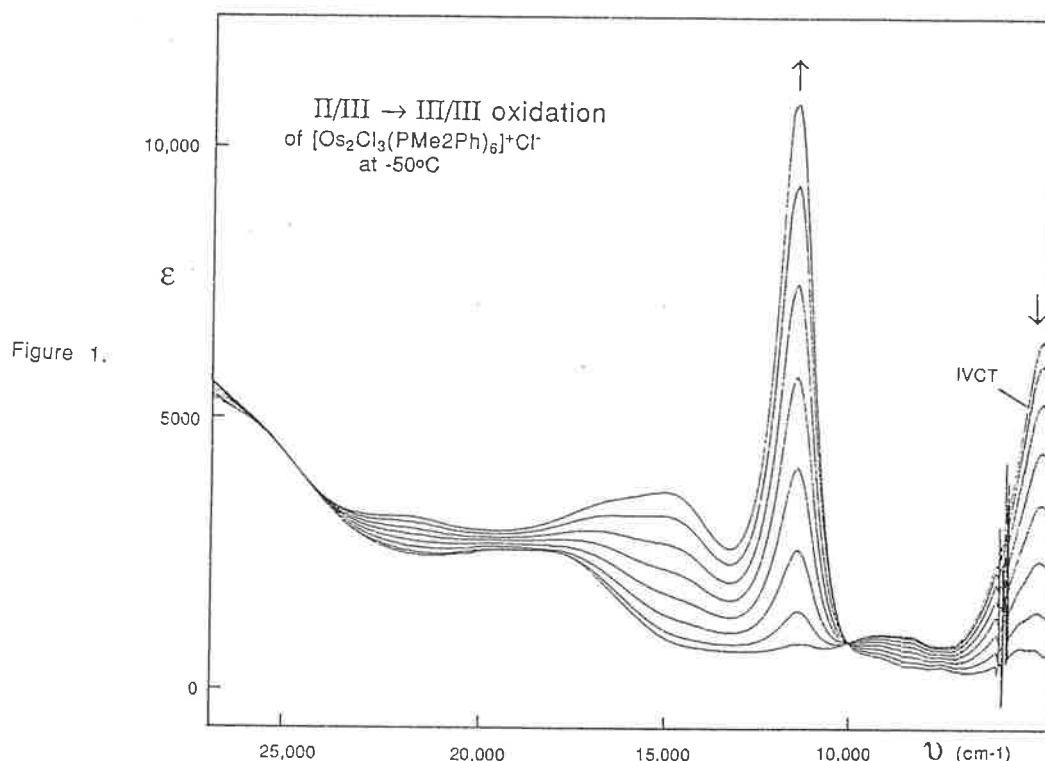
(G.A.HEATH and D.G.HUMPHREY)

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The electrochemistry and electronic spectra of the triply halide bridged binuclear species $[P_3MX_3MP_3]^+X^-$ ($M=Ru, Os$; $X=Cl^-, Br^-$; $P_3=(PMe_2\phi)_3$ or triphos) are described. Each of the dimeric complexes exhibits two reversible oxidative couples, corresponding to successive oxidations of the metal centres, i.e. $II/II \rightarrow II/III \rightarrow III/III$. The solution electronic spectra ($45,000 \rightarrow 4,000 \text{ cm}^{-1}$) of each dimer in successive oxidation states have been recorded in an optically transparent thin-layer electrode (OTTLE) cell at -50°C . This in-situ method of electrogenerating the required oxidation states provides us readily with rigorous physical data on complexes unstable to isolation.

The spectra of the II/II species are all closely related, being dominated by MLCT bands, while at the mixed valence level we observe the characteristic near-infrared IVCT transitions, i.e. $M_2^{II/III} \rightarrow M_2^{III/II}$. Interestingly, this band is little affected by bridge identity (Cl^-/Br^-), while the band maximum shifts from $8,100 \text{ cm}^{-1}$ ($Ru_2^{II/III}$) to $5,100 \text{ cm}^{-1}$ ($Os_2^{II/III}$). At the III/III level, each Os_2 complex is characterized by a remarkable strong band at $11,000 \text{ cm}^{-1}$ (Figure 1) which has no obvious counterpart in the $4d^5/4d^5$ complexes.

The parallel study of monomeric *fac*- $[Os(III)Cl_3(\text{triphos})]$ (triphos = $MeC\{CH_2P\phi_2\}_3$) has proved useful in interpreting the dimer spectra since it essentially models one metal site of the trigonally symmetric $[P_3OsX_3OsP_3]^+X^-$ complex and does not contain the near-ir band referred to above.



METAL-METAL INTERACTIONS AND MIXED VALENCY IN $[\text{Ru}_2\text{X}_9]^{n-1}$

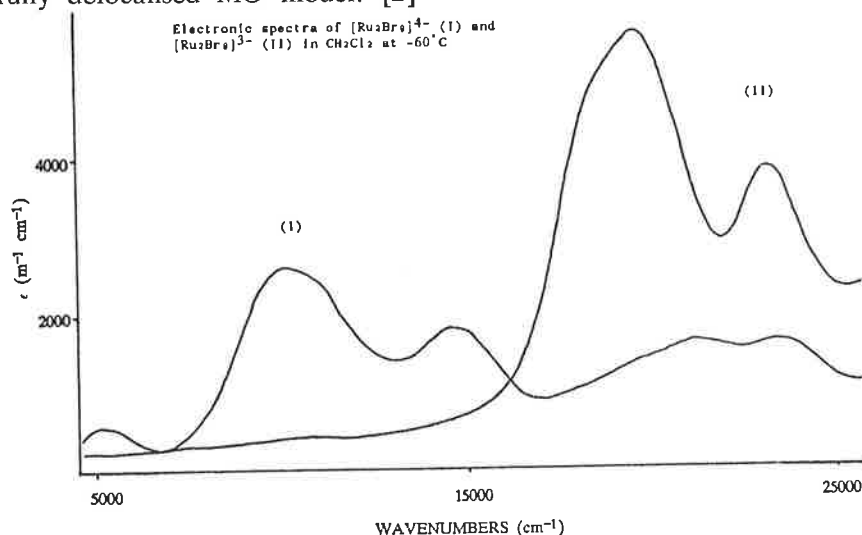
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Interactions between metals in dinuclear complexes of the type $[\text{M}_2\text{X}_9]^{n-}$, which have a highly symmetrical cofacial bioctahedral arrangement, have been extensively studied over the past two decades. One of us recently described [1] the electrochemical properties of $[\text{Ru}_2\text{Br}_9]^{n-}$ where a range of valence levels from $\text{Ru}_2^{\text{II/III}} 35\text{e}$ to $\text{Ru}_2^{\text{IV/IV}} 32\text{e}$ were found to be accessible. Using an OTTLE we measured the electronic spectra of these, and of the analogous chloro complexes at -60°C . These studies show an intriguing transition from a fully delocalised situation at the 35e level to isolated charges at the 32e level.

The 35e dimers for both $\text{X} = \text{Cl}$ and Br form intense blue solutions, reminiscent of classical "Ruthenium Blues". The low energy electronic spectra of the mixed valence $[\text{Ru}_2\text{Br}_9]^{4-}$ ion shows, Fig. 1, multiple transitions at 5300 , 10250 and 14750cm^{-1} which is considerably more complex than is found [2] in the related $[(\text{NH}_3)_3\text{RuX}_3\text{Ru}(\text{NH}_3)_3]^{2+}$ ions. These bands and the weaker features near $23,000\text{cm}^{-1}$ are assignable within the framework of a fully delocalised MO model. [2]



The electronic spectra of $[\text{Ru}_2\text{Br}_9]^{3-}$ is dominated by two intense $\text{Br} \rightarrow \text{Ru}$ CT bands near $20,000\text{cm}^{-1}$. Two extremely weak transitions are observed at 5250 and 12500cm^{-1} and these bands support the presence of a $S'=0$ ground state. Variable temperature susceptibility measurements ($4 \rightarrow 310\text{K}$) on powder samples of $(\text{TBA})_3\text{Ru}_2\text{Br}_9$ and $(\text{TBA})_3\text{Ru}_2\text{Cl}_9$ show increasing paramagnetism above 200K indicative of increasing thermal population of a low lying $S'=1$ excited state.

Electrochemical oxidation to the mixed valent 33e $\text{Ru}_2^{\text{III/IV}}$ dimer also yielded a blue solution, the spectra of which is dominated by a single intense low energy IVCT band near 10000cm^{-1} . The extent of delocalisation as gauged from the band parameter $\alpha^2 = [(4.24 \times 10^{-4})\epsilon(\Delta\nu_{1/2})]/(d^2\nu_{\text{max}}) = 6.76 \times 10^{-2}$ shows this to be essentially a trapped valence situation. Solution susceptibility measurements support a $S'=3/2$ ground state from the non-interacting $S=1$ Ru^{IV} and $S=1/2$ Ru^{III} sites. The absence of multiple IVCT bands results from the small spin-orbit coupling constant of Ru . All the other spectral features arise from CT processes to the isolated Ru centres. Further oxidation to the 32e $\text{Ru}_2^{\text{IV/IV}}$ dimer confirms this assignment of the band at 10000cm^{-1} .

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A Reassessment of the Electrochemical Behaviour of Transition Metal Porphyrin Complexes

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Since a classical study by Fuhrhop *et al*¹ in the early 1970s the interaction between the metal ion and the tetraaza macrocycle in metalloporphyrins has been viewed by electrochemists (with one exception!²) as a simply inductive one. In contrast π back-bonding effects have been invoked by spectroscopists to explain bathochromic shifts in the ligand-based visible absorption spectra of these complexes.³

Fuhrhop reported that for a series of metallooctaethylporphyrins (MOEP) the measured $E^{1/2}$ values for the first ligand-based reduction and the first ligand-based oxidation become less cathodic in parallel as the electronegativity (polarising power) of the metal increases. An explicit consequence of this behaviour is that ΔE^0 , the difference between E^0 (RED 1) and E^0 (OX 1), remains constant (~ 2.25 V) for both main group and transition metal complexes. This purely inductive model for metalloporphyrins of course excludes any metal π -bonding contributions in such complexes, which should differ for the HOMO and LUMO frontier orbitals.

We report here a re-examination of the redox properties of an orderly series of metalloporphyrins, spanning the progressions $3d^8$, $3d^9$, $3d^{10}$, and $3d^8$, $4d^8$, $5d^8$, in strictly non-coordinating aprotic media. The voltammetric properties of the meso-tetraphenylporphyrin (TPP) and OEP complexes of Ni, Cu, Zn, Pd and Pt have been studied in both CH_2Cl_2 (20°C) and liquid naphthalene (150°C). Each complex undergoes two one-electron reductions and two one-electron oxidations. The primary electrode products have been confirmed and characterised *in situ* by esr and uv/visible spectroscopy.

The intrinsic trends in E^0 are not as described hitherto, and demonstrate, for the first time, that π donation of electron density from the metal to the ligand may greatly affect the energy manifold of the porphinato moiety. Importantly it was found that E^0 (OX 1) and E^0 (RED 1) tend in opposite directions (with a resultant increase in ΔE) moving from $3d^8$ to $4d^8$ to $5d^8$ metals in each series. A single Fuhrhop-style inductive parameter cannot accommodate these data.

An observation of special interest is that the first oxidation of PtTPP leads to the paramagnetic Pt(III) complex rather than the macrocyclic cation radical.

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* Author to whom correspondence should be addressed.

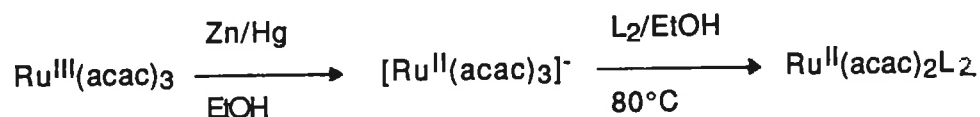
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Electrochemistry and Electronic Spectra of Ruthenium Bis(acetylacetonato) Complexes Ru(acac)₂L₂: Generation of Ruthenium (III) Alkene Complexes

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Coordinated water in the ruthenium(II) ions [Ru(NH₃)₅H₂O]²⁺ and [Ru(H₂O)₆]²⁺ is readily replaced by typical π -acceptor ligands (L¹) to give [Ru(NH₃)₅L¹]²⁺ and [Ru(H₂O)₅L¹]²⁺ (L¹ = CO, N₂, MeCN, pyridine, PR₃, alkenes and alkynes)[1]. Similarly, an acetylacetonate ligand is readily removed from the anion [Ru^{III}(acac)₃]⁻ by π -acceptor ligands to form stable complexes of the type Ru(acac)₂L₂ (L₂ = 2,2'-bipyridyl, 2MeCN [2], 1,5-cyclooctadiene):



These complexes display Ru(III)/(II) and Ru(IV)/(III) couples at room temperature, the former being completely reversible. The potentials increase as expected with decreasing σ -donor ability and increasing π -acceptor ability of L₂.

	E°(Ru(III)/II) ^a	E°(Ru(IV)/III) ^a
Ru(acac) ₃	-0.64 V	+1.13 V
Ru(acac) ₂ (bipy)	-0.02 V	+1.65 V
Ru(acac) ₂ (MeCN) ₂	+0.28 V	+1.74 V
Ru(acac) ₂ (COD)	+0.87 V	-

^a In CH₂Cl₂ with 0.5M Bu₄NClO₄ vs Ag/AgCl

The ruthenium(III) species have been electrogenerated and their electronic spectra recorded. Correlations of the electrochemical and spectroscopic data for the Ru(III) and Ru(II) complexes will be presented.

The electrogenerated species [Ru^{III}(acac)₂(COD)]⁺ and the similarly generated halide compounds [Ru^{III}Cl₅(norbornene)]²⁻ and [Ru^{III}Cl₅(COD)]²⁻ are the first examples of ruthenium(III)alkene complexes.

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STERIC CONTRIBUTIONS TO THE ENERGETICS OF ELECTRONIC PROCESSES IN TRANSITION METAL COMPLEXES.

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Intramolecular electron transfer processes such as oxidation/reduction and excitation of *d* electrons are often accompanied by large changes in metal-ligand bond lengths. Ligands which have a steric preference for the final or excited state will promote the electron transfer and thus this steric preference can be reflected in the energy change associated with the electron transfer. In order to quantify the steric contribution it is necessary to calculate the strain energies of both the 'ground' and 'excited' states. This can be done by use of molecular mechanics if models exist for both states, and the steric contribution can then be calculated as the difference between the two strain energies. Using this approach we have shown that for a series of hexaaminecobalt(III) complexes that E_0 for reduction to Co(II) varies by up to 1 V (98.5 kJ mol⁻¹) as a result of variation in the steric demands of the ligands [1].

This result has shown that in some cases strain-energy relaxation is a major contributor to the energetics of electronic reduction which needs to be taken into account and that molecular mechanics is an appropriate method for doing so. We have been extending this approach to other metals and to other electronic processes. The results obtained for Co(III)/Co(II) reductions has been confirmed by analysis of the reduction of hexaminechromium(III) complexes.

Electronic excitation of *d* electrons is also accompanied by changes in bond lengths and we have analyzed potential steric contributions to such processes. This necessitated the development of molecular mechanics models for electronically excited states which will be described. The role of steric contributions has been considered in terms of vertical and non-vertical electronic transitions.

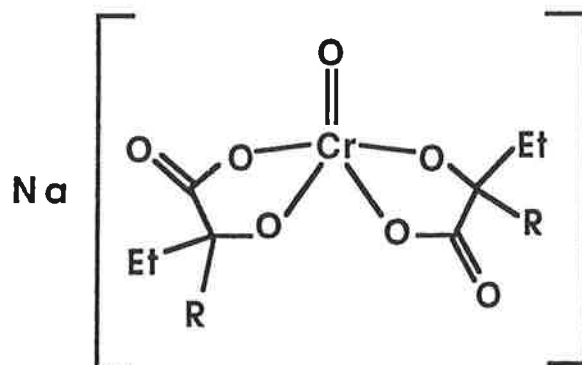
1. T.W. Hambley, *Inorg.Chem.*, 1988, 27, 2496.

THE ELECTROCHEMISTRY AND PROTONATION EQUILIBRIA OF CHROMIUM(V) COMPLEXES IN DIFFERENT SOLVENTS.

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Department of Inorganic Chemistry, The University of Sydney,
N.S.W., 2006.

Richard Bramley and Ji-Ying Ji;
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GPO Box 4, Canberra, ACT, 2601.

Complexes I and II are remarkably stable for Cr(V) complexes [1,2]. In non-aqueous solvents, such as DMSO, solutions of I are stable for a year or more at room temperature when stored in the dark. The Cr(IV) oxidation state is much less stable, but is stable enough for the quasi-reversible Cr(V)/(IV) redox couple to be studied in a range of solvents. This enabled the effects of hydrogen bonding on an anionic system to be studied (previous studies have only dealt with hydrogen bonding to cationic couples) [3,4]. A shift to negative potentials of E_f (vs Fc^+/Fc) was observed over a potential range of >1 V depending on the hydrogen-bonding donor properties and the polarity of the solvent. This variation is mainly due to hydrogen bonding between the solvent molecules and the anionic ligands of the complex, with a smaller, but statistically significant effect contributed by the solvent polarity.



(I), R = Et; (II), R = Me

The stabilities of I and II appear to depend on protection of the axial coordination site (in a square pyramid position) in the sixth position. The difference in stability between I and II due to this effect was explored further by means of crystallography and cyclic voltammetry. These results will be discussed in this poster.

Consistent with the formation of strong hydrogen bonds with the complexes, protonation/deprotonation equilibria are observed involving the alcohol groups of the ligand. These equilibria are slow on the ESR timescale. ESR, spectroscopic and electrochemical characterization of these equilibria will also be discussed.

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2. J.M. Eckert, R.J. Judd and P.A. Lay, *Inorg. Chem.*, 1987, 26, 2191.
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ELECTRONIC PROPERTIES OF BINUCLEAR COPPER COMPOUNDS.

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Faculty of Chemistry, P.Catholic University of Chile, Santiago, CHILE.

The electronic properties of binuclear Copper compounds have been studied by spectroscopical and electrochemical technics, with the final goal of getting some insight with respect to the factors that govern the stability and electronic interaction between the metal centers. Two types of systems have been studied:

a). Copper I dimers with a soft[1] bridge as S.- The first compound obtained was with 3-Mercapto-1,2-propane diol as ligand, and its cyclic voltammogram is shown in Figure 1. No reduction signal shows up if the sweep is started cathodically. By doing electrolysis at 240mV, both oxidation signals diminish in intensity after one electron has passed, while after the passage of two electrons both signals disappear completely. This behaviour is mainly interpreted as the generation (at 240mV) of a mixed-valence (MV) compound, that disproportionates during the course of the electrolysis. Theoretical X_α calculations support the behaviour observed.

In a second stage, thiol-bridged compounds were synthesized, and the structural and electronic influence of different phosphine ligands was studied. Table 1 summarizes the electrochemical results of this series of compounds, and three oxidation signals can be observed. The first one of these is assigned to the oxidation of the thiol group, the second to the Cu(I) oxidation and the third to phosphine. The results permit to conclude that the order of stability of the Cu(I) compounds is $P(Ph_3)_3 > DPPE > DPPP$.

b). Mixed valence compounds with carboxylate bridges.- A series of MV compounds with o-, m- and p-methyl benzoate (omb, mmb, pmb) were obtained, and the influence of the position of the methyl group was studied. Comparisons with respect to the fully oxidized methyl benzoate compounds and with respect to the unsubstituted benzoate MV compound were also done. Spectroscopically, all the MV compounds behave similarly, showing bands at 514nm and 870nm, that are not present in the fully oxidized complexes. The electrochemistry of this series of complexes is characterized by an oxidation assigned to $MV \rightarrow Cu(II)-Cu(II)$, and two reductions ($MV \rightarrow Cu(I)-Cu(I)$ and $Cu(I)-Cu(I) \rightarrow 2Cu^0$). The corresponding Cu(II)-Cu(II) compounds show the appearance of an additional reduction and no oxidation signal, as expected. The results obtained permit to postulate that the structure of the fully oxidized compounds is similar to the one of the MV compounds, and that the stability of the MV compounds increases in the order $mmb > pmb > omb > b$.

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2. I.G.Dance, P.J.Guerney, A.D.Rae and M.L.Scudder, *Inorg.Chem.*, 1983, 22, 2883.

Cyclic voltammogram for the Cu(I)dimer.
(0.1M TEAP in DMSO, $\nu = 200mV/s$).

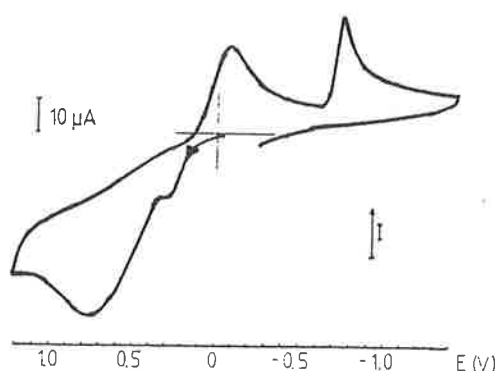


Table 1. Electrochemical data for the thiol bridged series.
(0.1M TEAP in DMF; DPPE=1,2 bis(Diphenylphosphine) ethane, DPPP=1,3-bis(Diphenylphosphine)propane).

Phosphine	Signal
PPh_3 [2]	0.34V 0.64V 1.05V
DPPE	0.35V 0.6 V 0.93V
DPPP	0.35V 0.44V 1.09V

MECHANISM OF ELECTRON TRANSFER REACTIONS OF AMINOPOLYCARBOXYLATO MONODIAMINE COBALT(III) COMPLEXES WITH ASCORBIC ACID.

C. Chattopadhyay and M.R. Mondal

Department of Chemistry, I.I.T. Powai, Bombay-400 076

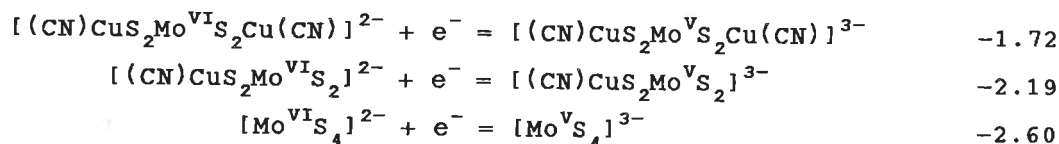
Ascorbic acid, despite a long and fascinating history, is still chemically and biologically puzzling. Its chemical redox behaviour, particularly with metal complexes, is not well resolved. The aminopolycarboxylate ligands have donor groups similar to more common amino acid residues. Hence, the electron transfer reaction at metal centre in amino-polycarboxylate environment with ascorbic acid has considerable physiological significance. The kinetics of oxidation of ascorbic acid (H_2A) to dehydroascorbic acid (A) by N,N bis-(carboxymethyl)glycinato diamine(1,2 diaminoethane and 1,3 diaminopropane)cobalt(III) complexes have been studied spectrophotometrically over the temperature range from 25.0 to 45.0 C, at an ionic strength of 0.10 mol dm^{-3} ($NaClO_4$), and over the pH range from 6.0 to 8.3. The following stoichiometric equation, $2 \text{ Co(III)} + H_2A = 2 \text{ Co(II)} + A + 2H^+$ was found to hold for both the oxidants. The formation of aminopolycarboxylatodiaminecobalt(II) complex as reduced product has been confirmed by ion exchange chromatography. The formation of ascorbate radical anion($A^{\cdot-}$) during the course of reaction has been inferred on the basis of spectral analysis. The observed first-order rate constants (k_{obs}) were found to increase linearly with initial ascorbic acid concentration. The second order rate constants, $k_{obs}/[H_2A]_0$ increased with a decrease in the acidity of the experimental solution. The complexes were reduced by both HA^- (k_1 path) and A^{2-} (k_2 path) ions. The second order rate constants at 25.0 C are ($k_1 = 2.82 \pm 0.05 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and ($k_2 = 0.71 \pm 0.2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the $[Co(NTA)tn]$ complex and ($k_1 = 0.71 \pm 0.06 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and ($k_2 = 0.46 \pm 0.1 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the $[Co(NTA)en]$ complex. The relative contributions of these two paths are related to the reduction potential of ascorbate ions. As the cobalt(III) complexes are substitutionally inert, the electron transfer reaction is considered to occur through an outer-sphere activated complex.

INTERCONVERSION OF CYANOCOPPERTHIOMOLYBDATE ANIONS OCCURS UPON REDUCTION.

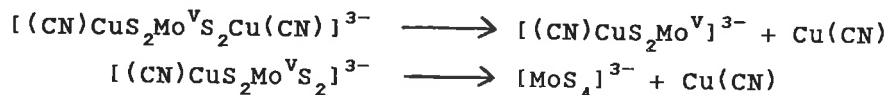
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The following couples are electrochemically reversible at scan rates ≥ 500 mV at glassy carbon electrodes in MeCN [1]:

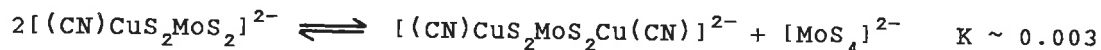


On longer timescales, the reduced species are unstable to dissociation:-



The reduced dissociation products appear in solution at potentials at which they are immediately oxidised. Consequently, the oxidised tri-, bi- and mono-nuclear thiomolybdate anions interconvert upon reduction in a most interesting way.

The simple behaviour described above is complicated by the presence of the following equilibrium:-



and the influence of redox cross-reactions.

1. $E_{1/2}$ quoted relative to SCE; electrolyte, 0.1 M Bu_4NBF_4 .

SYNTHESIS AND CHARACTERIZATION OF A FAMILY OF PARAMAGNETIC σ -ACETYLIDE IRON(II) AND IRON(I) COMPLEXES

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We recently discovered that the σ -acetylide iron(II) complexes $[(PP_3)Fe(C\equiv C-R)]BPh_4$ [$PP_3 = P(CH_2CH_2PPh_2)_3$; $R = Ph, n-C_3H_7, n-C_5H_{11}, SiMe_3$] are excellent catalyst precursors for the selective reduction of 1-alkynes to the corresponding alkenes [1]. Herein we report a detailed study of the physicochemical properties of this family of paramagnetic organometallics [these iron(II) complexes exhibit magnetic moments corresponding to two unpaired spins (μ_{eff} ranging from 3.28 to 3.42 B.M.)]. The molecular frame of these complexes, prepared according to reaction (1), is shown in the PLUTO drawing reported in Figure 1, which refers to $[(PP_3)Fe(C\equiv C-Ph)]^+$.

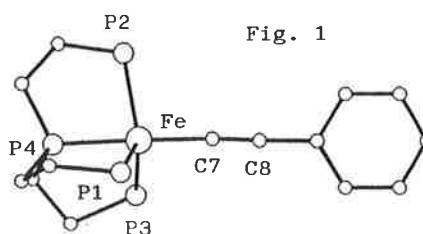
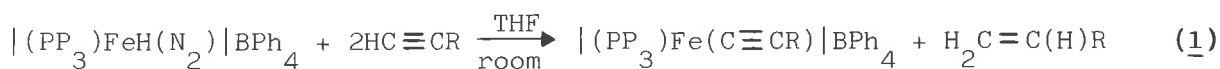


Fig. 1



Electrochemistry of the σ -acetylide complexes in nonaqueous solvents has shown that they undergo one-electron reduction to the corresponding iron(I) species $(PP_3)Fe(C\equiv CR)$. As an example Figure 2 shows the cyclic voltammetric response exhibited by $[(PP_3)Fe(CC-C_5H_{11})]^+$ in tetrahydrofuran solution (a), as well as the X-band EPR spectrum (recorded at 240 °K) of the electrogenerated neutral species $(PP_3)Fe(CC-C_5H_{11})$ (b).

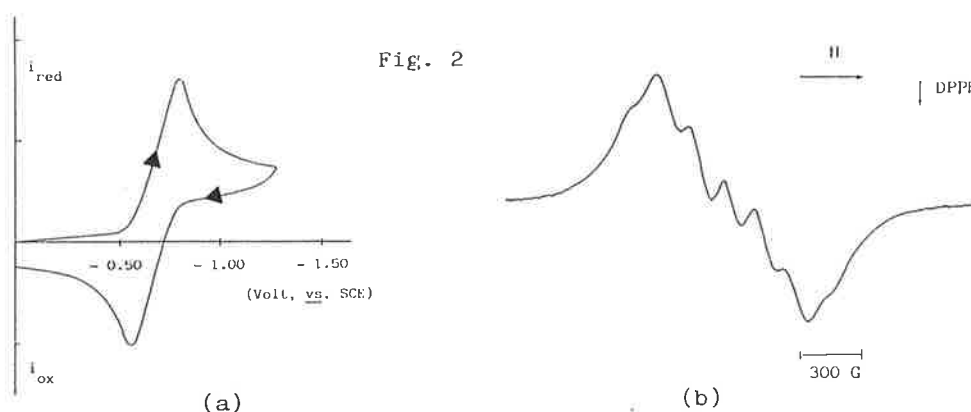


Fig. 2

The spectrum puts in evidence a well-resolved lineshape showing a superhyperfine splitting due to coupling of the unpaired electron $[Fe(I)]$ with the four phosphorus atoms of the tripodal ligand.

Studies are in progress to characterize crystallographically the iron(I) complexes in order to evaluate the stereochemistry of the iron(II)/(I) redox change.

STRUCTURAL REORGANIZATIONS ACCOMPANYING THE NICKEL(II)/(I) REDOX CHANGE IN NICKEL COMPLEXES WITH TRIPODAL LIGANDS

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We present here structural redox/relationships in nickel(II) complexes with tridentate $|\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3|$ and tetradentate $|\text{NP}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3|$; $\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$; $\text{NAS}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{AsPh}_2)_3|$ tripodal ligands of general formula $|(\text{tripod})\text{NiX}|^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

As shown in Figure 1 for $|(\text{triphos})\text{NiI}|^+$, the tetrahedral complexes $|(\text{triphos})\text{NiX}|^+$ undergo a quasireversible one-electron reduction at potentials unusually high for the Ni(II)/Ni(I) couple ($\text{X} = \text{I}$, $E^\circ' = -0.05 \text{ V}$; in CH_2Cl_2 solution, vs. S.C.E.). The most significant variation of the tetrahedral assembly, upon one-electron reduction, involves weakening of the Ni-I bond (from 2.41 \AA to 2.55 \AA), while the Ni-P bonds remain nearly unchanged (from a mean value of 2.24 \AA to 2.22 \AA) [1,2].

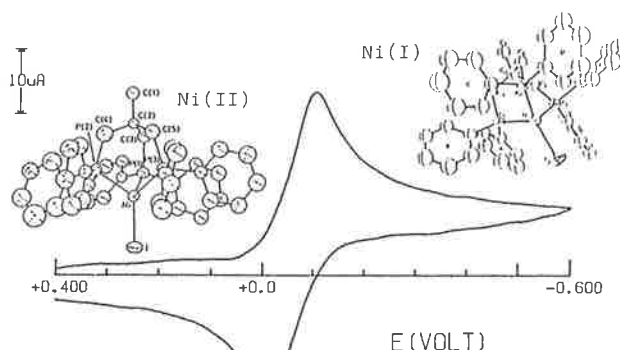


Fig. 1

A wider structural/redox relationship holds as far as the pentadentate $|(\text{NP}_3)\text{NiX}|^+$ complexes are concerned. As shown in Figure 2 for $|(\text{NP}_3)\text{NiI}|^+$, access to nickel(I) is slightly more difficult ($E^\circ' = -0.22 \text{ V}$, in CH_2Cl_2 solution). Reorganization from the regular trigonal-bipyramidal nickel(II) geometry to the distorted trigonal-bipyramidal nickel(I) geometry is again accompanied by a marked elongation of the Ni-I bond (from 2.71 \AA to 3.02 \AA), but significant bond weakening also occurs in the Ni-P bonds of the trigonal plane (from 2.22 \AA to 2.27 \AA), as well as in the axial Ni-N bond (from 2.13 \AA to 2.26 \AA) [3, 4].

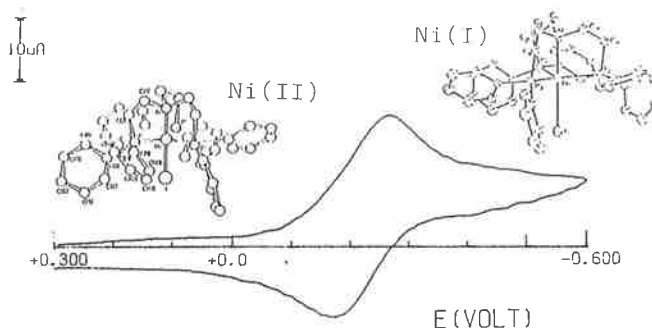


Fig. 2

X-ray investigations are in progress to understand whether structural features are responsible for the propensity of $|(\text{PP}_3)\text{NiX}|^+$ complexes to undergo irreversible single-stepped nickel(II)/(0) reduction.

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4. P.Dapporto and L.Sacconi, *Inorg.Chim.Acta*, **39** (1980) 61.

Synthesis and properties of dinuclear ruthenium/osmium compounds with triazole ligands.

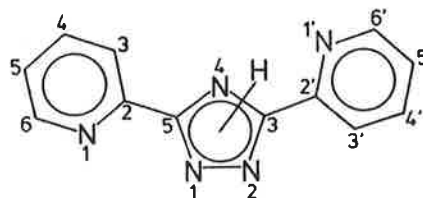
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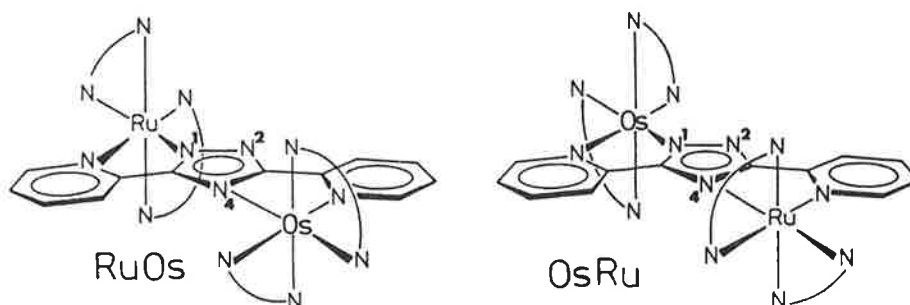
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A number of mononuclear and dinuclear $\text{Ru}(\text{bipy})_2$ and $\text{Os}(\text{bipy})_2$ complexes with bpt will be discussed (Hbpt=3,5-bis-(pyridin-2-yl)-1,2,4-triazole; see figure).

NMR spectroscopy and X-ray crystallography revealed [1] that for the mononuclear compounds, the metal centers are bound via N1 of the triazole ring (and N1 of the pyridine ring), while for the dinuclear systems the metal ions are coordinated via N1 and N4 of the triazole ligand (and via the two pyridine rings). The asymmetric coordination geometry induces a large splitting in oxidation potentials of the ruthenium dimer.



The isomeric mixed-metal ruthenium-osmium dimers with formula $\text{RuOs}(\text{bipy})_4(\text{bpt})(\text{anion})_3$ (anion = PF_6^- , CF_3SO_3^-) show different electrochemical properties, again caused by the asymmetric triazole ligand (see below).



Finally, some photophysical and spectroscopic properties of the ruthenium mononuclear and dinuclear ruthenium compounds will be discussed.

Acknowledgement

The authors wish to thank Johnson & Matthey (Reading, UK) for their generous loan of RuCl_3 .

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Reduction of Coordinated Molecules in Heteroleptic Polypyridine Ru-Complexes

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Following extensive electrochemical and photochemical studies of tris-diimine Ru-complexes, heteroleptic polypyridine complexes have attracted interest and investigations of various sets of complexes have been started. The main goal of these studies is either the estimation of electron localization accompanying reduction processes or determination of redox potentials related to the redox properties of excited states and their structural tuning. Whereas the latter problem is mainly straightforward, the estimation of electron localization is not always unambiguous. In all cases investigated up to now the general rules [1] regarding the number of redox states in the series and their general pattern hold fully. However, the differences in position of redox potentials indicate a rather complicated dependence upon the nature of individual ligands.

By detailed analysis of existing data it can be stated that

1) orbital energy of the most positively reduced ligand L' depends in most cases only slightly upon the nature of the fragment to which it is bonded

2) redox potentials of more negatively reducible ligand L depend

upon the orbital energy of ligand L bonded to the fragment in which L' is already reduced, i.e. overall charge of the fragment and detailed charge distribution in $(L')^-$ is to be taken into account

upon the interligand $(L-L')$ exchange term, representing the influence of electron localized on L' upon the electron incoming onto L ,

i.e. the reduction of L in $RuL'L_2^n$ might differ considerably from that of the homoleptic complex.

3) intraligand $(L-L)$ exchange terms increase for reduction sequence $L'L \rightarrow L'L$, i.e. for first reduction of L interposed between first and second reduction of L' and decrease for reduction sequence $L'L' \rightarrow L$, i.e. for full reduction of L' before the first of L .

Taking the above factors into consideration it is possible to analyze genetic diagrams, relating the reductions of free ligands with those of their homoleptic and heteroleptic complexes, and to estimate the localization of electrons. However, in cases when the reduction of free ligands, i.e. their redox orbital energies, are very close the problem of localization becomes more intricate not only theoretically but also experimentally as in these cases the spectra of ligands L and L' and of their mono- or dianions are mostly very similar.

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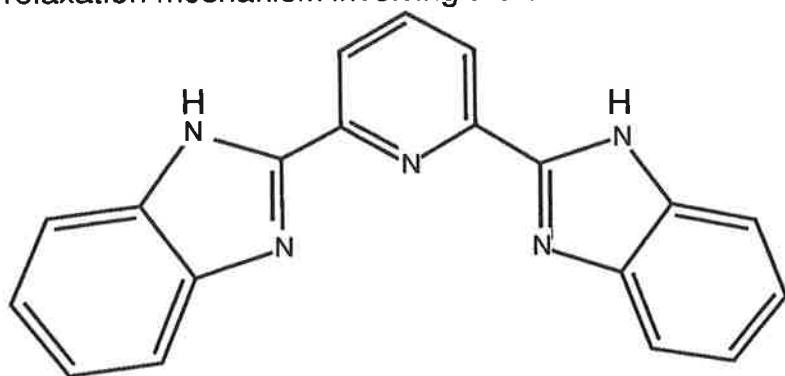
Rev. de Chim. minérale, 1983, 20, 612.

RUTHENIUM CHELATES OF 2,6-BIS(BENZIMIDAZOL-2'-YL)PYRIDINE AND RELATED BENZIMIDAZOLYL- AND PYRIDYL-LIGANDS: ENERGY TRANSFER, AND SOLVENT EFFECTS ON ELECTRON TRANSFER PROPERTIES.

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Ruthenium(II) complexes of several tridentate and bidentate benzimidazole- and pyridine-derived ligands have been prepared, including mixed-ligand tris-chelates of some substituted 1:10-phenanthrolines. ^1H -nmr served well for their characterization. The compounds undergo reversible oxidation and reductions in nonaqueous media, the nitrophenanthroline complexes having several redox processes detectable by cyclic voltammetry. Similarly to the corresponding iron(II) complex¹, the unsubstituted bis(benzimidazol-2-yl)pyridine [*below*] complex of ruthenium(II), $[\text{Ru}(\text{H}_2\text{Bzimpy})_2]^{2+}$ acts as a weak Brønsted-Lowry acid in solution, being titratable by alkoxide ion. The majority of the complexes exhibit luminescence emission *via* excitation into the MLCT and/or $\pi\text{-}\pi^*$ bands. A notable exception is $[\text{Ru}(\text{H}_2\text{Bzimpy})_2]^{2+}$, for which the low quantum yield is attributed to a relaxation mechanism involving the benzimidazole NH-protons.



Additionally, the redox chemistry of $\text{Ru}(\text{Bipy})_3^{2+}$ was studied in a variety of solvents. The results suggest that solvent polarity is a more important determinant of the solvent dependence of $E_{1/2}$ than are solvent donor or acceptor properties, though high dielectric solvents can actually react with the $[\text{Ru}(\text{bipy})_3]^{1+}$ anion (*via* an $\text{E}_\text{r}\text{C}_\text{i}$ mechanism). The effect on redox potential due to the dielectric constant of the medium surrounding a metalloprotein redox center is discussed in light of these results, and comment is made on the "ferrocene convention" for estimating the solvent dependences of the $E_{1/2}$ values of metal complexes.

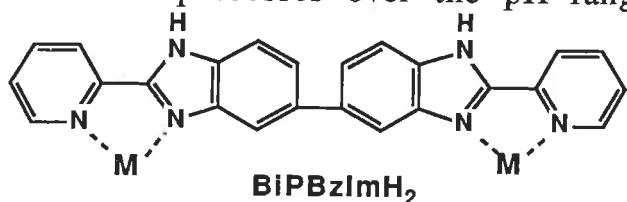
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PREPARATION AND ACID-BASE PROPERTIES OF BINUCLEAR RUTHENIUM AND OSMIUM COMPLEXES BRIDGED BY BIS-2,2'-(2-PYRIDYL)-BIBENZIMIDAZOLE.

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Many types of bridging ligand have been utilized for preparing Ru and Os binuclear complexes. The majority of the bridging ligands are π -acceptors, however, the π -donor bridging ligands are relatively sparse. Recently, we reported that 2,2'-bibenzimidazolate acts as a π -donor bridging ligand in the Ru and Os binuclear complexes.[1] In the present paper, we have extended investigations to synthesize a new bidentate bridging ligand, bis-2,2'-(2-pyridyl)-6,6'-bibenzimidazole(BiPBzImH₂). A series of Ru and Os binuclear complexes, $[M(L)_2(BiPBzImH_2)M(L)_2]^{4+}$ (M = Ru and/or Os)(1), was prepared by the reaction of $M(L)_2Cl_2$ (L = 2,2'-bipyridine(bpy) or 1,10-phenanthroline(phen)) with BiPBzImH₂. The binuclear complex 1 shows the pH dependence on the absorption spectra and oxidation potentials for the M(II)/M(III) couple, which is attributed to acid-base properties on the bridging BiPBzImH₂ moiety. Two stepwise acid-base equilibria are present, and the values of pK_{a1} and pK_{a2} obtained from the spectrophotometric titration are 5.61 and 7.12 for the complex 1(M= Ru(II); L= bpy). Electrochemical measurements (CV and DPV) of the homometallic binuclear complex 1 in CH₃CN/buffer(1:1 v/v) show two closely spaced one-electron oxidation processes over the pH ranges 0-12.



The potential difference between the first and second couple depends on the pH value of solution(50-100 mV).

The pK_a values for different oxidation states could be inferred from the oxidation potential, E_{1/2}, vs pH plots. The pK_a values for 1(M= Ru; L= bpy) are 1.4 and 6.7 for the mixed-valence Ru(II)-Ru(III) state, and 1.0 and 2.0 for Ru(III)-Ru(III) state, respectively. Spectroelectrochemistry in CH₃CN exhibits a very weak intervalence band at 1320 nm for the protonated form of 1(M= Ru; L= bpy). On the other hand, a relatively strong intervalence band at 1650 nm is observed for the deprotonated form of 1(M= Ru; L= bpy). These results indicate the electronic interaction between two sites can be switched by protonation.

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Studies of the Oxidative Processes for Mercury (II) Dithiocarbamate Complexes at Mercury and Platinum Electrodes

A. M. Bond¹, R. Colton², B.F. Hoskins², K. McGregor³ and E.R.T. Tiekink⁴.

Contribution from: (1) The Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria, 3217; (2) Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052; (3) Department of Chemistry, Monash University, Clayton, Victoria, 3168 and (4) Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia, 5001.

Extensive electrochemical studies for the mercury (II) diethyldithiocarbamate system, $\text{Hg}(\text{Et}_2\text{dtc})_2$, have demonstrated that the unusual polymeric species $[\text{Hg}_3(\text{Et}_2\text{dtc})_4]^{2+}$ is produced upon oxidative controlled potential electrolysis of $\text{Hg}(\text{Et}_2\text{dtc})_2$ at either mercury or platinum electrodes [1]. Attempts to isolate this mercury-rich trimeric species resulted in the unexpected product $[\text{Hg}_5(\text{Et}_2\text{dtc})_8][\text{ClO}_4]_2$. Recently, the oxidative processes for several different mercury dithiocarbamate complexes, $\text{Hg}(\text{Bz}_2\text{dtc})_2$ and $\text{Hg}(\text{pipdtc})_2$, have been examined to determine the effect, if any, of the nature of the R group of the ligand on the products of oxidation.

Oxidative controlled potential electrolysis of 5×10^{-4} M $\text{Hg}(\text{Bz}_2\text{dtc})_2$ or $\text{Hg}(\text{pipdtc})_2$ in dichloromethane (0.1M NBu_4ClO_4) at mercury produce solutions which on the basis of extensive electrochemical studies are shown to contain $[\text{Hg}_3(\text{Bz}_2\text{dtc})_4]^{2+}$ and $[\text{Hg}_2(\text{pipdtc})_3]^+$ respectively. The mercury-rich dibenzyl- and piperidylthiocarbamate species may also be generated via interaction of the appropriate mercury (II) dithiocarbamate with mercury (I) perchlorate. Variable temperature mercury-199 and chlorine-35 NMR studies have been used to investigate the nature of the mercury-rich $[\text{Hg}_3(\text{R}_2\text{dtc})_4]^{2+}$ ($\text{R} = \text{Et}, \text{Bz}$) and $[\text{Hg}_2(\text{pipdtc})_3]^+$ species in solution. Oxidative controlled potential electrolysis at platinum for $\text{Hg}(\text{Bz}_2\text{dtc})_2$ and $\text{Hg}(\text{pipdtc})_2$ produce solutions containing the same $[\text{Hg}_3(\text{Bz}_2\text{dtc})_4]^{2+}$ and $[\text{Hg}_2(\text{pipdtc})_3]^+$ species generated by electrolysis at mercury, but in this case they are believed to be formed by a mercury (III) intermediate.

The pentamercury species $[\text{Hg}_5(\text{Bz}_2\text{dtc})_8][\text{ClO}_4]_2$ is isolated from solutions of $[\text{Hg}_3(\text{Bz}_2\text{dtc})_4]^{2+}$, similar to the behaviour observed for the analogous diethyldithiocarbamate system. Evaporation of solutions of $[\text{Hg}_2(\text{pipdtc})_3]^+$ produces crystalline $[\text{Hg}_2(\text{pipdtc})_3][\text{ClO}_4]$, which has been characterized by an X-ray crystallographic study.

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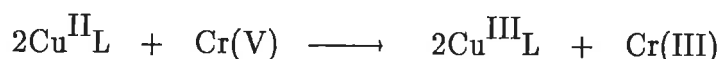
INNER-SPHERE ELECTRON TRANSFER BETWEEN CHROMIUM(V) AND COPPER(II) COMPLEXES

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We have previously reported that the complex $\text{cis-Cr}^{\text{III}}(\text{phen})_2(\text{H}_2\text{O})_2^{3+}$ (phen = 1,10-phenanthroline) is readily oxidized by PbO_2 or iodosobenzene (PhIO) to give the dioxo-bis(1,10-phenanthroline)chromium(V) [1]. The chromium(V) complex is stable in aqueous solutions for hours.

The chromium(V) complex was found to react readily with N,N'-ethylenebis-(isonitrosoacetylacetoneimine)copper(II) ($\text{Cu}^{\text{II}}\text{L}$) in acidic solutions to give the blue copper(III) complex [2]. The stoichiometry of the reaction is consistent with eq. 1.

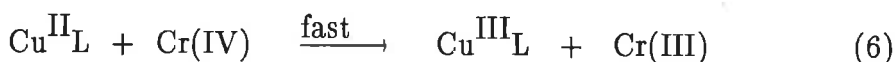
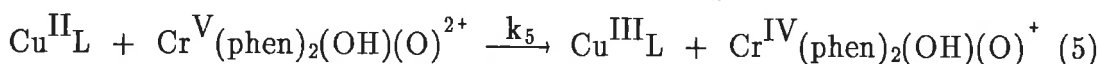
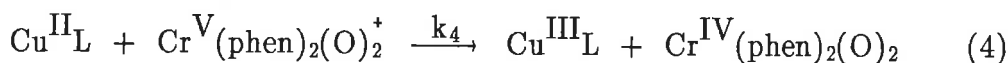
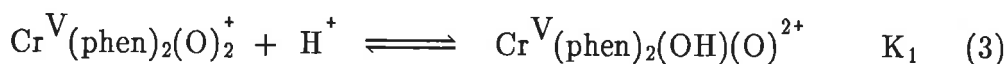


Kinetic studies showed that the reaction is of the first-order in each reactant at a constant pH. The second-order rate constant, k_2 , varies with $[\text{H}^+]$ according to eq. 2.

$$k_2 = k_2' + k_3[\text{H}^+]$$

Stopped-flow traces showed that the formation of Cu(III) was preceded by a faster step which was accompanied by a decrease in absorbance. This indicated that a substitution process precedes electron transfer.

A mechanism consistent with the kinetics is given in eqs. 3-6.



Both the protonated and unprotonated forms of the Cr(V) complex may bridge the $\text{Cu}^{\text{II}}\text{L}$ complex via an oxo ligand prior to electron transfer.

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THE ELECTROCHEMICAL PREPARATION OF METAL COMPLEXES

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The poster describes a direct electrochemical synthetic method for the preparation of inorganic and organometallic compounds. In each case the metal was used as the sacrificial anode of a simple cell and oxidized in an organic solution of a ligand or ligand precursor to yield an array of complexes. In some cases compounds have been obtained which have been difficult or impossible to prepared by other routes.

Examples are illustrated on the poster for the following types of preparations:

(a) The preparation of dithiolates is exemplified by the oxidation of metals in an organic solution of ethyl dioxanthogen or tetramethylthiuram disulphide to produce metal xanthates and dithiocarbamates. Results are reported for the dithiolates of a number of transition metals as well as a variety of main group metals.

(b) The one-step oxidation of cobalt in an acetonitrile-hydrohalic acid solution of neutral mono and di-phosphines produced complexes of the types $(R_3PH)_2(CoX_4)$ and $(HPPH_2(CH_3)_2PPh_2H)(CoX_4)$ as blue crystalline solids. Large isotropic NMR shifts were observed for these complexes.

(c) The synthesis of neutral transition metal complexes of imidazole, pyrazole and their derivatives was accomplished at room temperature by the oxidation of the metal in acetone solution of the diazole. This method of preparation is a significant advance over methods proposed so far. The temperature dependence of the magnetic susceptibility of the complexes of cobalt and of copper are interpreted in terms of a polynuclear arrangement in linear chains.

(d) Neutral transition metal chelates of pyridine-2-carbaldehyde pyridine-2'-ylhydrazone and related ligands were produced by oxidizing the metal in an acetone solution of the hydrazone. The magnetic data of the octahedral cobalt chelates fitted well to a known model expression for the susceptibility of a $E_{2g} - T_{1g}$ cross-over system.

(e) Metallocenes, polymethylmetallocenes, metal dimethylpentadienyls and metal phenyl phenylacetylides were synthesized by the oxidation of the metal in an appropriate organic solvent phase. The C-H bond is cleaved by electrical means rather than by alkali.

Some of this work has been published:

- A.T. Casey and A.M. Vecchio: Trans. Metal Chem., 1986, 11 366.
Inorg. Chim Acta, 1987, 131, 191.
Trans. Metal Chem., 1987, 12, 295.
J. Coord. Chem., 1988, 16, 375.

MULTIELEMENT DETECTION FOR HPLC SEPARATION OF SAMPLES FROM PATIENTS TREATED WITH GOLD DRUGS

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Chromatography, particularly HPLC, is a powerful tool for separation and identification of a variety of compounds. In many cases, element-specific detection of metals in individual chromatographic fractions is critical to the analysis. There are many situations such as analysis of biological or environmental samples in which metals are present at levels well below the detection limits for atomic absorption or atomic emission spectroscopy. We have adapted a Sciex Elan inductively coupled plasma-mass spectrometer (ICP-MS) for use as an HPLC detector. This instrument has the necessary element specificity and has detection limits for chromatography in the 5 ppb range. The Sciex instrument also has a multielement capability sampling each specific element for a few milliseconds. We have used this capability to simultaneously detect up to 4 elements in a single HPLC separation.

Our interest has been in analyzing gold containing samples from patients being treated with gold-based drugs. These drugs have been shown to be effective in the treatment of rheumatoid arthritis but little is understood about their mechanism of action or their mechanism of toxicity. The major difficulty in studying these drugs is the low level of gold found in patient fluids. Standard levels in the plasma, for example, are in the 500 ppb range. While this level is at the limit of detection of AA for gold it is well within the range of the ICP-MS for chromatography.

Using the ICP-MS as a detector, we have analyzed gold compounds in both urine and plasma samples from patients treated with the different gold drugs used. Weak anion exchange chromatography (WAX) of urine samples of an auranofin patient shows that there are three major peaks. Of particular interest is that the relative amounts of gold in these peaks changes as the patient continues through gold therapy. Identification of these gold components is currently underway. Analysis of plasma samples demonstrates that, independent of drug used, the bulk of the gold is bound to albumin. WAX chromatography reveals specific differences in minor components that appear to be related to the source of the gold. For analysis of plasma samples, the multielement capability of the ICP-MS has been particularly important. The drugs appear to differ in the effect they each have on Cu containing species in the plasma.

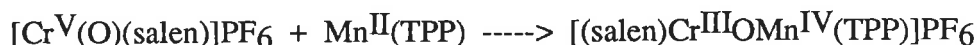
A significant problem for the use of the ICP-MS for reverse phase chromatography is that organic solvents can cause carbon accumulation in the instrument. The Sciex machine is equipped with an "organics kit" which is very useful for isocratic separations. For gradients, however, the changing organic concentration causes significant problems due to matrix effects. We have injected a series of standard slugs of a 100 ppb gold sample into a flowing gradient stream, 100% aqueous to 100% methanol. Comparing peak heights of individual injections, the relative standard deviation is up to 42%. This makes quantitation extremely difficult. We have developed an approach which corrects this problem by using a second set of HPLC pumps to build a reciprocal gradient. This is mixed with the HPLC effluent to create a constant composition flow into the ICP-MS. Using this method we obtain standard deviations of 5% for samples injected as above. Thus, the ICP-MS can also be used as an element specific detector for reverse phase separations.

SYNTHESIS OF MONOMERIC AND DIMERIC OXO AND ORGANO-IMIDO COMPLEXES OF CHROMIUM

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The synthesis of heterobinuclear oxo-bridged compounds of the type (porphyrin)CrOM(L) from the one electron redox reaction of CrO(porphyrin) and iron(II), manganese(II) or molybdenum(IV) complexes containing ligands such as salicylideneimine and dithiocarbamates has recently been reported [1]. A two electron redox reaction has now been found to occur between an oxochromium(V) salicylideneimine complex and manganese(II) porphyrin.

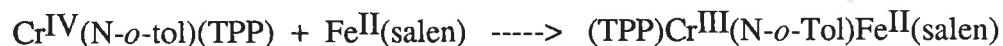


Elemental and Electron Microprobe analysis confirm the molecularity of the dimer. The μ -oxo complex has a room temperature moment of 5.2 B.M. and displays Curie-Wiess behaviour at low temperatures as expected for a Cr(d³) - Mn(d²) centre.

Similar heterobinuclear bridging by an organo-imido group has been sought by redox reactions between Cr^{IV}(NR) and Fe^{II} complexes. (Homobinuclear imido bridged species have been prepared by redox reactions [2]). The formation of Cr^{IV}(NR)(porphyrin) has been achieved by the reaction of Cr^{II}(porphyrin) and arylazides.[3]



The complexes are high spin d² systems (cf. Cr^{IV}(O)(TPP) which is low spin) and can transfer the organo-imido group to triphenylphosphine and styrene. Such organo-imido chromium complexes have been found to take part in redox reactions with metal compounds such as Fe^{II}(salen) to form products considered to be heterobinuclear μ -imido complexes.



These compounds have reduced magnetic moments and exhibit Curie-Wiess behaviour at low temperatures. Initial evidence has also been gathered for similar reactions between Cr^{IV}(NR)(TPP) and Mo^{IV}(O)(DTC)₂ and V^{IV}(O)(acac)₂.

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- [2] P.J. Nichols, G.D. Fallon and B.O. West. *Inorg. Chem.*, **1988**, 27, 2795.
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TRIAMMINE COMPLEXES OF CHROMIUM(III). SYNTHESIS AND CHARACTERIZATION OF THE TWO ISOMERIC SERIES.

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Synthesis of triammine complexes of chromium(III) with meridional configuration of the ammonia molecules have primarily been based on either thermal decomposition of higher ammines [1] or on treatment of $\text{Cr}(\text{NH}_3)_3(\text{O}_2)_2$ with strong acids such as hydrochloric acid or perchloric acid [2]. Complexes of the isomeric facial triammine series have been synthesized by treatment of chromium(III) ammine solutions with a high content of oligomers with hydrogen chloride [3]. The yields by these methods are, in our experience, moderate, and some of the products are mixtures of less well-defined species.

The procedures presented here are simple and give pure compounds in high yields of the meridional as well as of the facial series of chromium(III) triammines. The basis is that in mer- $\text{Cr}(\text{py})_3\text{F}_3$, made from $\text{CrF}_3 \cdot 9\text{H}_2\text{O}$ by treatment with pyridine [4], like in trans- $[\text{Cr}(\text{py})_4\text{F}_2]^+$ [5], the pyridine can easily be substituted by ammonia or other amine ligands and subsequently fluoride can be substituted by other acido ligands or water with or without isomerization.

Substitution with ammonia at 100°C quantitatively gives mer- $\text{Cr}(\text{NH}_3)_3\text{F}_3$. Hydrolysis of this compound with perchloric acid at room temperature nearly quantitatively gives mer- $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3](\text{ClO}_4)_3$ which can be purified for small amounts of the facial isomer via mer- $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$.

Treatment of the mer- $\text{Cr}(\text{NH}_3)_3\text{F}_3$ with triflic acid at 65°C quantitatively gives fac- $\text{Cr}(\text{NH}_3)_3(\text{O}_3\text{SCF}_3)_3$ which can be transformed to fac- $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3](\text{ClO}_4)_3$ with perchloric acid or to fac- $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ with hydrochloric acid.

Spectral, acid-base and other chemical properties of the compounds will be presented as well.

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Synthesis, Characterisation and Reactivity Studies on Transition Metal Oxo Compounds

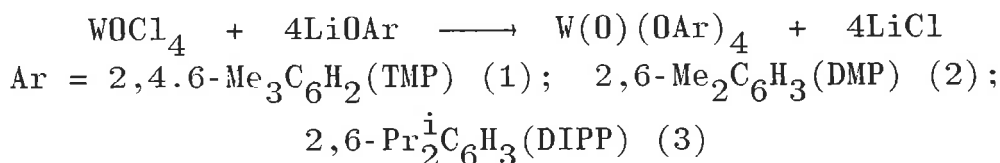
Vernon C. Gibson and Alan Shaw

Department of Chemistry, Science Laboratories, University of Durham, South Road, Durham DH1 3LE, U.K.

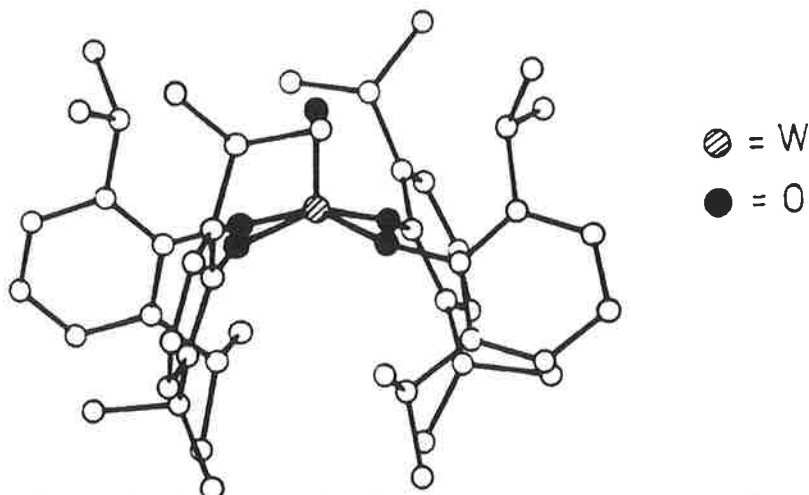
Convenient, mild syntheses of transition metal oxo compounds have been developed which exploit the reaction between metal halides and hexamethyldisiloxane, according to the general equation:



High yield preparations of a variety of base free and solvated oxyhalides of the heavier Group 5 and 6 metals have been achieved by this method,¹ including $WOCl_4$, MO_2Cl_2 ($M = Mo, W$), $WO_2Cl_2(CH_3CN)_2$, $NbOCl_3$ and $NbOCl_3L_2$ ($L = THF, CH_3CN$). These materials have been used to synthesise mononuclear oxo complexes by metathetical pathways e.g.



[3] has been shown by X-ray diffraction to possess a square based pyramidal geometry with the terminal oxo ligand occupying the axial site.



Gas phase alkylation of the terminal oxo group occurs for $W(O)(DMP)_4$ and $W(O)(TMP)_4$ but not for $W(O)(DIPP)_4$ in which access to the oxo ligand is sterically inhibited.

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PREPARATION AND STRUCTURAL CHARACTERIZATION OF
COMPLEXES OF LINEAR POLYAMINES WITH Mn(III) AND Mn(IV)

Rajumati Bhula^a, Susan Collier^a, Ward T. Robinson^b,
Richard Coll^b and David C. Weatherburn^a

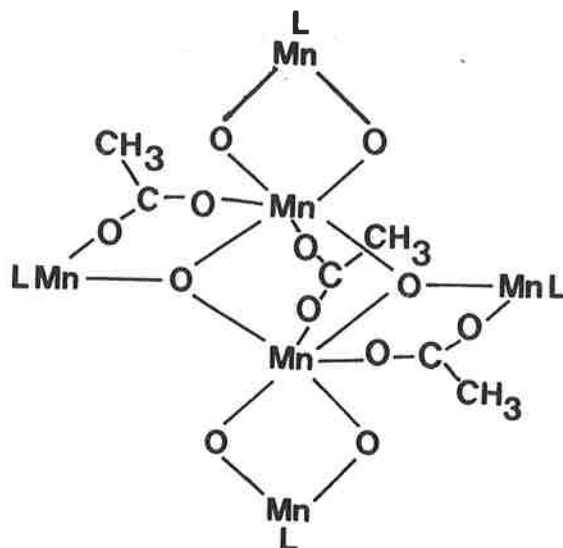
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Aerial oxidation of methanol solutions of Mn(II) carboxylates and linear polyamines such as diethylenetriamine, triethylenetetramine and 3,2,3-tet results in the formation of dark green or dark red solutions. Solid complexes may be precipitated from these solutions upon the addition of suitable precipitating anions. The solids are usually polynuclear Mn(III) or mixed valence Mn(III)/Mn(IV) complexes which are extremely difficult to fully characterize as crystals suitable for structural analysis are not easily obtained.

Details of the preparation and esr spectroscopic parameters of a wide variety of these complexes with a number of different amines and carboxylates will be described. Crystal structure determinations of two of these complexes with the ligand 3,2,3-tet will be presented. The monomeric lime green trans-bis-(*m*-iodobenzoato)(3,2,3-tet)Mn(III)(ClO₄) salt crystallizes in the monoclinic space group P2₁/c $a = 22.973$ $b = 12.029$ $c = 10.833\text{\AA}$ $\beta = 102.38^\circ$ $Z = 4$. The structure has been refined to an $R = 0.035$.

A hexanuclear mixed valence complex of formula Mn₆(3,2,3-tet)₄(μ₂-OOCCH₃)₃O₆I₅ crystallizes in the orthorhombic space group C2/c $a = 27.733$ $b = 13.663$ $c = 27.02\text{\AA}$ $\beta = 124.16^\circ$ $Z = 2$. The structure of the cation is illustrated below. This structure is of particular interest as it is to our knowledge the first polynuclear mixed valence complex of Mn to be diamagnetic.



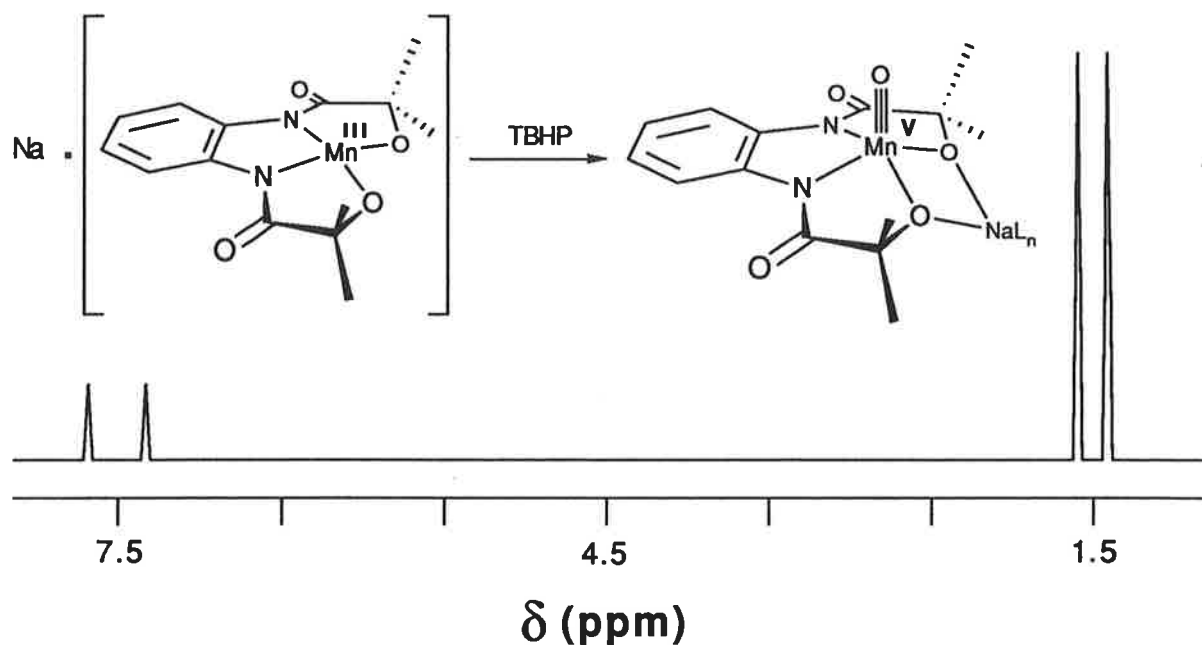
L = (3,2,3-tet)

A Manganese(V)-Oxo Complex

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Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213

The synthesis and characterization of the first stable manganese (V) monooxo complex is described. The manganyl complex has been isolated as a green crystalline diamagnetic material and characterization includes ^1H NMR and an X-ray crystal structure determination. Further characterisation by EXAFS, infrared and raman spectroscopy is underway.



IDENTIFICATION OF THE STRUCTURE OF TECHNETIUM-99M COMPLEXES IN THE CARRIER FREE STATE

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Because of its favourable physical properties, technetium-99m has been widely used in nuclear medicine for the preparation of complexes for use as diagnostic imaging agents. In these preparations, technetium concentrations are typically of the order of 10^{-8} M with the ligand concentration being several orders of magnitude greater. In order to identify the structure of these complexes, studies are often performed using the long-lived radionuclide technetium-99 at concentrations of 10^{-1} – 10^{-3} M with ligand concentrations generally at the same concentration. These results may not be directly applicable to the carrier free state.

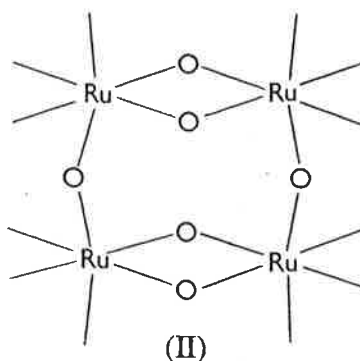
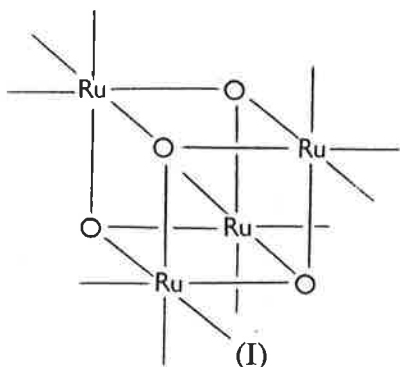
Technetium-99m complexes of dithiooxalate(dto) and maleonitriledithiolate(mnt) were prepared by ligand substitution of $^{99m}\text{TcNCl}_4^-$, dithionite reduction of $^{99m}\text{TcO}_4^-$ and ligand exchange of ^{99m}Tc -gluconate(Sn). All complexes were characterised by HPLC on a C18 column using gradient elution with a tetrabutylammonium phosphate buffer (40–85% methanol). HPLC was performed using mixtures of these complexes with structurally characterised ^{99}Tc -complexes of the same ligand. Results indicate that, at the carrier free level, labelling via $^{99m}\text{TcNCl}_4^-$ leads to the formation of $[\text{}^{99m}\text{TcN(dto)}_2]^{2-}$ and $[\text{}^{99m}\text{TcN(mnt)}_2]^{2-}$. Dithionite reduction and ligand exchange of $^{99m}\text{Tc(Sn)-gluconate}$ lead to the production of $[\text{}^{99m}\text{Tc(mnt)}_3]^{2-}$ and not of $[\text{}^{99m}\text{TcO(mnt)}_2]^-$ which would be the expected product from the results of studies with technetium-99. The product formed by dithionite reduction in the presence of dto was not identified, but it was clearly not $[\text{TcO(dto)}_2]^-$, the expected product from the results of studies with ^{99}Tc .

SOLUTION STUDIES ON AQUA IONS OF RUTHENIUM(II), (III) AND (IV)

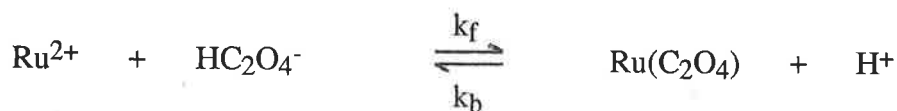
Ayyub Patel¹ and David T. Richens²

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The Ru(IV) Aqua Ion. First identified in 1950, the true solution structure for the red-brown aqua ion of Ru(IV) remains unknown although evidence from a number of sources provides support for a tetranuclear species. Following our successful use of ¹⁷O NMR to probe the structures of oligomeric aqua ions of Mo, W and Ir we have sought to characterize this diamagnetic species likewise with intriguing results. In our paper we show evidence for the tetranuclear structure following ¹⁷O NMR measurements and FAB MS characterization of a hydridotris(1-pyrazolyl)borate Ru(IV) complex. Our results provide evidence for a change in the number and type of bridging oxo group in the [Ru₄O_x] core structure from x = 4 (pH 1, μ₃-oxo) to 6 (pH 3, μ₂-oxo) with possible structures (I) and (II). Water exchange on Ru(IV)₄(aq) is fast (k = 30 s⁻¹, pH 1) and is accompanied by reversible fluctuation in the structure on warming to 60°C. Structures favoured by several workers based solely on μ-hydroxy groups can be ruled out.

**Complex Formation Studies on HexaquaRuthenium(II) and (III).**

(a) **Oxalate anation of [Ru(OH₂)₆]²⁺.** Reactions followed at 25°C with a 10 fold excess of oxalate show first order equilibration kinetics. The [H⁺] dependence suggests the following rate determining process:



Rate constants and activation parameters are in support of a dissociative interchange mechanism largely controlled by the rate of water dissociation from Ru²⁺.

(b) **Oxalate anation on [Ru(OH₂)₆]³⁺.** In the presence of excess oxalate reactions followed between 60° and 90°C proceed to completion to give [Ru(C₂O₄)₃]³⁻ with a dependence on [H⁺] suggestive of three parallel reaction paths involving Ru³⁺ with HC₂O₄⁻ and RuOH²⁺ with both H₂C₂O₄ and HC₂O₄⁻. The results are discussed in connection with similar studies performed on the aqua ions of Rh(III) and Ir(III) and with respect to the rate and mechanism of water exchange on Ru³⁺ and generally expected substitution mechanism on Ru(III). Some surprising conclusions are made.

PERIODIC TRENDS IN CHARGE DISTRIBUTION FOR TRANSITION METAL COMPLEXES CONTAINING CATECHOLATE AND SEMIQUINONE LIGANDS. SYNTHETIC, PHYSICAL, AND STEREODYNAMIC PROPERTIES OF THE TRIS(3,5-DI-TERT-BUTYLQUINONE) COMPLEXES OF RUTHENIUM AND OSMIUM.

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Tris(3,5-di-tert-butylbenzoquinone) complexes of Ru and Os have been synthesized in the interest of investigating periodic trends in charge distribution for tris(quinone) complexes of second and third row transition metals. Infrared spectra of the two complexes are similar but differ from spectra obtained on related semiquinone $[\text{Fe}(\text{DBSQ})_3]$ and catecholate $[\text{Re}(\text{DBCat})_3]$ complexes. Both complexes undergo two oxidation and two reduction reactions at similar potentials. Crystallographic characterization on the two complexes has shown that they crystallize as *trans* isomers and that they both have short M-O bond lengths, typical of complexes containing high oxidation state forms of Ru and Os. Ligand C-O bond lengths are found to be intermediate between semiquinone and catecholate values, with lengths that are more semiquinone-like for $\text{Ru}(\text{DBQ})_3$ and more catecholate-like for $\text{Os}(\text{DBQ})_3$. This subtle difference in charge distribution between the second and third row metals appears to contribute to marked differences in the stereodynamic properties of the two complexes. Both complexes are diamagnetic and show sharp NMR spectra at room temperature. Eight *t*-butyl and eight ring proton resonances are observed for $\text{Ru}(\text{DBQ})_3$ at room temperature indicating the presence of stereochemically rigid *cis* and *trans* isomers. Two *t*-butyl and two ring proton resonances are observed for $\text{Os}(\text{DBQ})_3$ at room temperature. At -85°C eight *t*-butyl and eight ring proton resonances appear as molecular rearrangement rates decrease on the NMR time scale. Analysis of the temperature dependence of the spectrum of $\text{Os}(\text{DBQ})_3$ has indicated racemization by a Bailar Twist mechanism at lower temperatures, with structural isomerization and racemization by the Ray-Dutt Twist mechanism at higher temperatures. The difference in activation energy for the two processes is estimated to be approximately 4 Kcal/mol.

STRUCTURAL STUDIES OF METAL COMPLEXES
WITH SOME MULTIDENTATE PYRIDINE N-OXIDE LIGANDS

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Australia

The *N*-oxide ligands 2-acetylpyridine 1-oxide oxime (pxo) and 2-pyridine carboxaldehyde 2'-pyridinylhydrazone 1-oxide (poph) have been shown, on the basis of spectroscopic and magnetic measurements, to function as ON and ONN donors, respectively, in their transition metal complexes [1,2]. In several cases, *N*-oxide-bridged cobalt(II) and nickel(II) complexes were identified, on the basis of the antiferromagnetic properties of the complexes.

X-ray structural studies are presented on a range of complexes of these ligands. These studies confirm ON and ONN coordination by the ligands. Both *cis*- and *trans*-dispositions of the ligand pxo are unexpectedly found in its bis-ligand $M(\text{pxo})_2X_2$ complexes. Hydrogen bonding involving the oxime hydrogen in pxo appears to be structurally important in the pxo complexes. *N*-Oxide-bridged structures involving out-of-ligand-plane bridging are described. The structures of the complexes are compared to those with other *N*-oxide ligands.

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Crystal Structure of Bis[aquabis(4-amino-3,5,6-trichloro pyridine-2- carboxylato)silver(I)] Dihydrate

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The problem that some auxin-type herbicides are difficult to crystallise for structure analysis may be overcome by preparing suitable metal complexes. This technique has been used to study the structure of 4-amino-3,5,6-trichloropicolinic acid, (Picloram or Tordon)[1,2,3,4]. In the current work, a silver(I) complex of Picloram, $[\text{Ag}_2(\text{picl})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ was prepared, and its crystal structure determined. The compound was prepared by mixing equimolar quantities of AgNO_3 and picl, Picloram (technical Tordon) as aqueous ammoniacal solutions. Loss of ammonia from the solution over a period of a few days in the dark gave pale brown crystals of the complex. *Crystal Data*: $[\text{Ag}_2(\text{picl})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $\text{C}_{12}\text{H}_{12}\text{Ag}_2\text{Cl}_6\text{N}_4\text{O}_8$, mol. wt. 768.7, triclinic, space group P-1, a 7.1197(8), b 8.924(2), c 9.493(1) Å, α 95.84(1), β 105.71(1), γ 108.68(1)°. The silver complex forms centrosymmetric dimers $[\text{Ag}_2(\text{picl})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ through bridging carboxylate oxygens [Ag-O, 2.810(2) Å]. Each silver has distorted tetrahedral coordination. The pyridine-2-carboxylate ligand chelates to the silver ion through its pyridyl nitrogen [Ag-N, 2.313(3) Å], and a carboxyl oxygen [Ag-O, 2.362(2) Å]. A water [Ow(1)] completes the coordination [Ag-O, 2.195(3) Å] with the five membered chelate ring planar [torsion angles: Ag-N(1)-C(2)-C(21), N(1)-C(2)-C(21)-O(21), C(2)-C(21)-O(21)-Ag, C(21)-O(21)-Ag-N(1), O(21)-Ag-N(1)-C(2), +5.6, -4.6, +2.0, +0.3, -3.1° respectively]. There is also a long range interaction between the silver ion and Cl(6), [Ag-Cl, 3.172(1) Å]. This structure is very different from that of silver picolinate, $[\text{Ag}(\text{picl})(\text{piclH})] \cdot \text{H}_2\text{O}$ [5]. In the latter structure, two pyridine-2-carboxylic acid groups are bound to the silver via the pyridyl nitrogens [Ag-N, 2.207(3) Å], and carboxyl oxygens [Ag-O, 2.524(4) Å] in a distorted tetrahedral arrangement.

In compounds of picloram where the picolinate ion is not complexed, the carboxylate group is synclinally related to the plane of the pyridine ring, as found in the structures of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{picl}^-)_2$ [2], and guanidinium picloramate[3]. This is also the case with the majority of compounds in which the picolinate ligand is directly bound to the metal centres. In $[\text{Mn}(\text{picl})_2 \cdot 2\text{H}_2\text{O}]$ [1], and $[\text{Cu}(\text{picl})_2(\text{pyra})_2]$ [4], (where pyra = 2-aminopyrimidine), distortion in the chelate ring is found. An exception is $[\text{Cu}(\text{picl})_2(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}]$ [4] and the current compound in which little distortion of the chelate ring is found. In the latter two examples, the metal coordination overcomes the repulsion between the carboxylate oxygen [O(22)] and the adjacent Cl atom [Cl(3)], and the ligands adopt a planar conformation. In picolinic acid hydrochloride, where no such repulsions exist a planar conformation also is found[6]. Although a number of ligating schemes appear possible with the picloramate ligand, in none of these examples is the 4-amino group involved in coordination. Thus the chelate effect due to the carboxylate oxygen and the pyridyl nitrogen are of prime importance.

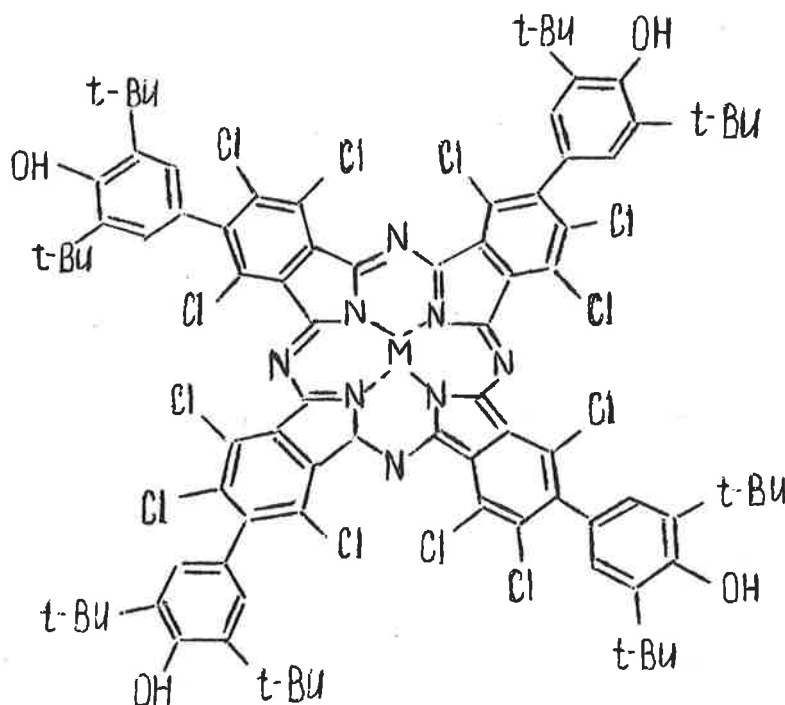
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COMPLEXES OF PLATINUM AND PALLADIUM WITH TETRASUBSTITUTED DODECAPHTALOCYANINE AS CATALYSTS FOR NITROAROMATIC COMPOUNDS HYDROGENATION

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Institute of Chemical Physics, Moscow 117977, USSR

Complexes of Pt(II) and Pd(II) with tetra(3,5-ditert butyl-4-hydroxyphenyl)dodecaphtalocyanine with the following structure:



have been synthesized.

All the complexes are paramagnetic in the solid state and in solution. A new ESR-signals have been observed due to transfer of Pt and Pd into oxidation state (I) after treatment of these complexes with $N_2H_4 \cdot H_2O$. The above complexes manifest high catalytic activity in the nitroaromatic compounds hydrogenation. Investigation of the nitrobenzene hydrogenation has shown that anion-radicals are formed in the course of the reaction. It is interesting to point out that these complexes also catalyze hydrogenation of chlorine-containing nitroaromatics without elimination of chlorine.

X-ray crystal structures of group VIII transition metal complexes with 4,7-diphenyl-1,10-phenanthroline.

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The presented investigation concerns the determination of x-ray single crystal structures of bidentate chelate complexes involving 4,7-diphenyl-1,10-phenanthroline (Bphen), $C_{24}H_{16}N_2$, and transition metals of group VIII.

Bphen is well known for its ability to form colourful complexes with numerous metal ions, and is used for quantitative analysis of especially Fe^{2+} (ref. 1). Some octahedral complexes of the form $[MeBphen_3]^{n+}$ exhibit high chemical stability as well as important interactions with the cell respiratory chain in that they strongly and reversibly inhibit the activity of mitochondrial F_1 -ATP-ase and are potent inhibitors of enzymes, catalyzing hydrolysis of pyrophosphate bonds, in general (2-4). Furthermore the racemic properties of the octahedral tris complexes can be used to perform chiral separation of right handed B-DNA helices from left handed Z-DNA helices (5), as well as site specific cleavage of Z-DNA upon photoactivation (6).

Finally, the photochemical properties of complexes involving the heavier complexing ions as Ru^{2+} , Rh^{3+} and Ir^{3+} have attracted the attention in connection with technological applications (7,8).

Complexes of the most stable oxidation numbers have been synthesized and crystallized and are subsequently being investigated by x-ray crystallography.

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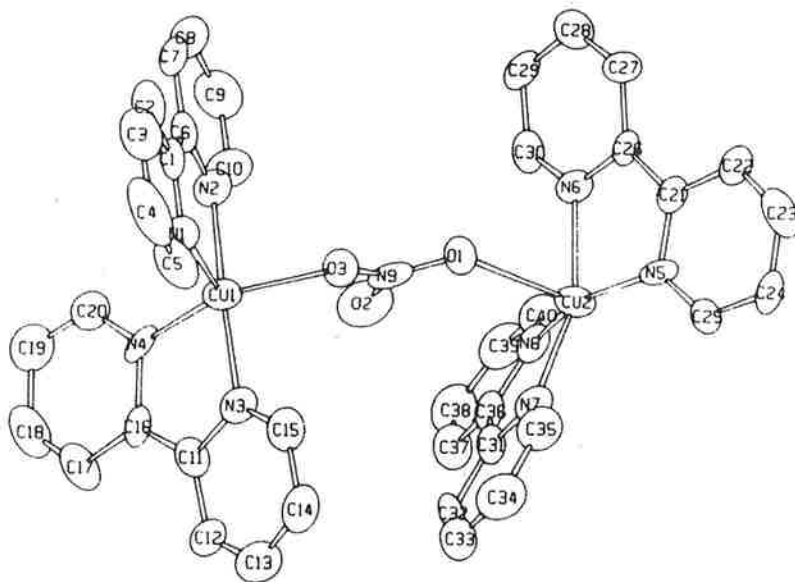
STRUCTURES OF $[\text{Cu}(\text{BIPY})_2\text{X}]\text{Y}$ COMPLEXES

Jorunn Sletten, Astrid Sørensen and Kristin Svardal,
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Complexes of the $[\text{Cu}(\text{bipy})_2\text{X}]\text{Y}$ type have been shown to possess a variety of coordination geometries. The angular changes at the copper atom have been related to the Berry Twist mechanism, and are shown to be correlated with changes in the electronic spectra. [1,2]

In the present work X-ray crystallographic structure determinations of two additional members of this group of complexes, are reported; $[\text{Cu}(\text{bipy})_2(\text{SCN})(\text{NO}_3) \cdot \text{H}_2\text{O}]$ (1) and $[(\text{Cu}(\text{bipy})_2)_2(\text{NO}_3)](\text{PF}_6)_3$ (2). Compound (1) is monomeric, SCN^- coordinating through N, and has a copper coordination-close to regular trigonal bipyramidal. Compound (2) is a dimer, bridged through the coordinating NO_3^- group. The two crystallographically independent copper atoms in (2) have distinctly different coordination geometries, - both may be described as distortions from the square pyramidal geometry. The structures will be compared with structures of related compounds.

Both crystals belong to the triclinic system, space group $P\bar{1}$, $Z = 2$. Data were collected on a CAD4 diffractometer using monochromatized $\text{MoK}\alpha$ radiation.



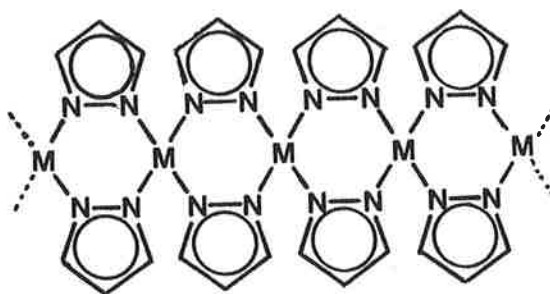
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TRANSITION-METAL PYRAZOLATE POLYMERS

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A number of pyrazolate-derived compounds of some first-row transition metals have been synthesised. Specifically, the compounds synthesised were of the general formula ML_2 , where $M = \text{Cu, Ni, or Co}$ and $L = \text{pyrazolate (pz), 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), or indazolate (indz)}$. These materials have been characterised by elemental analysis and infrared spectra. They are all thermally stable, insoluble in both polar and non-polar media, and, with the exception of Co(pz)_2 , they are air-stable. Powder magnetic susceptibilities have been measured between approximately 4.2 and 100 K for all of the compounds except Ni(pz)_2 . χ_m maxima, indicative of antiferromagnetic exchange, appear in Co(pz)_2 , Co(mpz)_2 , and Co(dmpz)_2 at 35, 28, and 9 K respectively. The copper compounds also show evidence for antiferromagnetic exchange in the form of exceptionally low χ_m values. Confirmation of exchange in these materials requires magnetic studies above 100 K and these are in progress. Modelling of the susceptibility data is required in order to elucidate the type and magnitude of exchange occurring in these metal pyrazolates. This modelling is also currently underway. The physical properties of these compounds suggest they are polymeric materials. This is in agreement with the fact that there are no known examples of endobidentate or monodentate pyrazolates of the first-row transition metals. It is suggested that these materials consist of linear chains of metal atoms bridged by pyrazolate moieties as depicted below.



A single-crystal X-ray diffraction study on the Cu(pz)_2 polymer is currently underway and should provide conclusive evidence for the structure proposed above.

SYNTHESES AND CHROMOTROPIC BEHAVIOR IN SOLUTIONS OF COPPER-(II) AND NICKEL(II)-DINUCLEAR MIXED LIGAND COMPLEXES WITH THE TETRAKETONE

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The branched tetraketone ligand (abbreviated as L) shown in Fig. 1a can form dinuclear mixed ligand complexes with N-alkylated ethylenediamine (N,N,N',N'-tetramethylethylenediamine = tmen); general formula = $M_2(L)(tmen)_2X_2 \cdot nH_2O$.

In this study, we have synthesized two tetraketones, $H_2(o-tax)$ and $H_2(p-tax)$, see Fig. 1b) derived from o- and p- α,α -dibromoxylene and an acetylacetonate ion and could obtain several complexes indicated above, where M = Cu(II) or Ni(II), $X = BPh_4^-$, ClO_4^- , or NO_3^- . Solid complexes obtained are soluble in various organic solvents and show the characteristic solvatochromism according to the donor and acceptor properties of the solvents used. These results are compared with the corresponding mononuclear mixed ligand complexes reported by us previously.¹⁾

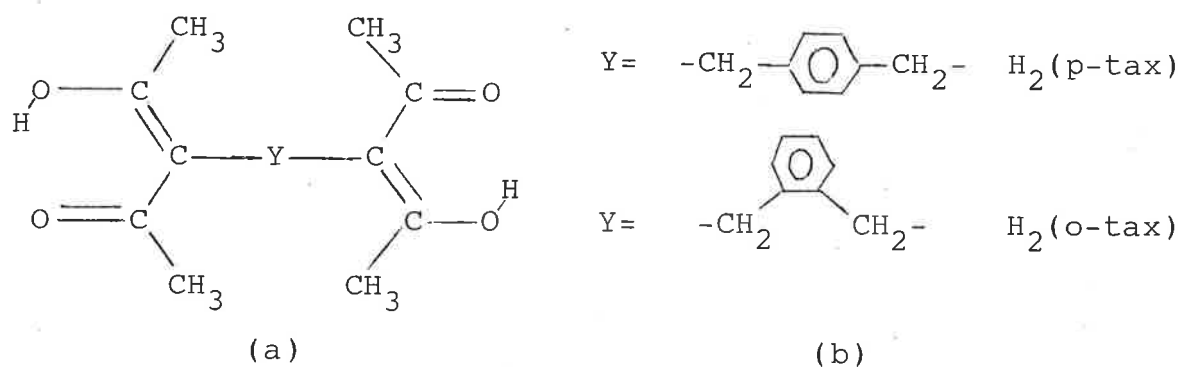


Figure 1.

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CADMIUM ARYLTHIOLATE MOLECULAR AGGREGATES IN SOLUTION

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$\text{Cd}(\text{SPh})_2$ and similar substituted aryl thiolate complexes, which are structurally non-molecular in three dimensions in the solid state, require polar coordinating solvents such as DMF for dissolution. The ^{113}Cd NMR spectrum of $\text{Cd}(\text{SPh})_2$ at 224°K shows a major line at 593.1 ppm, diagnostic of cadmium surrounded by four thiolate ligands, and a minor line at 130 ppm ascribed to cadmium with $\{\text{Cd}(\text{SPh})(\text{DMF})_n\}^+$ coordination. With increasing temperature only the major line is observed, broadening then narrowing to a line at 458 ppm (341°K). Analogous compounds $\text{Cd}(\text{SC}_6\text{H}_4\text{X})_2$ with 4-substituted arylthiolate ligands, X = CH₃, F, Cl, Br, give similar spectra. These spectral changes are interpreted in terms of the dynamics of interconversions between aggregated and de-aggregated cadmium species. The temperature dependent ^{13}C spectra have been measured.

Two proposals are presented for the structure of the more aggregated complex (or complexes) which prevail at low-temperature. In the fused tetra-adamantanoid structure $\text{Cd}_{10}(\text{SPh})_{20}$, all cadmium sites have $\{\text{Cd}(\text{SPh})_4\}$ coordination, but the *fused* cage structure presents difficulties in explaining the fast aggregation and de-aggregation reactions and the crystallisation/dissolution processes involving vertex-linked cages. The alternative proposal for the species in solution at low-temperature involves aggregates of vertex-linked adamantanoid cages. A variety of aggregates of different sizes and average $\{\text{Cd}(\text{SPh})_x(\text{DMF})_n\}$ coordination can be postulated, and all require some degree of solvent coordination at peripheral sites, which is in accord with the dissolution behaviour. It is proposed that "cascade" equilibria of these aggregated vertex-linked species occur, with different sizes and degrees of solvent coordination, giving rise to the changes in the ^{113}Cd NMR spectra. Addition of small amounts of halide (Cl^- , Br^- , I^-) to solutions of $\text{Cd}(\text{SAr})_2$ in DMF causes changes to the ^{113}Cd NMR consistent with coordinated solvent being replaced by halide.

CADMIUM THIOLATE CLUSTER IONS IN THE GAS PHASE: PLASMA DESORPTION MASS SPECTRA OF NON-MOLECULAR CADMIUM ARYLTHIOLATES

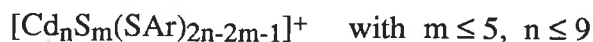
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Plasma desorption mass spectra (PDMS) of electrosprayed DMF solutions of bis-arylthiolates of cadmium $\text{Cd}(\text{SAr})_2$ (**1**) and $\text{Cd}(\text{SCH}_2\text{C}_6\text{H}_5)_2$ (**2**) reveal the existence of a large number of cluster cations and anions, containing up to nine cadmium atoms.

The aryl substituents are C_6H_5 (**1a**), 4-Me C_6H_4 (**1b**), 2-Me C_6H_4 (**1c**), 4-MeOC $_6\text{H}_4$ (**1d**), 4-Bu $^t\text{C}_6\text{H}_4$ (**1e**), 4-FC $_6\text{H}_4\text{F}$ (**1f**), C_6F_5 (**1g**)

Prominent in the positive ion spectra are ions belonging to the series:



which are formally related by ArSAr loss:



Many of the negative ions belong to the series $[\text{Cd}_n\text{S}_m(\text{SAr})_{2n-2m+1}]^-$ with $m \leq 4, n \leq 5$.

(**1a**), (**1b**), (**1c**) and (**1f**) crystallised from DMF have three-dimensionally non-molecular crystal structures.¹ In most but not all crystals the structural paradigm is vertex-linked adamantanoid cages, $[(\mu\text{-SAr})_6\text{Cd}_4(\mu\text{-SAr})_{4/2}]_\infty$. The density of bonds to be broken in the release of molecular fragments is relatively low in these crystals, but there is no marked prevalence of adamantanoid based Cd_4 ions in the PDMS spectra. Structural correlations between the crystals and the gaseous ions are likely to be tenuous for these compounds, in contrast with the mass spectra for binary compounds containing monatomic ions. Nevertheless, a large set of molecular structure types have been established by X-ray crystallography for $[\text{M}_x\text{S}_w(\text{SR})_y]$ compounds,² and examples and principles from this set can be invoked in assigning plausible structures to many of the ions in these PDMS experiments.

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SYNTHESIS AND PROPERTIES OF SOME NOVEL SOLUBLE METALLOCUBANE CLUSTERS

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We have been investigating the synthesis and properties of metallocubane clusters. Employing 4-substituted 2(1H)-pyridinethiones as ligands has facilitated the characterisation of bimetallic intermediates and tetrameric cubane products, due to the enhanced solubility of these ligands compared with 2(1H)-pyridinethione [1].

We have spectroscopic evidence that reaction of Cu(I) with potentially bidentate ligands 4-ethyl- and 4-methyl- 2(1H)-pyridinethione ((HL) and (HL¹) respectively) yields M_4L_4 and $M_4L_4^1$ species. The possible isomeric forms of these species are illustrated in figure 1. Variation of the reaction time has provided a degree of control over relative yields of each isomer.

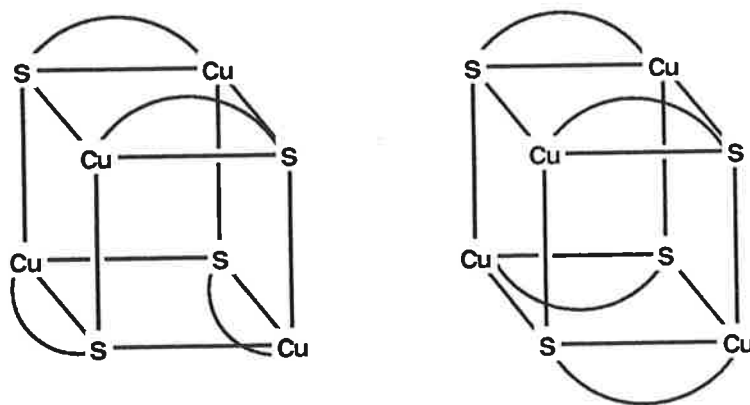


Figure 1

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SYNTHESIS AND REACTION CHEMISTRY OF TRANSITION-METAL S_2O COMPLEXES.

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We are interested in studying transition-metals' abilities to stabilize small reactive sulfur species, with the expectation that the reaction chemistry of the complexed species will be easier to study. Our initial goal within this research area has been to synthesize transition-metal complexes containing complexed disulfur monoxide (S_2O). Disulfur monoxide is then used in the synthesis of a class of organosulfur compounds called thiosulfinate esters.

To carry out this project, a reliable source of S_2O was needed and we have succeeded in synthesizing a molecule which liberates S_2O cleanly under very mild conditions. The S_2O precursor molecule apparently releases S_2O via a transition-metal induced retro Diels-Alder Reaction [1]. Use of this S_2O precursor in the synthesis of several transition-metal S_2O complexes will be reported along with our preliminary studies on the use of these S_2O complexes as building blocks for thiosulfinate ester synthesis.

Concurrently with the above complexation studies, we have been exploring the insertion of S_2O into transition-metal carbon bonds. Results of insertion of S_2O with simple metal alkyls will be reported along with several examples of cyclization of S_2O with transition-metal alkyl and propargyl complexes.

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SYNTHESIS AND COORDINATION PROPERTIES OF MEDIUM RINGS CONTAINING SULFUR AND PHOSPHORUS

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Medium sized rings with heteroatoms in the one and five positions have potentially strong intramolecular interactions and chelating ability. We have prepared a mesocycle containing a thioether and a sulfoxide group, one new mesocycle and one macrocycle containing both thioether and a phosphine groups and examined some of their complexes with metal ions. We also prepared and separated the *cis*- and *trans*-isomers of 1,5-diphosphacyclooctane and confirmed their identity by NMR.

Syntheses and crystal structures of *cis,trans,cis*- $\text{RuCl}_2(\text{DTCO-O})_2$ (DTCO-O = 1,5-dithiacyclooctane 1-oxide), *all-trans* - $\text{RuCl}_2(\text{DTCO-O})_2$, and a complex having four different ligands $[\text{RuCl}(\text{DTCO-O})(\text{DTCO})(\text{tht})]\text{BPh}_4$ (tht=tetrahydrothiophene; DTCO = 1,5-dithiacyclooctane) are described. The *all-trans*- $\text{RuX}_2(\text{R}_2\text{S})_2(\text{R}_2\text{SO})_2$ isomer is the first example of a ruthenium complex having halide, thioether and sulfoxide groups in a trans relationship to one another. This is the isomer which is thought to be the catalytic species in the ruthenium-catalyzed oxidation of thioethers. The *all-trans* isomer has a longer Ru-SO bond distance (2.298 (4) Å) than the *cis,trans,cis* isomer (2.239 Å), a shorter Ru-Cl bond distance (2.413 (4) Å) (compared to 2.467 (3) Å), and a shorter S-O bond distance of 1.459 (12) Å (compared to 1.485 (8) Å).

The synthesis of 5-phenyl-1-thia-5-phosphacyclooctane (1,5-PTPCO), its conformation in solution and the crystal structures of four platinum (II) complexes (dichloro(1,5-PTPCO)platinum (II), diiodo(1,5-PTPCO)platinum (II), chloro, methyl(1,5-PTPCO)platinum (II) and *cis*-bis (1,5-PTPCO)platinum (II) tetrafluoroborate) and several reactions of the chloro, methyl derivative are described. The cyclic dimer of 1,5-PTPCO, 5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane was also obtained and the crystal structure of its platinum complex was determined.

The Synthesis and Crystal Structure of Incomplete Cubane-Like Tungsten-Sulphur Cluster and Its Derivates

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Recently, research on the chemistry of incomplete cubane-like cluster has attracted the attentions¹⁻³ and many compounds with $Mo_3O_4-nSn^{4+}$ ($n=1-4$) cluster core have been synthesized. Hitter to, little research has been carried out on incomplete cubane-like tungsten-sulphur clusters.

We have synthesized an incomplete cubane-like tungsten-sulphur cluster compound $W_3S_4[S_2P(OC_2H_5)_2]_4 \cdot H_2O$ (I) and its reactivity has been studied. A series of reactions of (I) including replacement and addition are hereby reported.

In the compound (I) there is a "loose ligand" (H_2O) which can be easily replaced by some N-donor or O-donor ligands. In addition, the $S_2P(OC_2H_5)_2$ bridge ligand in (I) can also be substituted by some carboxyl ligands ($RCOO^-$).

It is obvious that on account of the presence of three coordinatively unsaturated μ_2-S atoms in the compound (I), some metal atoms can easily react with these sulphur atoms to form the cubane-like clusters. A series of compounds with $[W_3CuS_4]^{5+}$ cluster core have been synthesized in this way and characterized by IR, UV-Vis spectra and X-ray diffraction methods.

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SYNTHESES AND STRUCTURES OF METAL POLYSELENIDE COMPLEXES

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Reactions of selenium, sodium and metal halide in DMF yield solutions of anionic homoleptic metal polyselenide complexes, which can be crystallised with Ph_4P^+ . We have prepared the *bis*-tetraselenide M(II) complexes $[\text{M}(\text{Se}_4)_2]^{2-}$, M = Zn (1), Cd (2), Hg (3), Ni (4), Pb (5); two M(I) complexes $[\text{Cu}_4(\text{Se}_4)_{2.4}(\text{Se}_5)_{0.6}]^{2-}$ (6), $[\text{Ag}_4(\text{Se}_4)_{2.1}(\text{Se}_5)_{0.9}]^{2-}$ (7); two M(IV) complexes $[\text{Sn}(\text{Se}_4)_3]^{2-}$ (8) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{Se}_4)_2]^-$ (9), and one M(III) complex $[\text{Co}_3(\text{Se}_4)_6]^{3-}$ (10). Crystal structures for (1) to (10) have been determined and will be described.

(1), (2) and (3) contain pseudo-tetrahedral metal coordination, while in (4) the coordination is slightly distorted square planar. In (5) the coordination of lead is interpreted as comprised of primary trigonal orthogonal three coordination, plus one longer secondary bond in an approximately pseudo-octahedral location. The molecular clusters in (6) and (7) contain an M_4 tetrahedron, edge-bridged as $\text{M}_4(\text{Se}_x)_3$ by the terminal Se atoms of the three chelating polyselenide ligands. The coordination at each M atom is approximately trigonal planar. (8) possesses unremarkable octahedral coordination, while (9) is the first member of a new class of *mono*(cyclopentadienyl)-*bis*(polychalcogenide)metallates, distinct from previous similar compounds which are formulated $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{E}_x)]$, E = S, Se; x = 3, 4, 5. (10) contains two octahedral $\{\text{Co}(\text{Se}_4)_3\}$ moieties functioning as chelates to a third central Co atom which is also octahedrally coordinated.

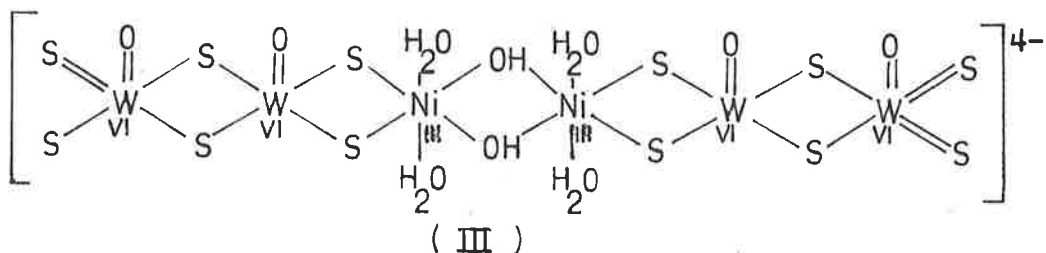
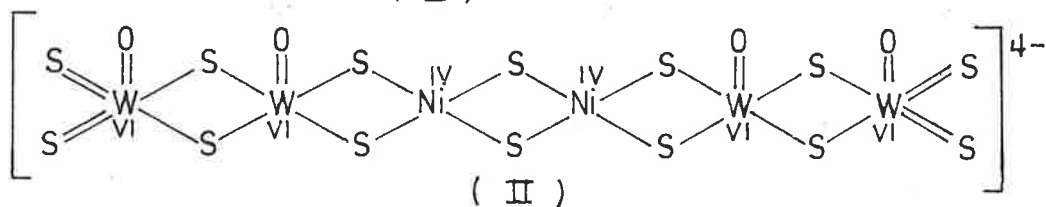
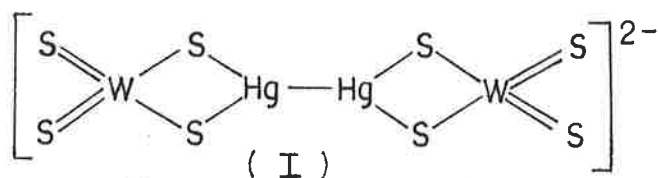
In all except (6) and (7) there is no evidence of the variability of polyselenide chain length which is characteristic of the analogous polysulfides complexes. Some disorder of chain length and conformation of metallapolyselenane rings occurs in the crystals of (6) and (7). Neither is there evidence yet of the coordination through non-terminal selenium atoms, as is known for sulfur in some metal polysulfides.

S,S BRIDGED HETERO POLY-METALLIC COMPLEXES: SYNTHESIS AND CHARACTERISATION.

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Hetero-trimetallic complexes in which the metal atoms are held by S,S bridges are well-known 1,2 in the systems $[S_2M'S_2MS_2M'S_2]^{2-}$ and to a lesser extent $[O,SM'S_2MS_2M'O,S]^{2-}$ and $[O_2M'S_2MS_2M'O_2]^{2-}$ where $M' = Mo, W$ and $M = Co(II), Ni(II), Pt(II), Pd(II), Zn(II)$ and sometimes $Fe(II)$. Herein is discussed the synthesis and characterisation of some closed shell (d^{10} or $d^{10}s^2$) - open shell (d^0) hetero bi- and tetra-metallic complexes, for instance I (a representative) and hexametallic $[Pb_2(WS_4)_4]^{4-}$ (isostructural with the structurally characterised $Sn(II)$ analogue [3]). Also a very interesting reaction has been discovered whereby a concerted and induced intra- and inter- molecular electron transfer occurs between $[W^V_2O_2S_2(S_4)_2]^{2-}$ and $[Ni^0(CO)_2(PPh_3)_2]$ affording the linear hexametallic complex II under non-aerobic condition, and then $Ni(IV)$ centres assume 6-coordination by absorbing H_2O , which on oxidative-hydrolysis in moist atmosphere affords III which ultimately degrades to a tetra-metallic $Ni(II)$ species. Interestingly, the nickel oxidation states have been characterised by X-ray Photoelectron Spectroscopy. Electrochemistry of these interesting complexes and probable mechanism behind their formation will be discussed.



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RHODIUM(III) AND PLATINUM(II) HALIDE COMPLEXES WITH 2,6-DIMETHYL-4H-PYRAN-4-THIONE.

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We have reported various platinum(II), palladium(II) and rhodium(III) halide complexes with thiocarbamic and dithiocarbamic esters [1-3], which were tested for "in vitro" cytostatic activity against KB cells, a line derived from a human epidermoid carcinoma. Of the thiocarbamic ester derivatives, the platinum adducts with EtOSCNHMe display significant activity also when dissolved in dimethyl sulfoxide (DMSO). In this solvent the mixed complexes $[\text{Pt}(\text{L})(\text{DMSO})\text{X}_2]$ (L = thiocarbamic ester; X = halide) are formed [4]. Owing to the detoxicant properties of sulphur donors the study is extended to the 2,6-dimethyl-4H-pyran-4-thione (DTP) complexes, which have been isolated and characterized by infrared and nmr (^1H and ^{13}C) spectroscopy and by thermogravimetric measurements.

The spectral data suggest for $[\text{Rh}(\text{DTP})_3\text{X}_3]$ (X = halide) an octahedral meridional configuration either in solution or in the solid state. The species $[\text{Rh}(\text{DTP})_2\text{Cl}_3]$ contains bridging Rh-Cl bonds. The platinum adducts $[\text{Pt}(\text{DTP})_2\text{X}_2]$ have generally a trans configuration, whereas the presence of DMSO favours cis geometry in the mixed species $[\text{Pt}(\text{DTP})(\text{DMSO})\text{X}_2]$.

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Synthesis, Characterization and Coordinating Properties of Aldehydthiosemicarbazone Complexes

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The use of thiosemicarbazones in the preparation of new coordination compounds has aroused much interest during the past several years, due to the pronounced biological activity and novel structural feature of their metal complexes. Several aldehydes viz (i) 4-hydroxy-3-methoxybenzaldehyde (vanillin), (ii) 2,3-indolinedione (isatin), (iii) 3-methoxysalicylaldehyde (o-vanillin) and (iv) 2-furaldehyde are employed to synthesise thiocarbazon Schiff base ligand when reacted with thio- or 4-phenylthiosemicarbazides. The ligands derived from (i) and (ii) act as bidentate chelators via S,N donors whereas those derived from (iii) and (iv) have an additional bonding site due to the presence of a phenolic/ketonic oxygen. The IR spectra of all the ligands show a strong band at $\sim 1600 \text{ cm}^{-1}$ which is assigned to $\nu(\text{C}=\text{N})$. The ligands have tendency to undergo enolization when they are in solution state. The presence of M-S stretching vibrations at $\sim 350 \text{ cm}^{-1}$ and the absence of S-H vibrations in the range of $2650\text{--}2500 \text{ cm}^{-1}$ indicate coordination by mercapto-sulphur atom of the thioenolate, tautomer of the ligands.

The thiosemicarbazone complexes show different stereochemistry as noticed for Cu(II), Ni(II) and Co(II) complexes. Ni(II) complexes formed by vanillin (VTSC) and 2-furaldehyde thiosemicarbazone (FTSC) are experimentally found to be diamagnetic and have been assigned square planar geometry. Similar is the case with the Cu(II)-VTSC complex indicating strong Cu-Cu interaction. The results are supported by d_{rs}, thermal, spectral parameters $10Dq, B', \beta, \beta^0$ and ν_1/ν_2 (or σ_1/σ_2) indicating largely to exhibit octahedral geometry. Pd(II) and UO₂(II) complexes with o-vanillin analogue are also characterized. The complexes formed by using 4-phenylthiosemicarbazone analogue are octahedral whereas those with VTSC and FTSC (with no phenyl group) are 4-coordinate. Stereochemical change in such complexes are investigated [1,2].

3-methoxysalicylaldehydthiosemicarbazone (ONS donor) yield mixed ligand complexes by mixing an ethanolic solution of a heterocyclic base bipy, phen or py in 1:1 molar ratio when added to copper(II) solution. The complexes formed are of the type $[\text{Cu}(\text{ONS}) \text{bipy}]$, $[\text{Cu}(\text{ONS}) \text{phen}]$ and $[\text{Cu}(\text{ONS}) \text{py}]$. Heterocyclic N is coordinated to the copper in every case as shown by their spectral bands at 450, 750, 1015, 1475; 450, 730, 885, 1468; 455, 680, 1026, 1225 and 1610 cm^{-1} due to coordinated heterocyclic bases respectively. Their electronic spectra in DMF-EtOH exhibit a broad band at $\sim 25000 \text{ cm}^{-1}$ ($\epsilon \sim 10^4 \text{ litre mol}^{-1} \text{ cm}^{-1}$) assigned to $L \rightarrow \text{MCT}$. The tridentate thiosemicarbazones coordinate to the central copper(II) ion followed by bipy or phen molecule with five-coordinate configuration. The sixth position is occupied by a water molecule as evident from tg analysis, to attain octahedral geometry. The results are discussed in the light of recent ESR studies and the determination of μ_{eff} values by Vibrating Sample Magnetometer (VSM). The values are checked by employing the ESR parameters $g, g_{\perp}, g_{\parallel}$ as well.

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^{13}C AND ^{59}Co NMR STUDIES OF THIOSELENO- AND DISELENOCARBAMATO COMPLEXES OF Co(III) AND In(III) IN CDCl_3 SOLUTION.

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The proton decoupled ^{13}C NMR spectra of several $\text{Co}(\text{Se}_2\text{CNR}_2)_3$, $\text{Co}(\text{SSeCNR}_2)_3$, $\text{In}(\text{Se}_2\text{CNR}_2)_3$ and $\text{In}(\text{SSeCNR}_2)_3$ (where R = organic substituent) have been measured in CDCl_3 solution (23-64 mM) at room temperature. Each of the diselenocarbamate complexes exhibited a single peak for the CSe_2 carbon at 188-197 ppm for Co(III) and at 186-198 ppm for In(III) complexes. The carbons alpha to the amine N also appeared as a single peak. The $\text{In}(\text{SSeCNR}_2)_3$ complexes exhibited single peaks for the CSSe carbons (192-202 ppm), but the carbons alpha to the amine N appeared as two distinct singlets (e.g., 54.35 and 49.12 ppm for $\text{In}(\text{SSeCN}(\text{CH}_2\text{CH}_3)_2)_3$), indicating hindered rotation about the SSeC-NR_2 bond. The $\text{Co}(\text{SSeCNR}_2)_3$ complexes exhibited four peaks of approximately equal intensity for the CSSe carbon (e.g., 198.95, 198.52, 197.98 and 197.45 ppm for $\text{Co}(\text{SSeCN}(\text{CH}_2\text{CH}_3)_2)_3$) which is interpreted as evidence for the stereochemical rigidity of the *fac* and *mer* isomers. The carbons alpha to the amine N appeared as six peaks (e.g., 45.00, 44.80, 43.37, 43.29, 43.12 and 43.02 ppm for $\text{Co}(\text{SSeCN}(\text{CH}_2\text{CH}_3)_2)_3$) (except for occasional accidental degeneracy) which is interpreted as evidence for hindered rotation about the SSeC-NR_2 bond in these two isomers.

The ^{59}Co NMR spectra of the $\text{Co}(\text{Se}_2\text{CNR}_2)_3$ complexes exhibited signals (6690-7260 ppm) in close agreement with results reported in the literature.[1] The ^{59}Co NMR signals of $\text{Co}(\text{SSeCNR}_2)_3$ were approximately identical to those of the corresponding $\text{Co}(\text{S}_2\text{CNR}_2)_3$ complexes [2] but were generally at lower field than for the corresponding $\text{Co}(\text{Se}_2\text{CNR}_2)_3$ complexes (e.g., 6780 ppm for $\text{Co}(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_3$, 6790 ppm for $\text{Co}(\text{SSeCN}(\text{CH}_2\text{CH}_3)_2)_3$ and 6830 ppm for $\text{Co}(\text{Se}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_3$). Similar to the dithiocarbamate complexes [3], there was a correlation between the ^{59}Co resonance and $(\mu_B)^2$ for the corresponding $\text{Fe}(\text{SSeCNR}_2)_3$, although only solid magnetic moments were available.[4]

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SYNTHESIS, STRUCTURE AND PROPERTIES OF
 $\text{Mo}(\text{NC}_6\text{H}_4\text{NH}_2)\text{Cl}_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$ AND RELATED COMPOUNDS

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$\text{MoOCl}_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$ reacts with PhNPPPh_3 or PhNCO to form $\text{Mo}(\text{NPh})\text{Cl}_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$ (A) [1]. Refluxing $\text{MoOCl}_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$ with aniline in the presence of base does not give an aryl nitrene complex, but when the the oxo-complex is refluxed with 1,2-phenylenediamine with two equivalents of base, $\text{Mo}(\text{NC}_6\text{H}_4\text{NH}_2)\text{Cl}_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$ (B) is formed. The structure of A [1] differs from the structure of B as indicated below:

Compound	Mo-NR (pm)	Mo-Cl ₁ (pm)	Mo-Cl ₂ (pm)	>Mo-N-C
A	173.4	246.7	246.9	166.8°
B	170.2	249.7	244.2	176.8°

The ^{95}Mo NMR data show that the molybdenum nucleus in B is deshielded compared to A. The reverse trend is observed for the nitrene nitrogens in the ^{14}N NMR spectra. The UV-Vis and electrochemical properties of A and B also show significant differences.

The reaction of $\text{MoOCl}_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$ with o-aminothiophenol yields $\text{MoOCl}(\text{SC}_6\text{H}_4\text{NH}_2)(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2$. The structure, NMR, UV-Vis and electrochemical properties of this complex will also be discussed.

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The Crystal Structure of $\text{Cd}_2(\text{S}_2\text{CO}^i\text{Pr})_3\text{I}$

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The structure of $\text{Cd}_2(\text{S}_2\text{CO}^i\text{Pr})_3\text{I}$ consists of cadmium atoms linked by xanthate bridges to form chains which extend in the c-direction. Adjacent chains link together through $(\text{S}_2\text{CO}^i\text{Pr})_2\text{CdI}_2(\text{S}_2\text{CO}^i\text{Pr})_2$ bridges to form a polymeric net-like structure which contains four-membered Cd_2I_2 rings, six-membered Cd_3S_3 rings and sixteen-membered $\text{Cd}_8\text{I}_2\text{S}_6$ rings.

There are two unique cadmium atoms in the structure. The first cadmium atom is coordinated by five sulphur atoms in a distorted trigonal bipyramidal environment while the second cadmium atom is in an octahedral environment formed by four sulphur and two iodine atoms.

Each of the three unique xanthate ligands asymmetrically chelates a cadmium atom in addition to forming a strong bond to an adjacent cadmium atom. Both of the iodine atoms symmetrically bridge two cadmium atoms.

Although a two-dimensional net-like structure is also adopted by many bisxanthates of the zinc triad, the tetrahedral coordination geometries normally found in these structures differ from the more highly coordinated cadmium atoms in $\text{Cd}_2(\text{S}_2\text{CO}^i\text{Pr})_3\text{I}$.

MULTINUCLEAR MAGNETIC RESONANCE STUDIES OF THE REACTIONS OF BIDENTATE LIGANDS WITH $\text{Pt}(\text{S}_2\text{CNEt}_2)_2$. COMPARISONS WITH THE REACTIONS OF $\text{Pt}(\text{S}_2\text{P}(\text{OEt})_2)_2$.

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The interactions in dichloromethane solution of $\text{Pt}(\text{S}_2\text{CNEt}_2)_2$ with a number of potentially bidentate ligands have been studied by multinuclear (^{31}P , ^{77}Se , ^{195}Pt) magnetic resonance techniques. The ligands used (L-L') were $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dpe), $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$ (ape), $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dpm), $\text{Ph}_2\text{PCH}_2\text{P}(\text{E})\text{Ph}_2$ (E = S, Se to give dpmS, dpmSe), $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{P}(\text{E})\text{Ph}_2$ (apeS, apeSe).

In 1:1 proportions the ligands dpe, ape and dpm all eventually give $[(\eta^2\text{-L-L'})\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$. With dpe the reaction is fast and no intermediate is observed, with ape $(\eta^1\text{-ape})\text{Pt}(\eta^1\text{-S}_2\text{CNEt}_2)(\eta^2\text{-S}_2\text{CNEt}_2)$ is observable and kinetic and thermodynamic data for its conversion to the final product were obtained. The overall reaction with dpm is very slow and involves both $(\eta^1\text{-dpm})\text{Pt}(\eta^1\text{-S}_2\text{CNEt}_2)(\eta^2\text{-S}_2\text{CNEt}_2)$ and the dimer $\text{cis,cis-}[\text{Pt}_2(\text{S}_2\text{CNEt}_2)_2(\mu\text{-dpm})_2]^{2+}$. In 1:2 proportions $[(\eta^1\text{-L-L'})_2\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$ (L-L' = ape, dpm) are formed but there is no further reaction in the dpe system. The relative instability of chelated ape and dpm is confirmed by reaction of $[(\eta^2\text{-L-L'})\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$ with PPh_3 to give $[(\eta^1\text{-L-L'})(\text{PPh}_3)\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$.

The reaction between $\text{Pt}(\text{S}_2\text{CNEt}_2)_2$ and dpmSe in 1:1 proportions is extremely complicated and is determined by the reactivity of the $\text{P}=\text{Se}$ bond. The initial products include $(\eta^1\text{-L-L'})\text{Pt}(\eta^1\text{-S}_2\text{CNEt}_2)(\eta^2\text{-S}_2\text{CNEt}_2)$ (L-L' = dpmSe, dpm) and dpmSe_2 . The reaction proceeds slowly to give $\text{cis,cis-}[\text{Pt}_2(\text{S}_2\text{CNEt}_2)_2(\mu\text{-dpm})_2]^{2+}$ and $[(\eta^2\text{-dpm})\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$ which then react with the generated dpmSe_2 to re-insert Se into a Pt-P bond to give $[(\eta^2\text{-dpmSe})\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$ as the final product. In contrast, dpmS reacts cleanly to give $(\eta^1\text{-dpmS})\text{Pt}(\eta^1\text{-S}_2\text{CNEt}_2)(\eta^2\text{-S}_2\text{CNEt}_2)$ and then $[(\eta^2\text{-dpmS})\text{Pt}(\eta^2\text{-S}_2\text{CNEt}_2)]^+$ due to the lower lability of the $\text{P}=\text{S}$ bond. No further reaction occurs with either ligand in 1:2 proportions. The ligands apeE do not react with $\text{Pt}(\text{S}_2\text{CNEt}_2)_2$ in dichloromethane solution.

Comparison with similar reactions of $\text{Pt}(\text{S}_2\text{P}(\text{OEt})_2)_2$ shows that the dithiocarbamate is more strongly bound to platinum than the dithiophosphate since several of the ligands studied can displace both dithiophosphate groups.

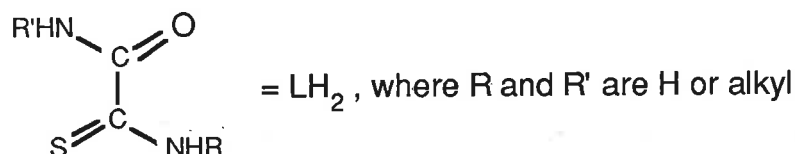
NEW COMPLEXES WITH PLANAR MONOTHIOOXAMIDES

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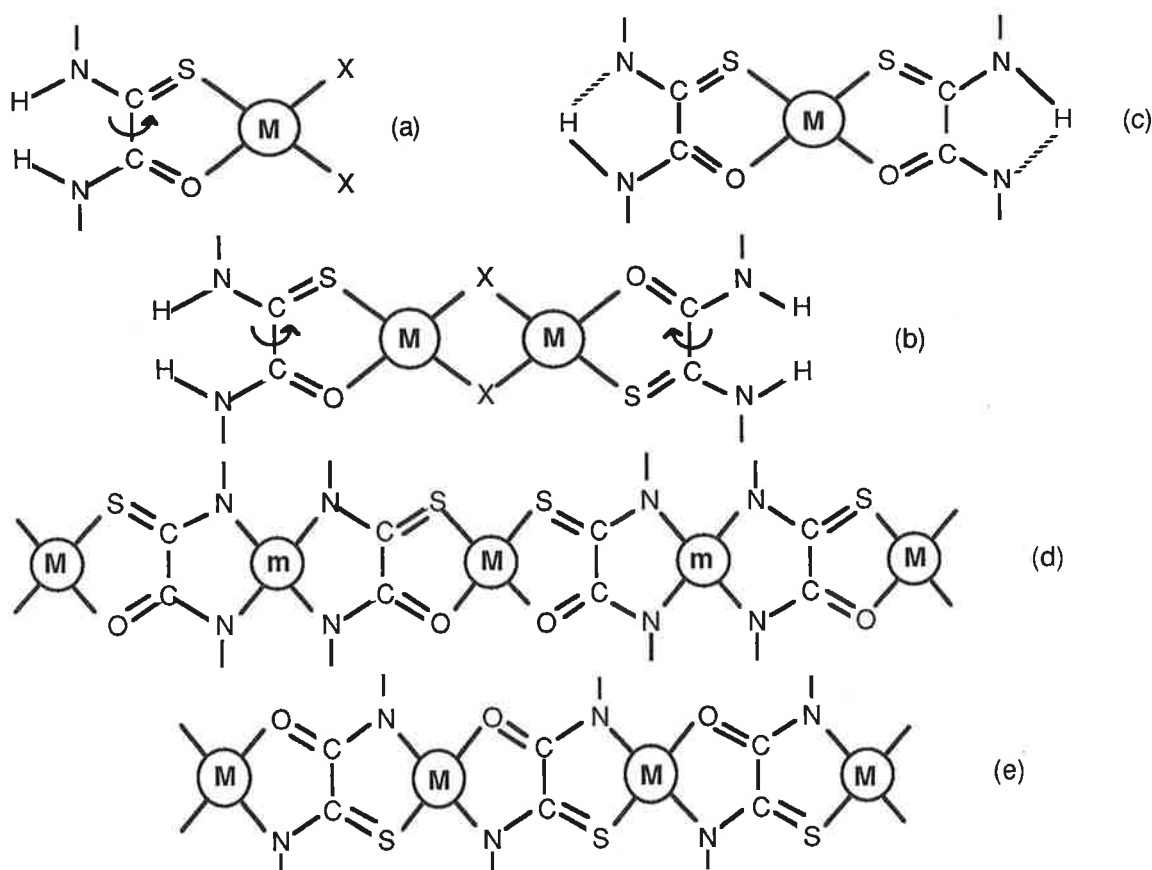
Planar monothiooxamides appear in the S,O trans configuration.



Coordination can occur with or without deprotonation through the N and/or O of the amide and the N and/or S of the thioamide group.

Different complexes can consequently be formed depending on the metal/ligand ratio the solvent and the pH.

Tetrahedral $\text{M}(\text{LH}_2)\text{X}_2$ (a), bridged $\text{M}_2(\text{LH}_2)_2\text{X}_2$ (b) and planar $\text{M}(\text{LH})_2$ (c) mixed polymers $\text{M}_{n/2}.\text{m}_{n/2}.\text{L}_n$ (d) and polymers $(\text{ML})_n$ (e) can be formed.



These compounds are studied by the vibrational spectra, U.V. spectra and thermal analysis.

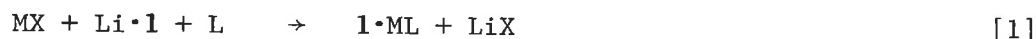
COORDINATION CHEMISTRY OF THE ANIONIC LIGANDS $\{[\text{Ph}_2\text{P}(\text{X})]_3\text{C}\}^-$, WHERE $\text{X} = \text{S}$ AND/OR O .

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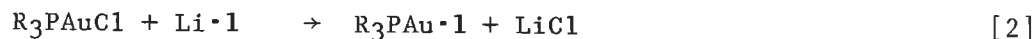
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The new anionic ligands, $\{[\text{Ph}_2\text{P}(\text{X})]_3\text{C}\}^-$, where X is various combinations of the chalcogens O , S and Se have recently been reported¹ along with some coordination chemistry of the trisulfide.² We report here recent progress in the coordination chemistry of the ligands $\{[\text{Ph}_2\text{P}(\text{S})]_3\text{C}\}^-$, **1**,; $\{[\text{Ph}_2\text{P}(\text{O})]_3\text{C}\}^-$, **2**; and $\{[\text{Ph}_2\text{P}(\text{S})][\text{Ph}_2\text{P}(\text{O})]_2\text{C}\}^-$, **3**. In the case of **1**, complexes with $\text{Cu}(\text{I})$, $\text{Ag}(\text{I})$ and $\text{Au}(\text{I})$ are reported along with NMR and structural aspects. The complexes are prepared by metathesis of metal halides or nitrates with the Li^+ or R_4N^+ salt of **1** as shown in equations [1] and [2].



where $\text{M} = \text{Cu}, \text{Ag}$; $\text{X} = \text{NO}_3, \text{Cl}$; $\text{L} = \text{R}_3\text{P}$



In $\mathbf{1} \cdot \text{Ag}(\text{PBU}_3)$ the ligand is a tridentate tripod bonded via three sulfur atoms to the silver. In the case of $\mathbf{1} \cdot \text{Au}(\text{PPh}_2\text{Bu})$, however, the ligand is sesquidentate, i.e., with one short Au-S bond, one long Au-S bond and one uncoordinated P-S group.

Complexes of **2** and **3** can be prepared by metathesis as above but also (and often preferentially) by ligand exchange with a metal betadiketonate and the neutral protonated ligand as shown in equation [3]. This reaction is successful with, for example, $\text{M} = \text{MoO}_2^{2+}$, VO^{2+} , Y^{3+} and Al^{3+} (although for Al^{3+} only two acac ligands are exchanged). The synthesis and properties of these complexes are discussed.



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CYCLOPENTADIENYLCHROMIUM COMPLEXES OF PHOSPHORUS.

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The reaction of $[\text{CpCr}(\text{CO})_3]_2$ with elemental P_4 under thermolytic conditions yielded a mixture of $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{P}_2$ (1), $\text{CpCr}(\text{CO})_2\text{P}_3$ (2), $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$ (3), $\text{Cp}_2\text{Cr}_2\text{P}_5$ (4) and $[\text{CpCr}(\text{CO})_2]_2$ (5). The composition of the mixture depends on detailed reaction conditions. Experimental evidence indicates that (1) - (3) are the primary products from a mechanism involving two pathways, whereas (4) is the ultimate product from the thermolysis of (1) - (3). Thermolysis of (1) also generates (2) and (5) as minor products. The structural features of (1) - (4) will also be illustrated.

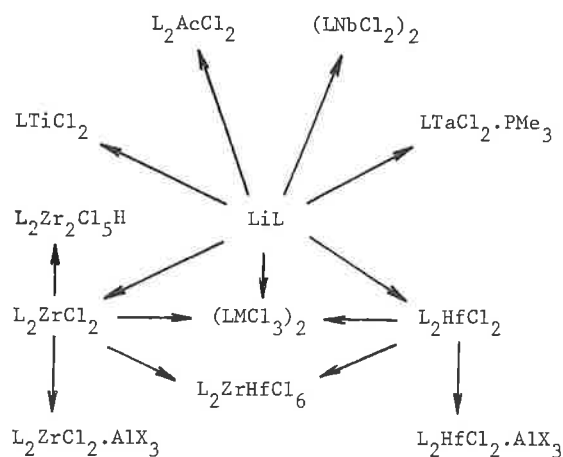
New Complexes of Electropositive Metals with Chelating Terdentate Phosphido-diphosphino Ligands

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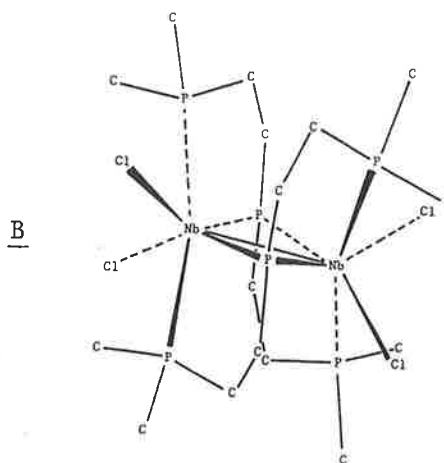
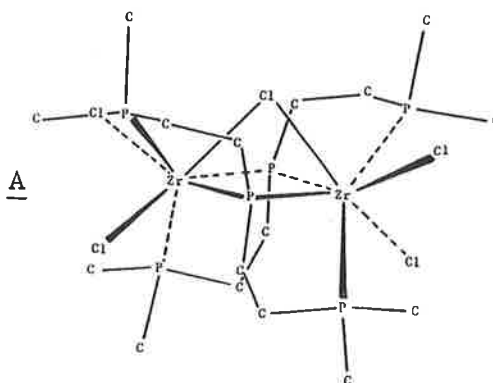
In view of the interesting coordination chemistry and reactivity [1] of complexes stabilised by linear terdentate amido-diamino/diphosphino ligands $\{^-\text{N}(\text{CH}_2\text{CH}_2\text{ER}_2)_2\}$, E = N, P and R = alkyl, we have undertaken a study of electropositive transition metal and actinide compounds stabilised by the new, analogous phosphido-diphosphino ligands $^-\text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$ L (R = Me, Et). We are interested in these ligands as they may be capable of stabilising unusual ternary systems, i.e. complexes containing other functions available for further reactions. In addition, phosphido ligands are well known to bridge; the new ligands L may provide access to heterobimetallic compounds containing functions available for a wide range of subsequent manipulations.

By the interaction of LiL with a variety of halides of metals in transition groups (IV) and (V) and actinides, and by appropriate control of conditions, mononuclear or binuclear complexes can be prepared (Scheme). In some of the mononuclear complexes, control of stoichiometry can provide compounds with pendant tertiary phosphine donors. These compounds may be used as precursors for the preparation of homo- or hetero-bimetallic systems. Spectroscopic and crystallographic [2] studies of $\text{L}_2\text{Zr}_2\text{Cl}_5\text{H}$ (A) and $(\text{LNbCl}_2)_2$ (B), reveal the bridging nature of the ligand. Further studies of these ligands and complexes are being undertaken.



X = Cl, Me; Ac = U, Th; M = Zr, Hf

SCHEME



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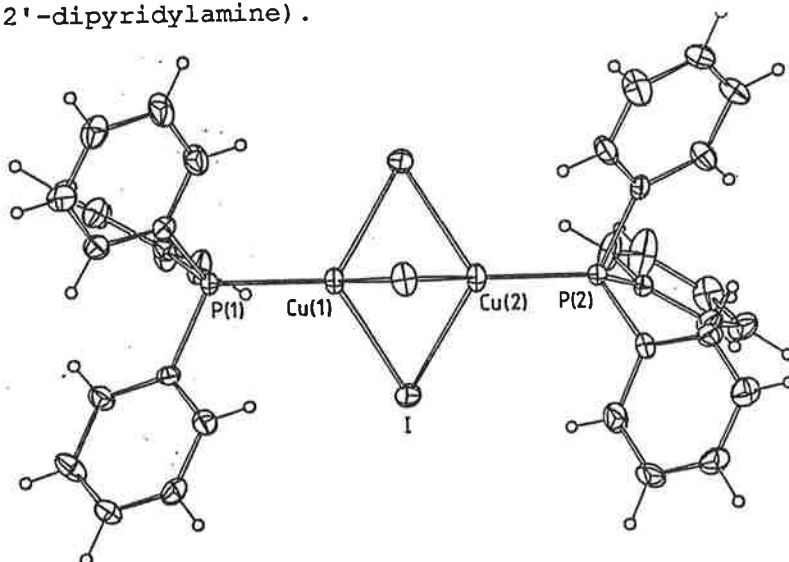
SOLID STATE NMR, FAR-IR AND STRUCTURAL STUDIES ON COPPER(I) COMPOUNDS

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P.C. Healy

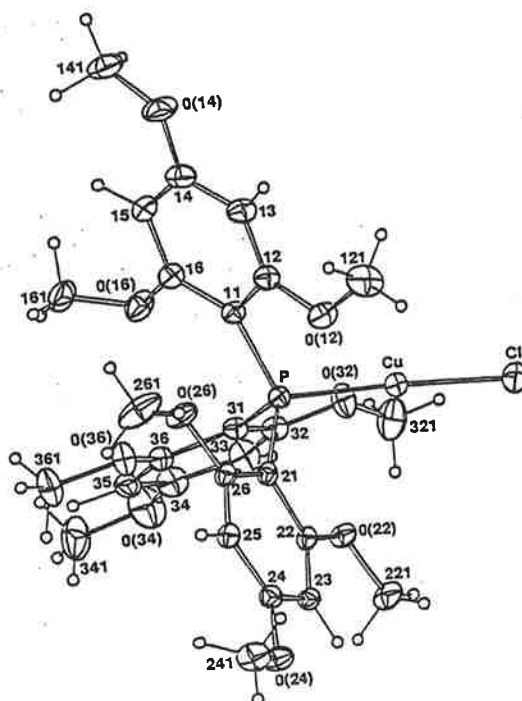
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Brisbane, AUSTRALIA.

Solid State ^{31}P NMR, Far Infrared spectra and single crystal X-ray diffraction techniques have been used to characterize a range of new and novel copper(I) compounds.

These compounds include the anionic species: $[(\text{PPh}_3)\text{CuBr}_2]^-$; $[(\text{PPh}_3)\text{CuI}_3\text{Cu}(\text{PPh}_3)]^-$; $[(\text{PPh}_3)_2\text{CuI}_2]^-$; $(\text{dpa})\text{CuCl}_2$ and $[(\text{dpa})\text{CuBr}_2]^-$.
(dpa = 2,2'-dipyridylamine).



and the two coordinate neutral compounds: (tris(2,4,6-trimethoxyphenyl)phosphine)copper(I) chloride and bromide.



GOLD(I) PHOSPHINE COMPLEXES: STERIC AND ELECTRONIC FACTORS IN ADDUCT FORMATION

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Phosphine complexes of gold(I) of the type $[LAuX]$, where $L = R_3P$ and $X = \text{halide or thiocyanate}$, can undergo either addition or substitution reactions in the presence of excess L . When $L = Ph_3P$, ($Ph = \text{phenyl}$), the adducts $[L_2AuX]$ and $[L_3AuX]$ can be isolated. [1-5] However, when $L = Cy_3P$, ($Cy = \text{cyclohexyl}$), only the substitution products $[L_2Au]X$ have been isolated. [6-8] There are both electronic and steric differences between Ph_3P and Cy_3P , so a series of complexes of Au(I) with other phosphines was prepared. The phosphines included mixed alkyl-aryl phosphines, such as Ph_2CyP and $PhCy_2P$, and *para*-substituted triphenylphosphines, $(Y-Ph)_3P$. The substituents on the phenyl rings were chosen so as to vary the electronic character of the phosphine.

For each phosphine (L), the linear $[LAuX]$ was prepared, and then excess L was added to the $[LAuX]$. The complexes were characterized by IR and UV-Vis spectra, ^{31}P -NMR spectra, and elemental analyses. Single-crystal X-ray diffraction was used to determine structures for several complexes.

Of particular interest were the complexes with $L = PhCy_2P$. The structures of $[LAuCl]$, $[L_2AuCl]$, and $[L_3Au]ClO_4$ have all been determined. Addition of one L to the linear complex gives a distorted trigonal planar complex $[L_2AuCl]$, [9] and efforts to add another L were only successful when perchlorate was used instead of Cl . The structure of the resultant $[(PhCy_2P)_3Au]ClO_4$ will be presented. A comparison of structural parameters for these complexes with the tendency for adduct formation will be made.

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REDOX STABLE TRIPHENYLPHOSPHINE, TRIPHENYLARSINE AND THIOUREA COPPER(II) DIOXIMATES.

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The formation of tetragonal pyramidal adducts of Cu(II) dimethylglyoximate with nitrogen donor ligands prompted us to investigate the preparation of redox stable triphenylphosphine (PPh_3), triphenylarsine (AsPh_3) and thiourea (tu) Cu(II) complexes, using butanedionedioximate (Hbd) and 3,4-hexanedione-dioximate (Hhd) as ligands stabilizing Cu(II) relative to Cu(I).

A series of pentacoordinate complexes $\text{Cu}(\text{Hbd})_2\text{L}$ ($\text{L} = \text{tu}$, Metu, 1,1- Me_2tu , 1,3- Me_2tu) and $\text{Cu}(\text{Hhd})_2\text{L}$ ($\text{L} = \text{tu}$, Metu, 1,1- Me_2tu , 1,3- Me_2tu , Me_3tu , PPh_3) as well as hexacoordinate complexes $\text{Cu}(\text{Hbd})_2\text{L}_2$ ($\text{L} = \text{entu}$, PPh_3 , AsPh_3) and $\text{Cu}(\text{Hhd})_2\text{L}_2$ ($\text{L} = \text{tu}$, Metu, 1,3- Me_2tu) has been prepared by the reaction of Cu(II) dioximates with the ligands in organic solvents and characterized by elemental analysis, electronic, infrared, and ESR spectra, as well as by magnetic susceptibility and thermal decomposition data.

The results of the above mentioned measurements indicate tetragonal pyramidal (TP) and tetragonal bipyramidal (TBP) polyhedra for pentacoordinate and hexacoordinate complexes, respectively. These polyhedra have been proved by X-ray structure analysis of pentacoordinate $\text{Cu}(\text{Hbd})_2\text{tu}$ and hexacoordinate $\text{Cu}(\text{Hbd})_2(\text{AsPh}_3)_2$ and $\text{Cu}(\text{Hhd})_2(\text{tu})_2$. The structure of the complexes consists of the molecules. In each molecule four nitrogen donor atoms of dioximate ligands are placed in the tetragonal plane, whereas sulphur and arsenic atoms occupy apical positions of TP (tu, Cu-S 247.0 pm) and TBP (tu, Cu-S 294.0 pm, AsPh_3 , Cu-S 304.4 pm) coordination polyhedra.

The stabilizing effect of dioximate ligands on Cu(II) relative to Cu(I) is associated with the formation of strong hydrogen bonds between dioximates ligands, assuring a pseudo-macrocyclic stability of the planar configuration of this part of the molecule. The PPh_3 , AsPh_3 and tu ligands are restricted to the apical coordination sites, unfavourable for the reduction process.

Silver(I) Complexes with Ligands Co-ordinating via P Donor Atoms. A Thermodynamic and Spectroscopic Investigation.

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Department of Chemistry, University of Udine, viale Ungheria, 43. I-33100 Udine, Italy.

Silver(I) is a typical soft acceptor which displays the affinity sequence $N \ll P > As > Sb > Bi$ for ligands co-ordinating via donor atoms of the nitrogen group. Thermodynamic investigations carried out in aprotic solvents on the complex formation of silver(I) with aliphatic and aromatic mono-phosphines show that the affinity of silver(I) for phosphorous is indeed very strong [1,2].

No thermodynamic data have so far been reported for the interaction, in solution, between silver(I) and phosphorous multidentate ligands. Because of the very low solubility of these compounds in water, thermodynamic measurements can only be performed in non aqueous solvents. In this work we report a thermodynamic investigation on the complex formation between silver(I) and a series of ligands co-ordinating via two or more phosphorous atoms in the aprotic solvent dimethyl sulphoxide (dmsO).

The ligands investigated are: bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), of general formula $PPh_2(CH_2)_n PPh_2$ $n=1-3$, bis(2-diphenylphosphinoethyl)phenylphosphine (etp) and tris(2-diphenylphosphinoethyl)phosphine (PP_3), respectively a ter- and tetra- dentate ligand. The aim of this work was to obtain information on the nature and thermodynamic stability of the species formed in dmsO solution between silver(I) and ligands possessing different steric properties and basicities and compare the data obtained with those previously reported [3,4] for analogous silver(I) complexes with nitrogen donor ligands.

The stabilities of the complexes have been determined by potentiometry by means of the silver electrode, the heats of formation by calorimetry. The thermodynamic data have been combined, when possible, with ^{31}P NMR studies in order to obtain further information on the bonding mode and structural aspects of the complexes formed.

The potentiometric and calorimetric measurements have been performed at 25°C in an ionic medium 0.1 M with NEt_4ClO_4 .

The ^{31}P NMR measurements have been performed in the range 308-183 K. Preliminary results indicate that the complexes are enthalpically stabilized, that the entropy terms counteract the complex formation and that the stabilities of silver(I) complexes with phosphorous ligands are larger than those with analogous nitrogen donor ligands. Spectroscopic data allow conclusions about the structures of the complexes formed.

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3. A. Cassol, P. Di Bernardo, P. Zanonato, R. Portanova, M. Tolazzi and G. Tomat, *J. Chem. Soc., Dalton Trans.*, 1988, 1781.
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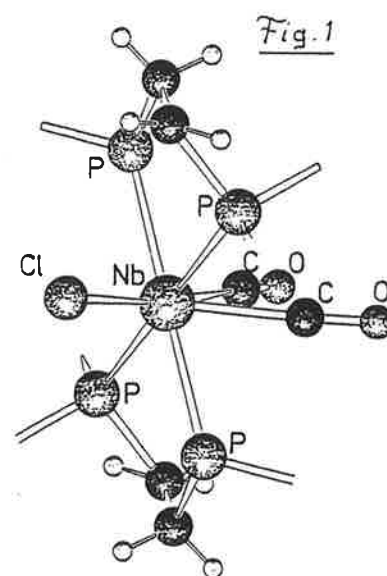
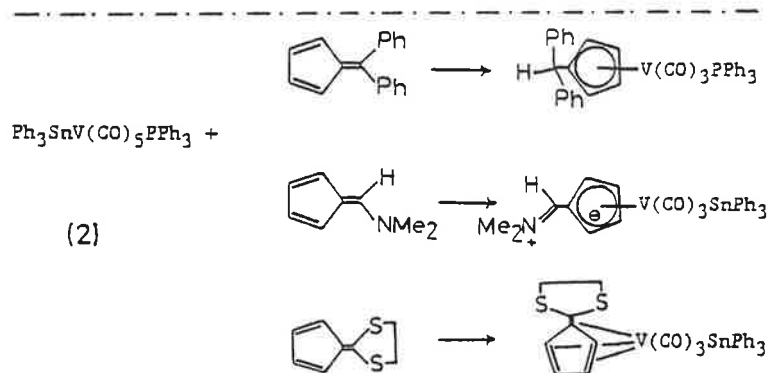
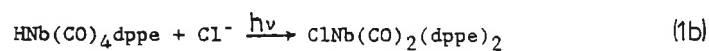
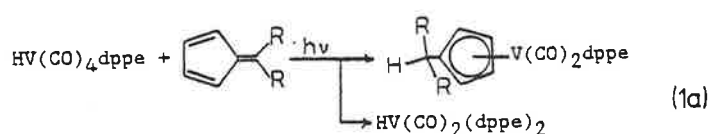
STRUCTURE AND REACTIVITY OF THE SEVEN-COORDINATED COMPLEXES $YM(CO)_6-nP_n$ ($Y = H, Hal, Alkyl, SnR_3$; $M = V, Nb, Ta$)

Dieter Rehder, Michael Fornalczyk, Christian Felten, Detmar Wenke, Peter Oltmanns and Wolfgang Pribsch.

Department of Chemistry, University of Hamburg, W.-Germany

The hydrido complexes $HM(CO)_6-nP_m$ (P_m is an n -dentate phosphine; $n, m = 1-4$) are obtained from the anionic precursors by ion exchange chromatography on silicagel. Their solution structure, according to NMR analyses, is the face-capped octahedron with a restricted fluctuallity. Reaction of carbonyl-metalates with alkylbromides leads to σ -alkyl, π -alkene and hydrido complexes. Photo-induced reaction of the hydrido complexes with pentafulvenes yields η^5 -cyclopentadienyl complexes (eq. 1a). In the presence of Hal^- , the halide complexes $Hal-M(CO)_2P_4$ are formed (eq. 1b). For $M = Nb$ and $Hal = Cl$, the X-ray structure analysis (Fig. 1) reveals the geometry of a face-capped trigonal prism, which is also the structure in solution. Halide and pseudo-halide complexes are further obtained by treatment of $[M(CO)_6]^-$ with $(Hal)_2$, $NbCl_5$ or $Hpy \cdot Hal$ in the presence of P_m and from hydrido complexes and $H(Hal)$.

The product of the reaction between the stannyl complexes $R_3SnV(CO)_5PPh_3$ and pentafulvenes largely depends on the polarity of the latter and is summarized in eq. 2.



D. Rehder, M. Fornalczyk, P. Oltmanns, *J. Organomet. Chem.*, **1987**, 331, 207.

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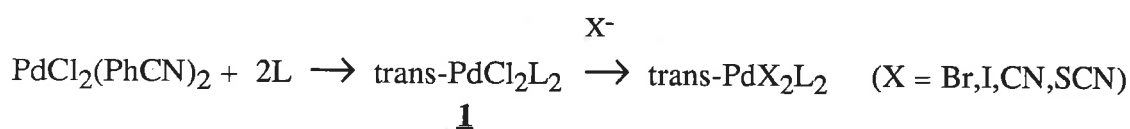
C. Felten, P. Oltmanns, W. Pribsch, *Chem. Ber.*, in press.

FORMATION OF A *p*-HYDROQUINONE SUBSTITUTED PHOSPHINE COMPLEXED TO PALLADIUM(II)

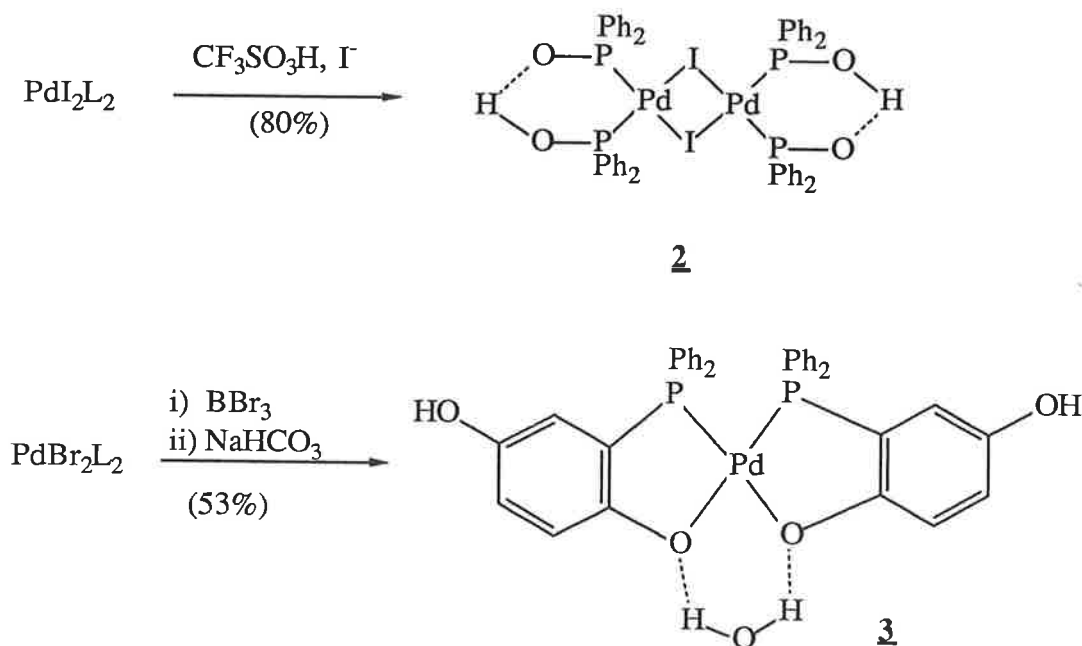
S.B. Colbran, D.C. Craig and S.B. Sembiring
University of New South Wales, Sydney, AUSTRALIA

We have prepared 1-diphenylphosphino-2,5-dimethoxybenzene (L), a phosphine with a protected hydroquinone moiety, as part of an investigation of co-operative effects arising between metal centres and ligands substituted with electrochemically active groups.

Complexes of L are readily formed. For example, simple Pd(II) derivatives have been synthesised by the following reactions:



Several methods of deprotecting the hydroquinone function have been attempted. Two of the more interesting results are:



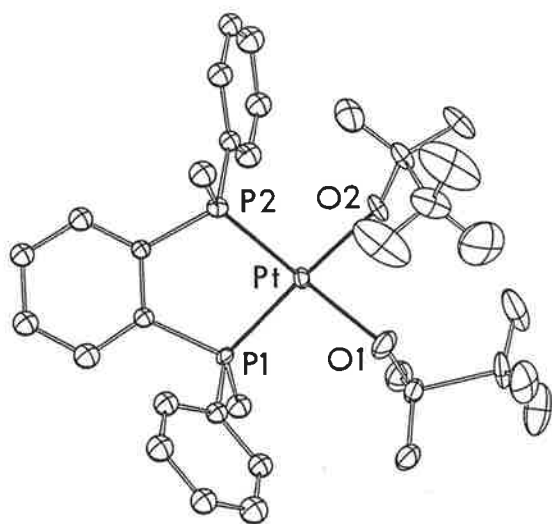
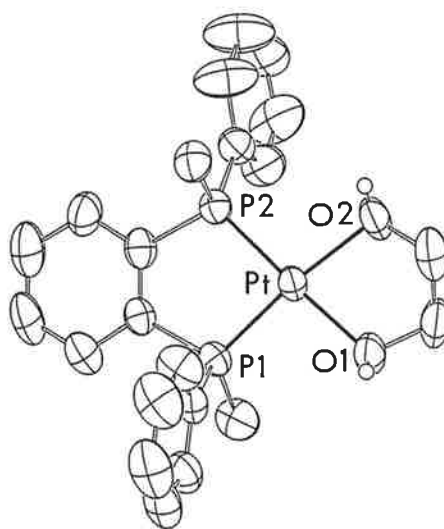
The X-ray crystal structures and chemical properties of **1**, **2** and **3**.2DMSO will be described in detail as will the full spectroscopic characterisation of all complexes.

ALCOHOL COMPLEXES OF PLATINUM(II)

A.M. Appelt, V. Ariaratnam, P.A. Duckworth, A.C. Willis and S.B. Wild

Research School of Chemistry, Australian National University, Canberra, Australia.

The crystal structure of $[S-(R^*, R^*)][Pt(O_3SCF_3)_2\{1,2-C_6H_4(PMePh)_2\}]$ (**1**) has been determined by X-ray diffraction. There are two molecules to the asymmetric unit, referred to below as **1a** and **1b**. This complex, the first structurally authenticated triflate of a platinum metal, reacts with ethane-1,2-diol to give $[S-(R^*, R^*)][Pt\{HO(CH_2)_2OH\}\{1,2-C_6H_4(PMePh)_2\}](O_3SCF_3)_2$ (**2**), which has also had its crystal and molecular structure determined. Complex **2** is the first example of a platinum complex of a simple alcohol.

**1a****2**

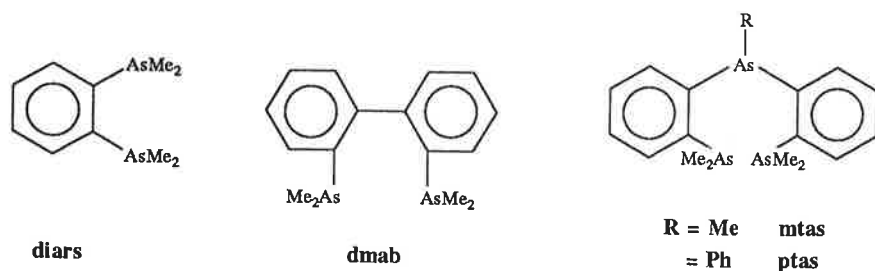
	1a	1b	2
Pt-P(1)	2.207(3)	2.201(3)	2.200(2)
Pt-P(2)	2.204(3)	2.216(3)	2.210(2)
Pt-O(1)	2.142(9)	2.125(7)	2.105(6)
Pt-O(2)	2.091(8)	2.112(8)	2.109(5)

LONG RANGE BONDING IN FIVE-COORDINATE NICKEL(II)-ARSINE COMPLEXES.

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A series of five-coordinate nickel(II) complexes containing the bidentate and tridentate ligands

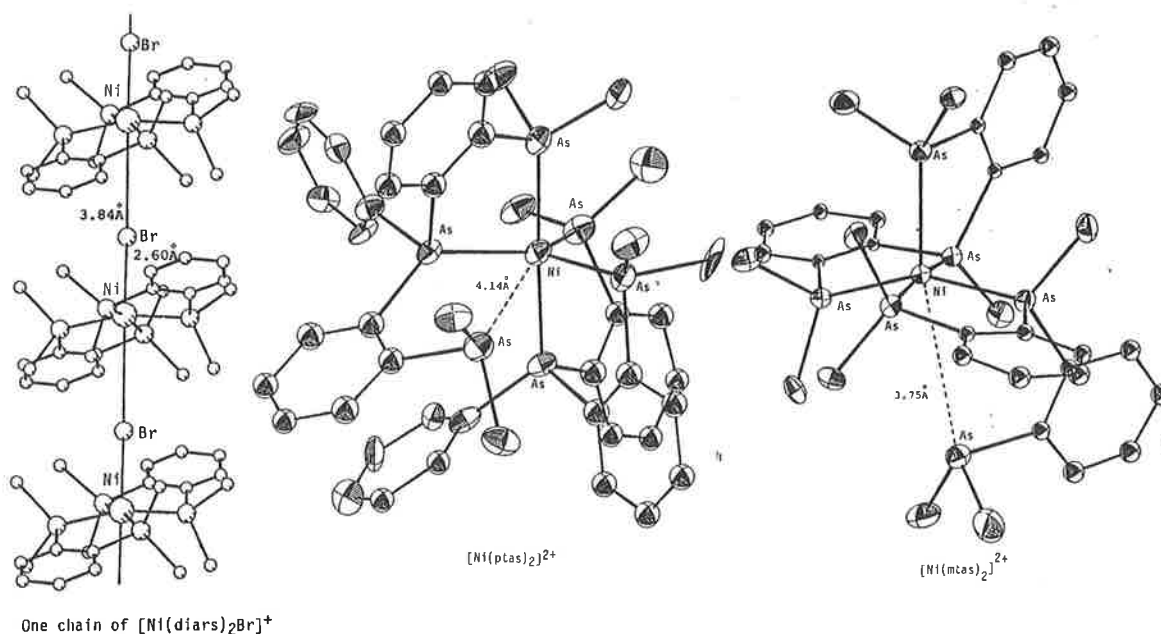


and having the donor sets $[\text{NiAs}_4\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $[\text{NiAs}_5]^{2+}$ can be prepared. With the exception of one poorly resolved X-ray structure [1], no complexes with these donor sets have been structurally examined.

A number of X-ray structural studies of systems of the above type will be reported. Some of the structures can be considered as coordinatively unsaturated. In those complexes where a potential extra ligand is available for coordination, eg a halide or dangling arsenic, that ligand is often weakly bound to the central nickel; distances for the long bonds are in the range 3.8–4.2 Å (see Figures).

The five coordinate $[\text{NiAs}_4\text{X}]^+$ complexes of the ligand **dmab** exist in two forms: a blue form [2] and a red discretely five coordinate form. Details of the two forms will be reported. The blue form is believed to be structurally similar to the linear chain $[\text{Ni}(\text{dias})_2\text{Br}]^+$ complex.

Many of the above systems are fluxional in solution and results from variable temperature ^1H nmr experiments will be presented.



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SYNTHESIS AND DETERMINATION OF SEVERAL NEW
POLYTUNGSTO (MOLYBDO) ARSONATES

Wang Zhangwen

Zou Qiaogen

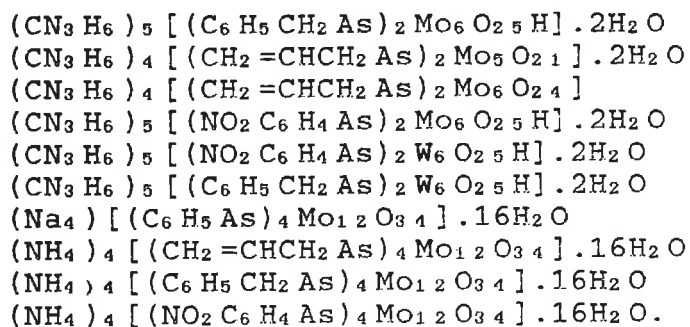
Nanjing Institute of Chemical Technology, China

The first polyanions containing covalently-attached organic groups to polytungsto(molybdo)phosphonates and polytungsto(molybdo)arsonates were reported by Miolati in 1908 and by Rosenheim and Bilecki in 1913, but the exact constitution and structure of these complexes were not established until recently. Since 1975 there has been an increasing interest in this area and the number of such complexes has multiplied accordingly. These derivatives may have potentially important applications in catalysis, biochemistry and medicine.

At first we obtained new guanidinium salts of molybdoarsinates corresponding to the formula $(\text{CN}_3\text{H}_6)_5 [(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{25}\text{H}]\cdot 2\text{H}_2\text{O}$. The IR spectra, X-ray data and DTA data are different from $[\text{N}(\text{CH}_3)_4]_2\text{Na}[(\text{CH}_3\text{AsO}_3)_2\text{Mo}_6\text{O}_{18}]\cdot 6\text{H}_2\text{O}$ and $(\text{CN}_3\text{H}_6)_4 [(\text{C}_6\text{H}_5\text{AsO}_3)_2\text{Mo}_6\text{O}_{19}\text{H}]\cdot 4\text{H}_2\text{O}$ which have been known.

Then we synthesized the guanidinium salt of the complexes with six metal atoms, corresponding to the general formula $(\text{CN}_3\text{H}_6)_5 [(\text{C}_6\text{H}_3\text{As})_2\text{Mo}_6-n\text{W}_n\text{O}_{25}\text{H}]\cdot 2\text{H}_2\text{O}$, ($n=0$ to 6). All compounds form good crystals. Our experiments show that these are true compounds and not isomorphic mixtures of heteropoly compounds.

Several new polytungsto(molybdo)organoarsonates which are unknown or different from those reported, have been synthesized and characterized. Crystals whose molecular structures have been determined are:



THE SYNTHESIS AND INVESTIGATION OF OPTICAL CHARACTERISTICS OF
COORDINATION COMPOUNDS OF f- AND d-ELEMENTS WITH NITROGEN-
AND OXYGENCONTAINING LIGANDS

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It was investigated the formation of complexes of lanthanide ions (Ln) and scandium with some bidentate electronegative ligands such as dicarbonilic reagents by means of spectrophotometric and luminescence methods.

It has been found the optimal condition of formation complexes including of lanthanide and ligand (L): acylic derivatives of indandione-1,3, phenol or dihydracetic acid. It was established that the complex compounds with the component ratio $Ln:L = 1:3$ are formed. It was interesting to study mixed ligand complexes of lanthanides in presence of aminopolycarbonic acids.

With help of spectrophotometric method was investigated changes of intensity of absorption bands of neodymium, holmium and erbium corresponding to the hypersensitive transitions in solutions of the some complex compounds. It was shown that by the variation of the ligand type with the intensity increase of the band of one element the proportional intensity increase of another absorption band is observed. It was calculated values of oscillator strength of the absorption bands for Nd^{3+} , Ho^{3+} and Er^{3+} . In all complexes which have been studied the ions of europium show intensity luminescence under ultraviolet radiation.

It was established the relation of intensities of luminescence bands of europium (η) for transition $^5D_0 \rightarrow ^7F_2$, $\lambda_{max} = 613$ nm, and for transition $^5D_0 \rightarrow ^7F_1$, $\lambda_{max} = 590$ nm. The correlation between values and oscillator strengths bands spectra of ions neodymium and holmium with ligands are observed. On the basis of these results it was assumed about similar influence of the arrangement on 4 f-shell in absorption and luminescence spectra.

The luminescence properties of europium complexes may be used for determination of their microquantities in industrial and nature objects.

COMPLEXES OF LANTHANOID METHANESULPHONATES (MS) AND PIRIDINE-N-OXIDE (pyO).

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The complexes, with composition $\text{Ln}(\text{MS})_3 \cdot 2\text{pyO}$ ($\text{Ln} = \text{La-Tm, Y}$) were prepared by reaction of a methanolic solution of the hydrated methanesulphonate with a solution of the ligand in triethyl-ortho-formate. The compounds were characterized by complexometric titration of the lanthanoid ions with EDTA, using xylenol orange as indicator. Microanalytical determinations of carbon, hydrogen and nitrogen were also performed. The melting ranges decrease with increasing atomic number and were correlated with ionic radii. Conductance measurements in methanol indicate a non-electrolyte behaviour. X-ray powder diffractions show that all the compounds are isomorphous. IR spectra suggest that the anions are coordinated to the central ions and that pyO is bonded through the oxygen. From the absorption spectra of the neodymium compound at room temperature and at 77K, the nephelauxetic, β , covalent factor, $b^{1/2}$, and Sinha's parameters were calculated and are indicative of essentially electrostatic bonds, with a very small 4f orbitals participation. From the emission spectrum of the europium compound, obtained at 77K, it was possible to suggest a C_{3v} symmetry for the complex species. Crystal-field parameters were also calculated and compared with those of the compounds of general compositions $\text{Ln}(\text{MS})_3 \cdot 2(3\text{-picNO})$ and $\text{Ln}(\text{MS})_3 \cdot 2(4\text{-picNO})$.

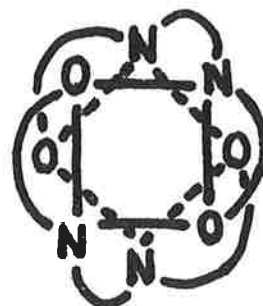
(FAPESP, FINEP and CNPq).

SYNTHESIS AND CHARACTERIZATION OF NEW LANTHANOID(III)
COMPLEXES WITH N,N'-ETHYLENE-BIS(SALICYLIDENEAMINATE)

Akira Takeuchi and Shoichiro Yamada

College of General Education, Osaka University, Toyonaka,
Osaka, Japan 560

The Schiff base, H_2salen , forms polymeric lanthanoid(III) complexes of the types $Ln_2(salen)_3$ and $Ln(salen)OH$, besides $Ce(salen)_2$ [1]. However, little has been reported about monomeric lanthanoid(III) complexes [2]. The present paper deals with synthesis and characterization of new monomeric lanthanoid(III) complexes $pipH[Ln(salen)_2]$, where $pipH$ =piperidinium and $Ln(III)=La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er$ and Tm . They have been synthesized by heating a mixture of an aqueous solution of lanthanoid(III) chloride and a methanolic solution of H_2salen and pip at about $60^\circ C$.



The structure of $pipH[Er(salen)_2]$ has been determined by single crystal X-ray analysis[3]. As shown in the Figure, the complex ion is eight-coordinate antiprismatic with quadridentate salen distorted from the planar configuration. It is reasonable to assume that the other lanthanoid(III) complexes also have a similar structure.

With the exception of $Sm(III)$ and $Eu(III)$ complexes, magnetic moments of the complexes agree with the formula $\mu = g\sqrt{J(J+1)}$ and susceptibilities in the temperature range 80-300K obey the Curie-Weiss law with a small value[4].

The f-f transitions (ν_{com}) are close to those of the aqua ions (ν_{aq}), the ratio ν_{com}/ν_{aq} being 0.99 to 1. The shapes of the hypersensitive bands are discussed in relation to the geometry of lanthanoid(III) is discussed. The frequency values decrease according to the sequence $[Ln(H_2O)_9]^{3+} > [Ln(salen)_2]^- > [LnCl_6]^{3-} > [Ln(Et_2dtc)_4]^-$.

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ON THE YTTRIUM CHLORIDE-1,10-PHENANTHROLINE INTERACTION:
SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE PRODUCT
 $[Y(OH)(H_2O)_2(phen)_2]_2Cl_4 \cdot 2(phen) \cdot MeOH$.

M.D.Grillone^a, F.Benetollo^b and G.Bombieri^c

^a Inst. of Chemical Engineering, University of Palermo-I

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^c Inst. of Pharmaceutical Chemistry, University of Milano-I

The rare earth elements are known to have, like the alkali metal ions, a greater tendency to give complex species with O-donors rather than with N-donors; there are still few complexes with the latter and very little is known about their structural environment.

Almost unknown are the structural features of the complex species with N-donor bidentate ligands such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) so far isolated; these have been repeatedly found to have a lanthanide ion/ligand stoichiometry ranging from 1:1 to 1:4, depending on the nature of the counter ion associated to the lanthanide. Most of them have been mainly investigated by infrared spectroscopy [1-3].

Our interest in the coordinating ability of yttrium(III) towards N-donors prompted this study on the interaction of such a pre-lanthanide with phen. Among the different experimental conditions (salt:ligand molar ratios from 1:3 to 1:9, solvents such as Me_2CO , EtOH or MeOH and solvent mixtures, and temperature from 25 to 60 °C), all using $YCl_3 \cdot 6H_2O$, those involving the interaction of 1:6-1:7 salt:ligand ratios in MeOH permitted the isolation of the title compound in crystals suitable for X-ray structural studies.

Crystal data - $Y_2(phen)_6Cl_4(OH)_2(H_2O)_4 \cdot MeOH$ triclinic $P\bar{1}$
 $a=13.970(2)$, $b=11.398(2)$, $c=10.818(2)\text{\AA}$, $\alpha=102.07(3)$,
 $\beta=94.96(3)$ and $\gamma=86.75(3)^\circ$, $Z=1$. Reflections used for structure solution and refinement 4849 with $I > 2.5\sigma(I)$. Diffractometer data and $MoK\alpha$ radiation. Final R value 0.042. The salt like structure is dimeric. The complex cation $[Y(OH)(H_2O)_2(phen)_2]_2^{4+}$ has C_i symmetry, each yttrium is coordinated² to four nitrogens¹ of the two phen moieties, two waters and two hydroxyls which are bridging the two yttrium ions complete the coordination sphere. Four chlorine anions balance the cation charges and two additional phen molecules and one disordered methanol are clathrated in the triclinic cell.

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- [3] D.M. Czakis-Sulikowska and J. Radwanska-Doczekalska, J. Monatsh. Chem., 117, 783 (1986), and refs. therein.

YTTRIUM TRI-TERTIARY ALKOXIDES

D.C. Bradley and H. Chudzynska

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London E1 4NS, UK.

According to the literature [1] the trialkoxides $[M(OR)_3]_n$ of several trivalent metals ($M = Ga, In, Y, La, Pr, Nd, Sm, Gd, Ho$, and Er) have been prepared from the reaction of sodium alkoxide with the appropriate MCl_3 .

Nevertheless we have found recently that for some metals (Sc, Y, In and Yb) the reaction of the metal trichloride with sodium isopropoxide gives not the tri-isopropoxide but a novel stable pentanuclear oxoalkoxide cluster of formula $[M_5(\mu_5-O)(\mu_3-OPr^1)_4(\mu_2-OPr^1)_4(OPr^1)_5]$ [2]. Further work with yttrium has now shown that an unstable tri-isopropoxide can be formed from the mild reaction of the 3-coordinated $Y[N(SiMe_3)_2]_3$ and isopropanol but it is readily converted to the pentanuclear cluster in boiling isopropanol. However, with tertiary alcohols the trialkoxides $[Y(OR)_3]_n$ [$R = CMe_3, CEtMe_2, CPr^1Me_2, CEt_3, C(CF_3)Me_2, C(CF_3)_2Me$ and $C(CF_3)_3$] are obtained as thermally stable sublimable (*in vacuo*) compounds with no tendency to form pentanuclear oxo species.

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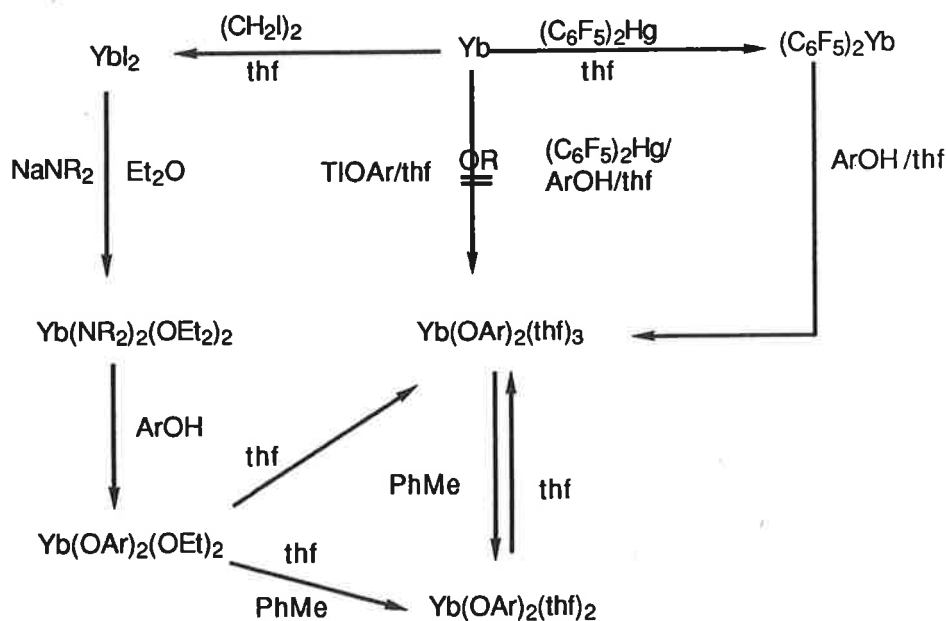
FOUR- AND FIVE-COORDINATE LANTHANIDE(II) ARYLOXIDES

Glen B. Deacon ^a, Peter B. Hitchcock ^b, Stephen A. Holmes ^b, Michael F. Lappert ^b, Peter MacKinnon ^a and Russell H. Newnham ^a

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Several syntheses for the preparation of hydrocarbon-soluble, monomeric ytterbium(II) aryloxides, $\text{Yb}(\text{OAr})_2\text{L}_2$ ($\text{Ar}=\text{C}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4}$; $\text{L}=\text{tetrahydrofuran (thf) (1) or Et}_2\text{O (2)}$ and $\text{Yb}(\text{OAr})_2(\text{thf})_3$ (3) have been achieved (Scheme 1; $\text{R} = \text{SiMe}_3$).



X-ray crystal structures have shown that $\text{Yb}(\text{OAr})_2\text{L}_2$ have tetrahedral stereochemistry, whereas $\text{Yb}(\text{OAr})_2(\text{thf})_3$ has square pyramidal stereochemistry (thf apical) with a distant methyl group possibly giving a pseudo-octahedral arrangement. $\langle \text{Yb} - \text{OAr} \rangle$ distances are 2.207 (12) Å (1); 2.137 (10) Å (2) and 2.154 (28) Å (3).

ORGANO-f ELEMENT COMPLEXES CONTAINING THE POTENTIALLY CHELATING, OR BRIDGING NEW DIANIONIC LIGAND: 2,6-BIS (METHYLENE-CYCLOPENTADIENYL)PYRIDINE.

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Recently we observed that organo-rare earth complexes containing silicon-bridged-bis cyclopentadienyl ligands may exist in two isomeric forms[1,2], i.e. in one form where the two Si-interlinked cyclopentadienyl rings coordinate to one metal ion in a chelating fashion (Type I), and in a second form where the two metal ions are bridged by this ligand (Type II).

In order to study the effect of the size of the group interlinking the two cyclopentadienyl rings in view of the prevalence of type I or of type II isomers, we have synthesized the disodium salt of the new ligand 2,6-bis(methylenecyclopentadienyl)pyridine ["LNa₂"], by reaction of 2,6-(chloromethyl)pyridine with sodium cyclopentadienide in THF. The ¹H nmr spectrum (THF-d₈) of the white crystalline product [LNa₂] crystallizing from THF/n-hexane, 5:1, v:v), shows a triplet centered at δ 7.54 (1H, pyridine-C4 proton), a doublet centered at δ 7.01 (2H, pyridine-C3,5 protons, J = 9.5 Hz), a pseudodoublet centered at δ 5.56 (8H, cyclopentadienyl protons) and a singlet at δ 4.06 (4H, methylene protons).

After reaction of LNa₂ with PrCl₃ in THF, in the molar ratio 1:1, a yellow product was isolated. The analytical data of the crystallized product (slightly soluble in THF) are in agreement with the formulation [LPrCl][I]. Its mass spectrum (E.I., 70 eV, 250°C) indicates the dimeric nature in gas phase (M⁺, m/z 818). In addition, a mass spectrometric study based on B/E and B²/E scans, respectively, suggests the presence of type I isomer, where the ligands coordinate the metal ion in a chelating fashion. Analogous results were obtained for the green product [II] isolated after reacting the ligand LNa₂ with NdCl₃ under the same conditions..

The chelating properties of the ligand have also been confirmed for the deep green product obtained by reaction of LNa₂ with UCl₄ in the molar ratio 1:1. However in this case the analytical and physico-chemical data (¹H nmr and mass spectra) suggest that the product is the monomer [LUCl₂] [III].

Both reactivity and spectroscopic properties of [I-III] (¹H nmr, MS, NIR/VIS) will be discussed in detail, inter alia in view of potential metal-N(pyridine) interactions.

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Synthesis of Tris(cyclopentadienyl)lanthanoids from
lanthanoid metals, Bis(pentafluorophenyl)mercury and
Cyclopentadiene

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The classical route to tris(cyclopentadienyl)lanthanoid(III) complexes from anhydrous lanthanoid trichlorides and sodium cyclopentadienide has the disadvantage of the use of two moisture and/or oxygen-sensitive reagents [1]. Simpler recent syntheses involve reactions of lanthanoid metals with thallium(I) [2,3] or mercury(II) [4] cyclopentadienides. We now report a new convenient synthesis by reaction of lanthanoid metals (Ce, Nd, Sm, Gd, Dy, Er, Tm, Lu) with bis(pentafluorophenyl)mercury and cyclopentadiene in tetrahydrofuran at room temperature. Yields of the complexes $(C_5H_5)_3Ln \cdot thf$ were 50-90%, and the products were identified by m.s., n.m.r., visible/near i.r., and i.r. spectroscopy. The reactions are considered to involve redox transmetallation giving pentafluorophenyl lanthanoid species which are trapped by ligand exchange giving $(C_5H_5)_3Ln$. An analogous reaction with ytterbium gave $(C_5H_5)_2Yb(thf)$ together with some $(C_5H_5)_2YbF$.

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Structural Studies of Coordination Complexes of Lithium Salts with Amines

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Structural studies concerning the coordination complexes formed between lithium halide or nitrate salts and uni- or polydentate amines have revealed striking similarities with those of the analogous copper(I) complexes. Species such as monomers with 3:1 ligand:salt ratio, 2:1 dimers and 3:2 'step' tetramers have been obtained with unidentate ligands, for example pyridine, 2-methylpyridine, 3,5-dimethylpyridine and quinoline, e.g. [1]. Differences in the complexes of lithium and copper have also been apparent, perhaps due to the difference in size of the two metals, as the lithium atom more easily accommodates the halide and three bulky ligands such as quinoline in its coordination sphere than does copper. In addition there is a greater range in the lithium to halogen bond lengths on moving from chloride to iodide than is observed for the analogous copper to halogen distances, resulting in a 'cross-over' of bond lengths for the two metals, with M-Br distances approximately equal. As a result of these factors, slightly different structures have sometimes been observed for lithium and copper salts with a given ligand.

Lithium also has a greater affinity for oxygen than does copper(I) and this has provided some interesting polymeric nitrate complexes for lithium, unlike any obtained for copper, as well as providing some experimental difficulty in the total exclusion of water from the reaction mixtures. The lithium atom remains coordinated to the oxygens of the nitrate group, with the nitrate group generally bridging lithium centres, and the amine ligands are disposed about the lithium nitrate framework [2].

Polydentate ligands such as N,N,N',N'-tetramethylethylenediamine (tmed) and N,N,N',N'',N''-pentamethyldiethylenetriamine (pmdet), originally believed to form only 1:1 or 2:1 complexes containing 4-coordinate lithium atoms [3], have provided some interesting 2:3 and 3:4 complexes with bridging and chelating ligands, as well as 1:1 dimers, e.g. [4].

Further work involving a variety of lithium salts and aromatic and aliphatic amines is continuing. A number of sodium halide complexes are also under investigation, with oligonuclear species being obtained with tmed and pmDET ligands, e.g. [5].

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SOLVENT ELECTRON-PAIR DONOR ABILITY AND STRUCTURE OF MERCURY(II) AND COPPER(I) DIHALIDE COMPLEXES IN SOLUTION

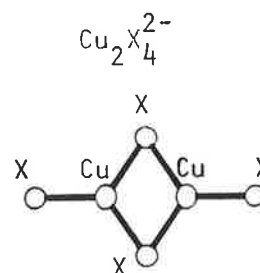
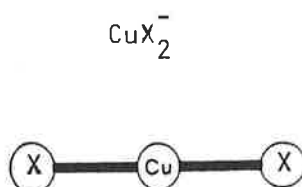
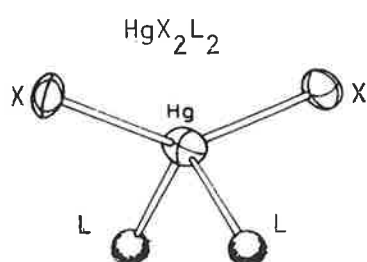
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Donor-acceptor interactions are of great importance for solvation and complex formation and are thus of interest for most chemical processes in solution. A number of scales ranking the Lewis base strength of solvents has been proposed previously, based on experimental measurements of changes in thermodynamic or molecular properties upon solvation. Especially soft-soft interactions have been difficult to characterise with the use of experimental probes, which often react with the solvent. However, the HgBr₂ molecule, with the Hg atom as the soft acceptor, has been found to be sufficiently stable and soluble in most solvents.

The structure of the solvated HgX₂ (X = Cl, Br or I) species formed in strongly coordinating solvents (L = DMSO, pyridine, tetrahydrothiophene, tributylphosphite etc.) have been determined in solution and in solid phase with X-ray diffraction methods and found to form pseudotetrahedral HgX₂L₂ complexes [1-5]. The XHgX angle gradually decreases from linearity to near tetrahedral values, and a correlation between the decoupling of the symmetric and the asymmetric stretching vibration frequencies and the XHgX angle allows the angle to be estimated in solution from measurements of vibrational frequencies. With the use of the shift in the Br-Hg-Br symmetric stretching frequency as a measure of the solvent donor-acceptor interaction, a relative scale (*D_s*) has been derived for about 70 solvents, including many with very soft donor properties [1]. The softness would in the first place be related to the π-bond donor properties of the Hg(II) ion to the solvent ligands, because its filled 5*d*¹⁰ electron shell prevents it from accepting π-bonds from the ligands. Comparisons with other measures of solvent Lewis basicity are given [2].

This behaviour of the solvated HgX₂ species is in contrast to that of the monomeric CuX₂⁻ complexes in solution, which do not seem to be solvated to any great extent [6]. An increasing (in the order Cl < Br < I) dimerisation tendency is found instead.



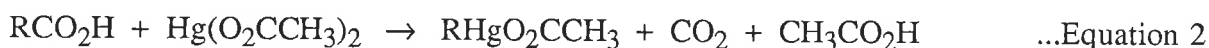
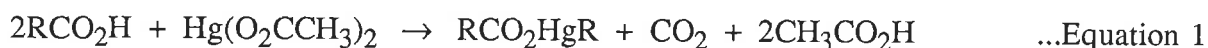
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PREPARATION OF SOME POLYMETHOXYPHENYLMERCURIC HALIDES BY NOVEL DECARBOXYLATION REACTIONS.

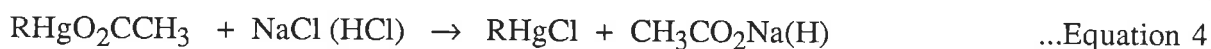
G. B. Deacon, C. L. Leseberg.

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Previous work [1] in the preparation of polymethoxyphenylmercuric chlorides and polymethoxyphenylmercuric polymethoxybenzoates has involved a two-step synthesis. The first step used the polymethoxybenzoic acid and mercuric acetate to prepare either the mercuric benzoate derivative or the acetate product (Equations 1 and 2).



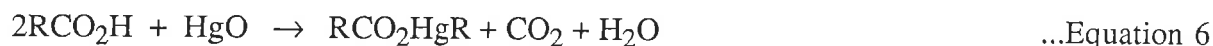
Conversion of these products to the desired mercuric chlorides was achieved by treatment with either dilute hydrochloric acid or a saturated sodium chloride solution (Equations 3 and 4).



We now report a novel one-step route to some of these compounds by ipso - decarboxylation of the polymethoxybenzoic acid by mercuric chloride in refluxing methanol / water (Equation 5).



Direct reaction of some polymethoxybenzoic acids with mercuric oxide gave the corresponding polymethoxyphenylmercuric polymethoxybenzoate in good yield (Equation 6).



The products have been characterized using FTIR, mass spectra, ^1H NMR, and ^{199}Hg NMR.

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THE SYNTHESIS AND ^1H NMR CHARACTERIZATION OF
 $\{\text{RN}(\text{CH}_2\text{CH}_2)_2\text{Hg}\}_2$ COMPOUNDS

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A series of $[\text{RN}(\text{CH}_2\text{CH}_2)_2\text{Hg}]_2$ ($\text{R} = \text{C}_6\text{H}_5$, $3\text{-ClC}_6\text{H}_4$, $2,4,6\text{-X}_3\text{C}_6\text{H}_2$, $\text{X} = \text{Br}$, Cl) compounds have been prepared by the symmetrization of the corresponding organomercurials, $\text{RN}(\text{CH}_2\text{CH}_2\text{HgX})_2$ using sodium stannite (NaSnO_2), according to Equation 1.



Equation 1.

The dominant feature in the identification of these novel products of symmetrization is the size of the J_{HHg} coupling constants in the ^1H nmr spectra. The $^2J_{\text{HHg}}$ and $^3J_{\text{HHg}}$ coupling constants of $[\text{RN}(\text{CH}_2\text{CH}_2)_2\text{Hg}]_2$ compounds are approximately half the size of those of $\text{RN}(\text{CH}_2\text{CH}_2\text{HgX})_2$ compounds.

The x-ray crystal structure of $[\text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{CH}_2)_2\text{Hg}]_2$ (Figure 1) has been determined and shows that a dimer rather than a polymer is present.



Figure 1:

The Structure of

Bis(μ -phenylnitrilobis(ethane-2,1-diyl)di[mercury(II)]).

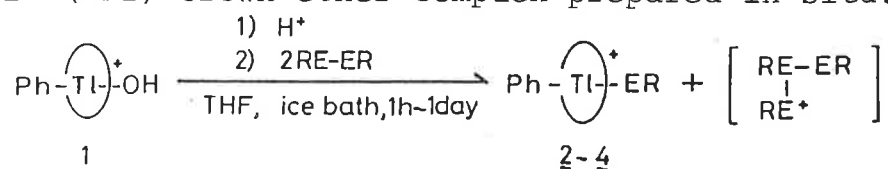
PREPARATION OF MONOPHENYLTHALLIUM(III) CROWN-ETHER COMPLEXES HAVING Tl-ER (ER= S, Se, Te) BOND

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We have found that stable monophenylthallium(III) complexes with a Tl-S bond [PhTl(III)(DBC)SR]ClO₄ could be isolated in the presence of crown-ether such as dibenzo-18-crown-6[1]. In this paper we will present the preparation of analogous complexes with Tl-Se and Tl-Te bonds and examine the nature of the Tl-E (E = S, Se, Te) bond on the basis of the ¹H NMR spectra.

The preparation of [PhTl(III)(18-crown-6)ER]BF₄ was used cleavage of the RE-ER bond with the dicationic monophenylthallium(III) crown-ether complex prepared in situ. Air



E= S 2, Se 3, Te 4 ; R= ⁿ-Pr a, ⁿ-Bu b, Ph c, p-tolyl d

stable complexes 2 and 3 were obtained after partial evaporation of solvent under reduced pressure and subsequent addition of ether as colorless crystals. The yellow complexes 4 with the Tl-Te bond were sensitive to light and decompose gradually in solution at room temperature.

The spin-spin coupling constants between the thallium nucleus and the ortho protons of the phenyl group, $^3J(\text{Tl-H}_o)$,

The Values of $^3J(\text{Ti-H}_\text{O})/\text{Hz}$ of Complexes 2 - 4 in CH_3CN

E \ R	n-Pr	n-Bu	Ph	p-tolyl
S	628 ^a	626 ^{a, b}	676 ^a	659 ^a
Se	— ^c	603	636 ^a	633
Te	543	540	573	562

^aCounter ion= ClO₄. ^bCrown-ether= DBC. ^cNot measured.

cf. [PhTl(III)(DBC)Cl]ClO₄; ³J(Tl-H_O) = 945.

[PhY1 (III) (DBC) CH₃] ClO₄; ³J (T1-H₀) = 444.

are shown in the Table. These values are smaller than that of chloro complex but larger than the methyl analogue. The $^3J(\text{Tl-H}_2\text{O})$ values of 2 - 4 decrease in the order $\text{S} > \text{Se} > \text{Te}$ and the Tl-Te bond has been considered to have the largest covalent character among these complexes. The Tl-Se bond is close to that of the Tl-S bond rather than the Tl-Te. In the ^{77}Se NMR spectra of 2c, $^1J(\text{Tl-}^{77}\text{Se})$ was found to be 9020 Hz.

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THE CHEMICAL AND STEREOCHEMICAL ACTIVITY OF THE LONE PAIR IN TIN(II) COMPLEXES

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The Structures of a selection of Sn(II) complexes from the crystallographic literature (including a series prepared and solved in our laboratories) were examined and compared, with a view to discovering general structural patterns, especially regarding intermolecular close contacts and the stereochemical activity of the tin lone pair. Certain patterns in coordination sphere geometries (primary and secondary) have emerged.

An attempt to measure the chemical reactivity of the tin lone pair in a series of complexes has been made, by studying adduct formation between the complexes and certain Lewis acids. Structural analysis of the resulting adducts may also provide information regarding the activity of the lone pair.

TIN-119 NMR INVESTIGATION OF THE FORMATION AND STEREOCHEMISTRY IN SOLUTION OF ORGANOYLTIN(IV)HALIDE COMPLEXES WITH DITHIOLATE LIGANDS

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As part of our ongoing program investigating the stability and stereochemistry of complexes derived from organoyltin(IV)halide compounds in solution [1, 2] we will present tin-119 NMR data for formation of several series of dithiolate complexes $R_2SnX(S-S)$, $R_2Sn(S-S)_2$ ($R = Me, ^nBu, ^tBu, Ph$; $X = Cl, Br, F$; $S-S = S_2CNEt_2, S_2COEt, S_2P(OEt)_2$) and $RSnX_n(S-S)_{3-n}$ ($R = Ph$; $n = 1-3$).

In many cases solution tin-119 NMR data establish the coordination number of the tin and are able to distinguish between monodentate and bidentate coordination modes from the dithiolate ligands. For example the xanthate ligands in $^nBu_2Sn(S_2COEt)_2$ are bidentate whereas in the more sterically restricted analogue, $^tBu_2Sn(S_2COEt)_2$, the dithiocarbamate ligands are apparently monodentate. Interestingly, the dithiolate ligand in $^tBu_2Sn(S_2COEt)Cl$ appears to be bidentate.

NMR data will be presented for what we believe to be unusual examples of organoyltin(IV) complexes containing one or more coordinated fluoride ions. Interestingly, halide exchange is slow at room-temperature for $PhSnX_n(S-S)_{2-n}$ when $X = Cl$ or Br (or a mixture thereof) but when $X = F$, cooling is required before halide exchange becomes slow enough on the NMR timescale to allow observation of Sn-F coupling.

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HYDROGEN BONDING IN ORGANOTIN (IV) COMPLEXES. SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL STRUCTURE OF SOME DIVINYLTIN COMPLEXES.

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The co-ordinating properties of organotin(IV) halides or pseudohalides toward N-donor ligands are of interest particularly because of their relevance to organotin interactions with biological system.

Moreover hydrogen bonding is an important feature of the structure of several organotin(IV) complexes[1].

In this contest some new adducts of $(\text{CH}_2=\text{CH})_2\text{SnX}_2$ ($\text{X}=\text{Cl}, \text{CNS}$) with N-bonded heterocyclic ligands (Pyrazole, Imidazole, 1-10 Phenanthroline) have been characterized by means of i.r , n.m.r. spectroscopy and X-ray diffraction methods.

The structure of the complex $(\text{CH}_2=\text{CH})_2\text{SnCl}_2 \cdot 2\text{C}_3\text{H}_4\text{N}_2$ (pyrazole) is described.

The configuration about the tin atom, centre of symmetry, is all trans octahedral. The $\text{C}_3\text{H}_4\text{N}_2$ ligands are bonded to the metal through the N(2) atom. The H atom on the N(1) atom of each pyrazole takes part in an intramolecular hydrogen bond with a chloride ligand and in an intermolecular hydrogen bond with chloride in a neighboring molecule.

The structure of other divinyln complexes is described on the bases of the infrared pattern.

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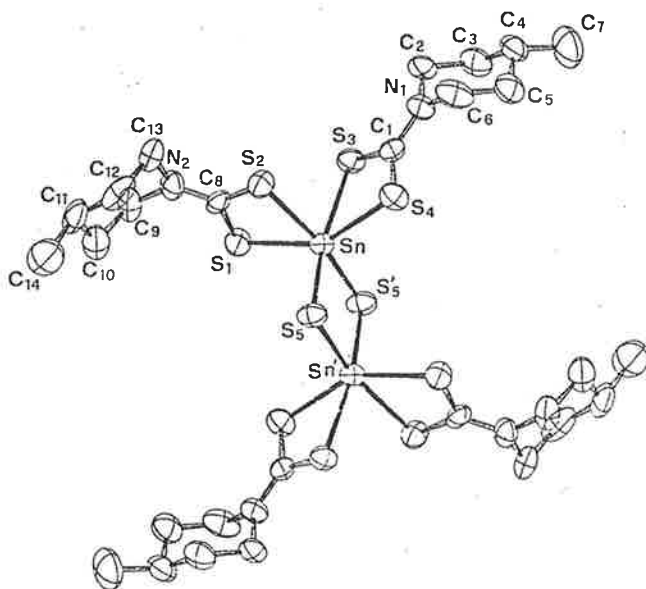
TIN METHYL-DITHIOCARBAMATE COMPLEX CRYSTAL STRUCTUREA.C.Fabretti and C.Preti

Department of Chemistry, University of Modena, Italy

Following our interest in the chemistry of the metal dithiocarbamate complexes we report the crystal and molecular structure of the compound di- μ -sulphido-bis 4-methyl-piperidine-dithiocarbamate tin(IV).

The crystal are monoclinic, space group $P2_1/n$, with $a = 12.330(2)$, $b = 11.930(1)$, $c = 17.055(2)$ Å, $\beta = 106.21(1)^\circ$ and $Z = 4$. The structure was solved by the heavy-atom method, and least-squares refinement of structural parameters led to a conventional R factor of 0.028 for 1284 independent reflections. The structure consists of discrete dimeric units with the metal coordinated to six sulphur atoms.

This is the first example of a tin dithiocarbamate complex bearing bridged sulphur atoms.



STRUCTURES OF MONO- AND BIS-(ETHYLENEDIAMINE)LEAD(II) HALIDES,
AND BIS-(1,10-PHENANTHROLINE)LEAD(II) HALIDES

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When powdered lead(II) halide(PbX_2) with appropriate concentration of Lewis base solution was sealed in a branched glasstube and the branch containing PbX_2 was heated to keep warmer than the other side, lead(II) complex was crystallized in cooler part of the glasstube after a several days. In this way, we obtained following ethylenediamine(en) and phenanthroline(phen) complexes: $Pb(en)Cl_2$, $Pb(en)Br_2$, $Pb(en)_2Cl_2$, $Pb(en)_2Br_2$, $Pb(phen)_2Br_2$, and $Pb(phen)_2I_2$. X-ray structure analysis shows that each pair of compounds are isomorphous.

In $Pb(en)X_2$, the Pb atom is surrounded by two N and five X atoms in distorted square-capped trigonal prism. But in PbL_2X_2 , the atom on two-fold axis is coordinated by four N and two X atoms in distorted octahedron, being X atoms in cis positions with largely expanded X-Pb-X bond angle ($\sim 147^\circ$ and $\sim 125^\circ$ for en and phen complexes, respectively).

En molecules in $Pb(en)_2X_2$ exhibit two coordination geometry as in the case of $Pb(en)_2I_2$ [1]: One is chelating and the other bridging. The latter are bonded to Pb at trans positions with Pb-N distance of $\sim 2.60 \text{ \AA}$ which is longer than those in chelating ones ($\sim 2.45 \text{ \AA}$). The difference is consistent with those observed in cis- and trans-forms of $Pb(\text{pyridine})_2I_2$ [2].

On the contrary, two of phen molecules are symmetrically chelated with Pb-N distance of $\sim 2.60 \text{ \AA}$.

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GROUP 15 (PHOSPHORUS, ANTIMONY, AND BISMUTH) PORPHYRIN COMPLEXES

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The chemistry of Transition Metal porphyrin complexes is well established as a focal point in inorganic chemistry. Recently, this interest has extended to complexes containing Main Group elements inserted into the porphyrin macrocycle. The importance of Main Group compounds in the semiconductor industry and as therapeutic agents in medicine, combined with the unique properties conferred by the porphyrin ligand, may result in compounds with novel properties. To date, the most notable advances in this area have been achieved for Groups 13 and 14 porphyrin complexes [1,2].

Although the insertion of all the heavier Group 15 elements into substituted porphyrin macrocycles has been reported in the literature, there has been some confusion over the identity and oxidation state of the products [2]. We have reinvestigated this chemistry, and have developed improved syntheses of cationic phosphorus(V) tetra-*p*-tolylporphyrin (TTP) complexes, $[P(TTP)Cl_2]Cl$ and $[P(TTP)(OH)_2]OH$. Antimony(V) and bismuth(III) species, $[Sb(TTP)(OH)_2]X$ ($X = Cl, SbCl_6$), $[Sb(TTP)(OH)_2]OH$ and $[Bi(TTP)]NO_3$, are the first fully characterised tetraarylporphyrin complexes containing antimony and bismuth to be prepared. The characterisation of these products resolves the confusion surrounding the oxidation states of the antimony and bismuth derivatives. Other new species include $[M(TTP)(OR)_2]^+$ ($M = P, R = CH_3, CH_2CH_3, p-C_6H_4CH_3, p-C_6H_4OH, o-C_6H_4OH$; $M = Sb, R = CH_3$) and $[P(TTP)(NH-p-C_6H_4CH_3)_2]^+$. For the first time, ^{31}P NMR data has been recorded for phosphorus porphyrin complexes. These data reveal the marked upfield shift of the coordinated phosphorus atom, and remarkable seven-bond P-H coupling. An NMR analysis of the bismuth complex $[Bi(TTP)]NO_3$ demonstrates temperature dependence of the NMR spectrum, related to exchange of the nitrate anion.

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TELLURIUM IV COMPOUNDS WITH SULFUR-CONTAINING LIGANDS

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Our group [1] and others [2, 3], both very recently and some time ago, have reported on the synthesis and structures of various tellurium IV compounds containing sulfur ligands such as $\text{Ph}_2\text{Te}[\text{S}_2\text{P}(\text{OMe})_2]_2$, $p\text{-MeOC}_6\text{H}_4\text{TeBr}_2[\text{S}_2\text{P}(\text{OMe})_2]$, $\text{Ph}_2\text{Te}[\text{S}_2\text{CNMe}_2]_2$, $\text{Ph}_2\text{TeCl}[\text{S}_2\text{CNEt}_2]$, $\text{Ph}_2\text{TeCl}[\text{S}_2\text{CN}(i\text{-Pr})_2]$ [1], $\text{Ph}_2\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]$, $\text{Ph}_2\text{Te}[\text{S}_2\text{CNEt}_2]_2$, $\text{PhTe}[\text{S}_2\text{CNEt}_2]_2[\text{S}_2\text{P}(\text{OEt})_2]$, $\text{MeITe}[\text{S}_2\text{CNEt}_2]_2$ [2] and $\text{PhTe}[\text{S}_2\text{CNEt}_2]_3$ [3].

Structurally, the compounds have been variously described as four, five, six, seven or eight coordinated depending on whether secondary interactions and/or lone pairs are counted along with the normal tellurium-carbon, -sulfur, or -halide bonds.

The poster will provide several additional examples of R_2TeL_2 species as well as RTeL_3 and R_3TeL compounds, where $\text{R} = \text{Ph}$, Cl , Br and $\text{L} =$ dithiocarbamate, dithiophosphate or xanthate. The preferred arrangements leading to specific secondary interactions will be explored.

The formation of crystals of many of these types of compounds may be considered fortuitous because of their tendency to undergo redox reactions to give R_2Te and diligand. Evidence of decompositions or rearrangements other than these will be presented.

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ADIABATIC ELECTRON AFFINITIES FOR TRIS(CHELATE) TRANSITION METAL COMPLEXES DETERMINED BY GAS-PHASE ION TECHNIQUES

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Electron affinity (EA) is defined as the absolute value of the enthalpy change for the adiabatic process $A(g) + e^- \rightarrow A^-(g)$ at 0 K and is equivalent to the adiabatic ionization potential of $A^-(g)$. Values for EA can be estimated by experimental determination of the enthalpy for the electron attachment at $T > 0$ K. Electron affinities can be combined with the thermodynamics of solvation to yield absolute reduction potentials. Thus, an EA value represents the "intrinsic reduction potential" of a molecule in the absence of solvation and is valuable for theoretical analysis of factors determining observed electrode potentials in solution. In addition, molecules that present experimental difficulties in determination of E^0 values due to irreversible electrode behavior or extremely large oxidizing or reducing potentials can often be studied readily by gas-phase methods. The EA values for a large number of organic molecules have been reported, but with the exception of several metal hexafluorides, $M(VI)F_6$, EA values have not previously been reported for transition metal coordination complexes.

In the present work, we have used Fourier transform ion cyclotron resonance mass spectrometry to estimate EA values for a number of pseudooctahedral $M(III)$ tris(chelate) complexes. In these studies, anionic charge-transfer reactions are observed between organic acceptors of known EA and a series of neutral complexes such as $M(\text{acetylacetonate})_3$ and $M(\text{hexafluoroacetylacetonate})_3$ ($M = \text{Sc} - \text{Co}, \text{Ga}$). The general reaction is $ML_3 + A^- = ML_3^- + A$, and if the value of EA is sufficiently small the reaction will come to equilibrium in the FTICR ion trap. Values of EA for the acac and hfac complexes are in the range $\sim 0.9 - 2.5$ eV and $2.7 - 4.5$ eV, respectively.

As expected, the general trend for the complexes is increasing EA from left to right (Sc - Co), with variations due to increasing number of electrons in predominantly metal d molecular orbitals. Variations from a smooth trend can be semi-quantitatively accounted for by consideration of electronic configurations for the $M(II)/M(III)$ couples via the ligand field theory model. Molecular orbital calculations can be used to estimate electronic relaxation effects that determine the dependence of the potentials on the nature of the ligands.

Similar approaches can be used to investigate the thermodynamics of gas-phase oxidation and reduction processes for other coordination complexes and organometallic species.

THERMODYNAMICS OF COMPLEX FORMATION OF URANYL(VI) WITH AMINES IN DIMETHYL SULFOXIDE. THE INFLUENCE OF SMALL AMOUNTS OF WATER.

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It is well known that in coordination systems involving metal ions classified as "hard" acceptors, like the actinide ions, in aqueous solution, most ligands coordinating only via nitrogen are so basic that they coordinate the protons of the water instead of the metal ion, thus causing the formation of metal-hydroxo complexes. This behaviour makes it impossible to carry out quantitative studies on the metal-nitrogen interactions in aqueous solutions. These interactions may be investigated, as a rule, in non-aqueous solvents. Experimental information about the nature and stability of complex species of actinide ions with neutral N-donors in solution is almost inexistent in the literature.

The purpose of the present investigation was to provide quantitative information about the existence and thermodynamic stability in dimethyl sulfoxide solution of complexes of the uranyl(VI) ion with the ligands n-butylamine, ethylenediamine, and propylenediamine. Extreme care was taken to work under anhydrous conditions and some measurements were performed to investigate the influence of small amounts of water on the coordination systems considered. The experimental methods used were calorimetric measurement of enthalpies of complexation, potentiometric measurements using an Ag/Ag⁺ electrode and Ag⁺ as competitor, and FT-IR spectra in solution.

The results consistently indicated that in the uranyl(VI) - n-butylamine system only a very weak interaction, if any, takes place between metal ion and ligand, and when water is present, even in small amount, the following hydrolytic reactions occur:

$$x\text{UO}_2^{2+} + y\text{RNH}_2 + y\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_x(\text{OH})_y^{(2x-y)+} + y\text{RNH}_3^+$$

In the uranyl(VI) - ethylenediamine and - propylenediamine systems chelate complexes are formed. Their composition, stability, and thermodynamic parameters are as follows:

Ligand	Reaction	log β	$-\Delta H$ kJ mol ⁻¹	$-\Delta S$ JK ⁻¹ mol ⁻¹
Ethylenediamine	M+L \rightleftharpoons ML	3.88(2)	41.4(6)	64(3)
	M+2L \rightleftharpoons ML ₂	5.88(5)	76.7(9)	145(4)
Propylenediamine	M+L \rightleftharpoons ML	1.15(4)	41(2)	117(8)

Water present at a concentration comparable to that of the metal ion does not interfere with formation of the 1:1 ethylenediamine complex, but hydrolytic reactions are competitive with formation of the second ethylenediamine complex and of the propylenediamine one.

The identified complexes are enthalpy stabilized whereas the entropy terms oppose the complex formation. This trend is the reverse of the one generally found in aqueous solution for the actinide ions and may be discussed in terms of the properties of the different coordination systems.

LINEAR FREE ENERGY RELATIONSHIPS: COPPER(II)-N-(META-SUBSTITUTED PHENYL)
IMINODIACETIC ACID- α -AMINOACIDS COMPETITIVE TERNARY SYSTEMS

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The formation constants of the competitive ternary mixed-ligand complex compounds Cu(II)-N-(meta-substituted phenyl) iminodiacetic acid (m-RPhIDA, R=CH₃, H, CH₃O, Cl)- α -aminoacids (L-Proline, α -aminoisobutyric acid, L-isoleucine, L-valine, glycine, L-serine) have been determined by pH method at 25°C and in the presence of 0.1 mol.dm⁻³ NaClO₄. Linear free Energy Relationships are found to exist between the following pairs

$\log \beta_{111}$ vs pK_2^a values of m-RPhIDA

$\log \beta_{111}$ vs pK_2^b values of the aminoacids

$\log \beta_{111}$ vs $\log \beta_{110}$ values of the parent binary complex compounds Cu(II)-m-RPhIDA

$\log \beta_{111}$ vs $\log \beta_{102}$ values of parent binary complex compounds Cu(II)- α -aminoacids

$\Delta \log \beta_M$ vs $\Delta pK_2'$ values

where β_{111} is the formation constant of the ternary complex compound

β_{110} is the formation constant of the parent binary complex compound Cu(II)-m-RPhIDA

β_{102} is the formation constant of the parent binary complex compounds Cu(II)- α -aminoacid

$\Delta \log \beta_M = \log \beta_{111} - \log \beta_{102}$

pK_2^a is the 2nd dissociation constant of m-RPhIDA

pK_2^b is the basic dissociation constant of α -aminoacid

$\Delta pK_2' = pK_2^b - pK_2^a$

The experimental results show that the higher is the base strength of the ligand the greater is its competitive ability in the formation of ternary complex compounds.

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STANDARD ENTHALPIES OF FORMATION OF BIS(8-HYDROXYQUINOLINATES) OF Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II). THE METAL-LIGAND BOND STRENGTHS.

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8-Hydroxyquinoline, (HOx), quelates to metal ions through the oxygen atom of the hydroxyl group and the nitrogen atom of the heterocycle. Although these complexes have been used in Analytical Chemistry for a long time, very little is known about the energetics of the metal-ligand bonds.

The standard molar enthalpies of formation, at 298.15 K, of some crystalline bis(8-hydroxyquinolate)metal complexes, $[M(Ox)_2]$, where $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$ and $Pb(II)$ were determined by solution-reaction calorimetry.

The standard molar enthalpies of formation in the gaseous state, of the same complexes, were derived using their enthalpies of sublimation.

The differences between the metal-ligand dissociation enthalpies, $\langle D \rangle(M-Ox)$, in the complexes and the (O—H) bond dissociation enthalpy in the parent ligand, $D(O-H)$, are calculated and compared with the corresponding differences for the complexes of the same metals with 8-hydroxy-5-nitroquinoline and with 8-hydroxy-5-methylquinoline.

The results are discussed in terms of structure of the complexes and of the energetics of the chelate bonds.

Thermochemistry Of Cationic Complexes Of Cadmium (II)

Trifluoromethanesulfonate in Acetonitrile solution

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Complexes of $\text{Cd}(\text{O}_3\text{SCF}_3)_2$ with phosphines in different solvents have been reported [1] . Results of calorimetric titration for the titled compound with different bases in acetonitrile solution at 30°C is summarised for the reaction:

$$\text{Cd}^{2+} + n\text{B} \rightleftharpoons [\text{Cd B}_n]^{2+}$$

Base	n	K (lmol^{-1})	$-\Delta H^\circ$ (kJmol^{-1})
Bu ₃ P	1-3	$>10^{12}$	60.61
	4	$>10^3$	24.39
2-mepy	1	80	22
4-mepy	1	423	27
	2	56	27
py	1	400	27
	2	57	27
1,10-phen	3	$>10^{12}$	133
2,2'-dipy	3	$>10^{12}$	94

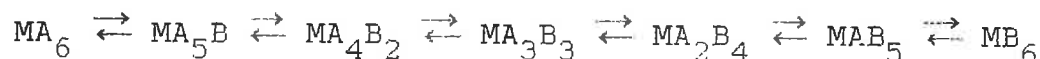
Conductometric titration of $[\text{Cd}(\text{DSMO})_6](\text{O}_3\text{SCF}_3)_2$ in Acetonitrile with the bases studied reveals 2:1 electrolyte solution and $[\text{O}_3\text{SCF}_3]^-$ is not coordinated. The Bidentate Nitrogen donors give 6-coordinate cationic Complexes, while one- and two-coordinated species are formed with 2-mepy , 4-mepy. Bu₃P can make 3- and 4 -coordinate adducts.

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SOLVATION OF METAL IONS IN MIXED SOLVENTS.
A CHEMOMETRICAL APPROACH

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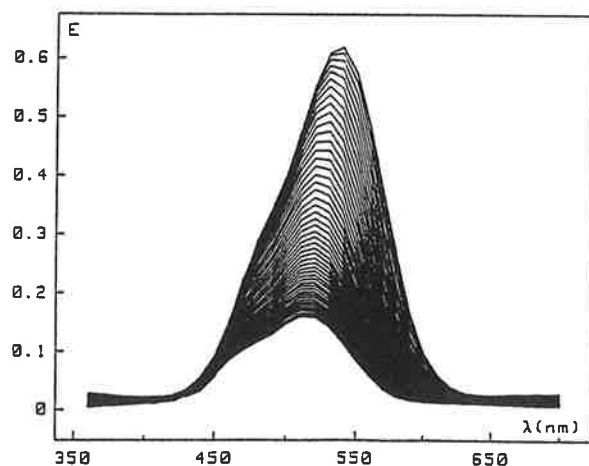
The solvation of transition metal ions of octahedral coordination geometry in a binary mixture of solvents A and B can be described in general terms by a series of equilibria



MA_6 is formed in pure A, MB_6 in pure B and all the other complexes exist to different degrees in the mixed solvents. No practicable functional relation can be used to describe the concentrations of the different complexes as the activities of all complexes as well as of both solvents are not known and are not constant at all throughout the whole range of solutions from pure A to pure B.

Evolving Factor Analysis has been developed to deconvolute overlapping concentration profiles in chromatography and equilibrium studies in a *completely modelfree* way [1,2] and therefore is ideally suited to analyse these coordination equilibria in mixed solvents.

Co^{2+} has been investigated spectrophotometrically in the solvent mixture DMSO/water and using *Evolving Factor Analysis*, the highly overlapping concentration profiles of all seven complexes together with their individual absorption spectra have been resolved.



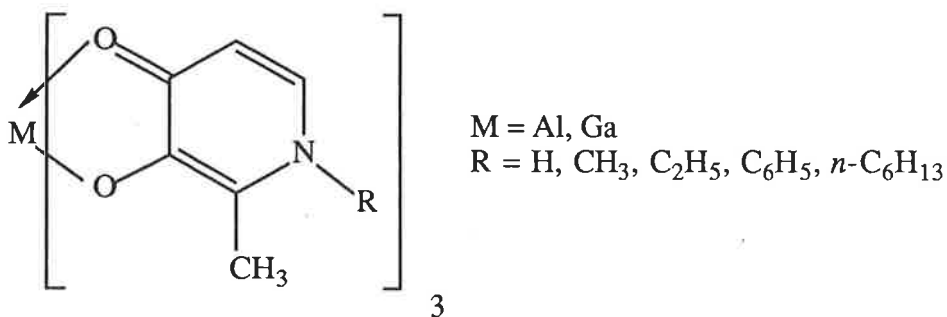
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SOLUTION CHEMISTRY OF ALUMINUM AND GALLIUM COMPLEXES OF 3-HYDROXY-4-PYRIDINONES.

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A series of 3-hydroxy-2-methyl-4-pyridinones and their complexes with aluminum(III) and gallium (III) have been characterized by potentiometric (glass electrode) titration. The equilibria have been examined at a temperature of $25.0 \pm 0.1^\circ\text{C}$ and an ionic strength of $\mu = 0.15\text{ M NaCl}$.



The pyridinones have a variety of substituents at the ring nitrogen atom (H , CH_3 , C_2H_5 , C_6H_5 , and $n\text{-C}_6\text{H}_{13}$), and the pyridinonate anions are characterized by two stepwise protonation constants of $\sim 10^{9.8}$ and $\sim 10^{3.7}$. These ligands form ML_3 complexes ($n = 1, 2, 3$) of high stability; the overall stability constants β_3 for the 3:1 complexes are all $\sim 10^{32}$ for $M = \text{Al}$ and $\sim 10^{38}$ for $M = \text{Ga}$. At ligand to metal ratios ≥ 1 , the ligands prevent M(III) hydrolysis at mM concentrations, even under slightly basic conditions, and the effective formation constants ($\beta_{3\text{eff}}$) of the various ligands for M^{3+} at physiological pH are $\sim 10^{24}$ for $M = \text{Al}$ and $\sim 10^{31}$ for $M = \text{Ga}$. The binding of these ligands to Al^{3+} is considerably enhanced (ten orders of magnitude) from their pyrone congeners. Several examples of the practical application of these data are discussed: confirmation of Al^{3+} speciation (particularly hydrolysis behaviour) as deduced from ^{27}Al NMR spectra; comparative metal binding in a simple blood plasma model is simulated; and an attempt will be made to predict the biodistribution of the ^{67}Ga complexes of these ligands.

RH(III) COMPLEXES WITH AROMATIC DIAMINES INTERCALATED IN LAYERED ION-EXCHANGERS : THERMAL, REDOX AND XPS CHARACTERIZATION.

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Rh-compounds are increasingly employed in different homogeneous catalytic processes. An eventual anchorage of these compounds on insoluble matrices should be of great interest in order to minimize their loss and facilitate the separation of the catalyst from the substrate.

α -Zirconium hydrogenphosphate (ZP) is an insoluble layered ion-exchanger able either to directly exchange Rh^{+3} ions or to anchor, between its layers, in situ formed complexes of Rh^{+3} with aromatic diamines, such as 2,2'-bipyridil (bipy), 1-10 phenanthroline (phen) or 2,9 dimethylphenanthroline (dmp).

With a Rh^{+3}/H^+ exchange process, a completely converted Rh-ZP phase can be prepared with formula $ZrRh_{0.65}(PO_4)_2 \cdot 2H_2O$

and an interlayer distance (d_{002}) of 11.6 Å, in comparison with the 7.6 Å value of the hydrogen form.

When the aromatic diamine-ZP intercalation compounds are contacted with Rh^{+3} solution, Rh-diamine complexes are formed and the new materials have composition and d_{002} depending on the ligand initially present in the interlayer region. The most common compounds obtained are : ZP-bipy_{0.25}Rh_{0.13}·1.8H₂O

(d_{002} =10.9Å) ; ZP-phen_{0.38}Rh_{0.38}·2.5H₂O (d_{002} = 13.58 Å) and ZP-dmp_{0.38}Rh_{0.38}·3.2H₂O with a d_{002} = 14.77 Å.

By heating below 100°C, the Rh-diamine-ZP compounds dehydrate reversibly, while the ligand decomposition begins above 280-300°C. Reduction experiments with H₂ at 100°C slowly lead to a partial Rh reduction to Rh⁰, without change of the interlayer distance. The X-ray diffraction patterns do not reveal presence of metallic Rh, that therefore must be still well dispersed between the layers of the host.

The XPS results give very interesting information on the ligands and on Rh-complexes formed between the layers of ZP. In the case of ZP-bipy-Rh compound the Rh 3d_{5/2} XPS spectra show a peak at 309.1 eV, typical of Rh^{+3} . The analysis of the N1s band for this compound gives three b.e. values at 399.2, 400.1 and 401.7 eV. The first b.e. value is to be ascribed to a free nitrogen, the second to a coordinated N (the greater part) and the third one to a N protonated to the P-OH groups, also present in the interlayer region.

After the reduction at 100°C, a marked decrease of the peak corresponding to the N-coordinated is observed together with a change of Rh b.e. value, which now has a maximum at 307.4 eV, ascribed to Rh⁰, main product of the reduction, and a shoulder at 308.9 eV., referring certainly to Rh^{+3} still present.

The behaviour of the ZP-phen-Rh and ZP-dmp-Rh intercalation compounds is very similar to that of ZP-bipy-Rh.

FT-IR EMISSION SPECTROSCOPIC INVESTIGATION OF SURFACE METAL-CARBONYL COMPLEXES

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In the past 15-20 years, a great number of excellent surface probing methods (various electron spectroscopies, surface enhanced Raman and reflection absorption IR spectroscopies etc.) have been developed for "clean", well-defined surfaces (e.g. metal single crystals) under ultra high vacuum conditions and at low temperatures. Unfortunately, most of the results obtained by the above techniques are not transferable to "real" catalytic systems (e.g. dispersed, supported metal catalysts). In such cases FT-IR spectroscopy with its fast signal accumulation possibilities offers a possible solution to measure IR spectra under very poor energy conditions. FT-IR emission spectroscopy seemed to be especially promising in the case of roughly absorbing or opaque substrates. The weak emission bands of small amounts of absorbed species may be masked, however, by the enormous background radiation of the support.

M-CO type surface complexes have been detected for Pt⁰/NaY (Zeolite) [1], Pt⁰/Al₂O₃ (alumina) and Pt⁺/Al₂O₃ [2,3], M(CO)₂ species have been established on the surface of Rh⁰/Al₂O₃ [2,3], Ru⁰/Al₂O₃ [4] and formation of [Re(CO)₃OH]₄ cubic tetramer complex has been identified on Re₂(CO)₁₀/Al₂O₃ systems [5].

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COMPLEX FORMATION AT A MODIFIED SILICA SURFACE

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DPA (Dipicolylamine) was bound to the surface of SiO₂ (I:Aerosil 300-5, Degussa; II:Nucleosil 100-5, Macherey-Nagel) [1]. The modified surface was characterized by elemental analysis, thermogravimetry and acid-base titration. A surface coverage of $5.3 \cdot 10^{-4}$ mol DPA/g of I and $5.6 \cdot 10^{-4}$ mol DPA/g of II was obtained. This corresponds to an identical surface density of one DPA per 10^{-18} m² for I and II. The binding capacity for Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ [Table 1] was determined by the distribution of these ions between surface and solution (pH = 4.7; KNO₃ = 0.5 M). The values indicate, that not each DPA group can complex a metal ion at the same time. The affinity constant of the surface for H⁺ was calculated from the titration curve. Each DPA can bind two H⁺ with the two conditional (0.5 M KNO₃) pK_a values of 2.0 - 2.4 and 5.5 - 6.5 respectively. These constants are slightly dependent of the degree of protonation, indicating only a small electrostatic interaction between different DPA. The affinity constants for the transition metal ions were deduced from competition equilibria between surface bound DPA and a ligand (NTA for Co²⁺, Ni²⁺ and Zn²⁺; EDTA for Cu²⁺) in solution (pH 4.7, 0.5 M KNO₃). They are compared with the conditional complex formation constants of DPA in solution [Table 1]. The absorption equilibria are reversible. The metal ions were completely desorbed by EDTA solution at pH 9. Competition between different metal ions for complexing sites at the surface confirm the order of the affinity constants.

Table 1

M ²⁺	Capacity mol/g SiO ₂	Surface bound DPA log K (pH 4.7, 0.5M KNO ₃)	DPA in solution [2] log K (pH 4.7, 0.1M KNO ₃)
Co	$2.5(3) \cdot 10^{-4}$	5.7	5.65
Ni	$2.6(3) \cdot 10^{-4}$	8.0	6.90
Cu	$3.1(3) \cdot 10^{-4}$	11.4	11.45
Zn	$2.7(3) \cdot 10^{-4}$	5.2	5.23

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PREPARATION AND PROPERTIES OF MONODISPERSED SPHERICAL-COLLOIDAL PARTICLES OF LANTHANUM HYDROXYCARBONATE.

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Colloidal lanthanum hydroxycarbonate particles of narrow size distribution were obtained by aging at elevated temperatures a solution of lanthanum chloride ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$) in the presence of urea. A basic carbonate sol consisting of amorphous spherical particles was produced.

The precipitated solids were characterized by their electrokinetic and optical properties. The size distribution was determined, and the spherical particles of lanthanum hydroxycarbonate were converted to the oxide, without a change in morphology, by calcination. Transmission electron micrograph and X-ray analysis results will be displayed.

SOLID STATE REDOX REACTIONS OF COORDINATION COMPOUNDS AT ROOM TEMPERATURE

Xinquan Xin and Xiaoping Wang

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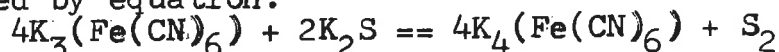
The study of solid state reactions of coordination compounds at relatively low temperature is concerned by both coordination chemistry and solid state chemistry. Synthesis of several compounds by solid state reaction has been reported in our labs last year. Here are listed some solid state redox reactions of potassium hexacyanoferrate (II) and (III) with various reductants or oxidants that have been studied:

1. $K_3(Fe(CN)_6)$ and KI

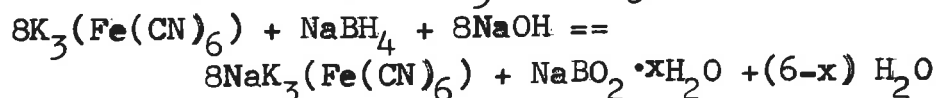
It is well known that in solution $K_4(Fe(CN)_6)$ react with I_2 to produce $K_3(Fe(CN)_6)$ and KI. The situation is just reversed in solid state reaction.

2. $K_3(Fe(CN)_6)$ and K_2S

The reaction of the system in solid state may be represented by equation:

3. $K_3(Fe(CN)_6)$ and $NaBH_4$

When the above solids are mixed, there is no reaction. If some base such as NaOH or KOH and the reductant are added in sufficient quantity, all $K_3(Fe(CN)_6)$ is well reduced:

4. $K_4(Fe(CN)_6)$ and $K_2S_2O_8$

$K_4(Fe(CN)_6)$ is easily oxidized by peroxosulfate ion in aqueous solution. But in solid state, the system reacts only slowly, and if solid $K_4(Fe(CN)_6)$ is first mixed with KOH, it gives no reaction with $K_2S_2O_8$.

Conclusion

1. Many redox reactions of the same reactants in solid state are quite different from those in aqueous solution.
2. Solid state redox reactions may be greatly changed by a strong base or an acid.

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SYNTHESIS AND STRUCTURE OF A BINUCLEAR COMPLEX OF COPPER (II) PERCHLORATE WITH N,N'-BIS(3-AMINO-PROPYL) OXAMIDE AND 1,10-PHENANTHROLINE

Zhi-Yong Zhang*, Song-Qi Hao** and Geng-Lin Wang

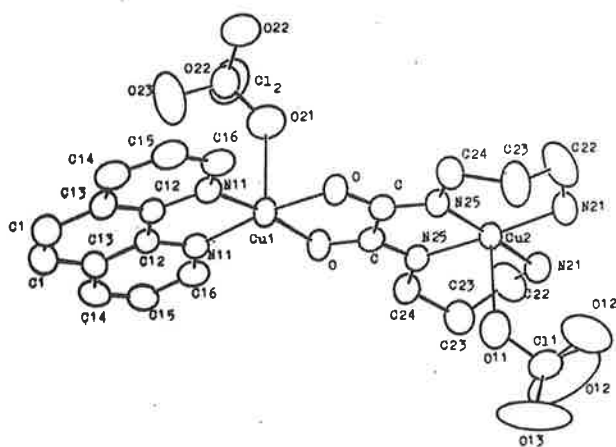
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A new binuclear copper (II) complex, $[\text{Cu}(\text{oxpn})\text{Cu}(\text{phen})](\text{ClO}_4)_2$, has been synthesized, where oxpn and phen are N,N'-bis(3-amino-propyl) oxamide and 1,10-phenanthroline respectively, and a royal purple single crystal having approximate dimensions of 0.3x0.3x0.4mm was obtained. The crystal is orthorhombic, space group Pnma, with $a=10.432(1)$, $b=11.458(2)$, $c=24.999(2)\text{\AA}$, $z=4$, 2654 independent reflections were collected by an Enraf-Nonius CAD4 diffractometer, in which 1575 observable reflections were used for refinement. The final deviation factor $R=0.047$ and $R_w=0.055$.

The structure consists of $[\text{Cu}(\text{oxpn})\text{Cu}(\text{phen})]^{2+}$ cations with weakly coordinated perchlorate anions. The two copper(II) ions are in square-pyramidal surroundings with almost coplanar basal planes. The dihedral angle between the two basal planes is $4.52\pm 0.97^\circ$. The molecule has a symmetric plane which is perpendicular to the basal planes and passes through Cu_1 and Cu_2 . The two copper ions are linked by μ -Oxamide and the separation of them is 5.208\AA . Further investigations are in progress.

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PREPARATION AND PROPERTIES OF A SERIES OF BIMETALLIC COMPLEXES WITH SCHIFF BASE LIGANDS

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In recent years considerable efforts have been directed towards syntheses of new type bidental Scheff base ligands and their bimetallic complexes. However, it appears that most of works in this area deal with homobimetallic complexes. We attempt to prepare N,N'-alkylene-bis-salicyl-3-formyl-dimine(alkylene=ethylene(ES), or propylene(PS)) which form a nearly planar binuclear complex in such a way that two phenolic oxygens of the ligand bridge two homo- or hetero-metal ions. Three types of complexes: mononuclear, homo-binuclear and heterobinuclear complexes have been prepared. Buecher's method^[1] and Poddar's method^[2] were modified for the preparations of ES and PS and their mononuclear complexes, respectively. Binuclear complexes were prepared by the reaction of mononuclear complexes of Cu(II) with $M(\text{Ac})_2 \cdot (\text{H}_2\text{O})_n$ ($M=\text{Cu}(\text{II}), n=1; M=\text{Mn}(\text{II}), n=4; M=\text{Co}(\text{II}), n=4; M=\text{Zn}(\text{II}), n=2$) in ethanol, all analysed reasonably well.

The IR, UV-VIS and magnetic moments are as below.

	IR Bands(cm^{-1})				d-d Bands(kK)		(B.M) μ_{eff}
	-COOH	-COO-	-C=N	Skeletal	in DMSO	in MeOH	
ES	1698		1651				
PS	1693		1650				
CuES		1595	1630	1544	17.5	18.2	1.85
CuPS		1595	1615	1548	15.4	15.6	1.86
Cu ₂ ES			1636	1558	18.9	19.2	1.03
Cu ₂ PS			1624	1569	13.5-16.1		0.97
CuMnPS			1623	1558	16.4	16.1	4.16
CuCoPS			1619	1563	16.1	16.1	3.20
CuZnPS			1620	1565	16.1	15.9	1.93

A new IR band appeared around $1544\text{--}1569\text{cm}^{-1}$ upon complexation could be assigned to the skeletal vibration of aromatic rings^[3]. The fact that all the bands of binuclear complexes compared with those of mononuclear complexes move to higher frequencies indicates that binuclear complexes were formed^[4].

The lower energy d-d band of CuPS, compared with that of CuES, suggests that the configuration around the Cu(II) ion in CuPS is slightly distorted from planarity. Cu₂PS has a wider band around $13.5\text{--}16.1\text{kK}$ which could be attributed to the differences of steric environment of the two Cu(II) ions.

The values of magnetic moments support that the Cu(II) in CuPS is in a environment of distorted planarity, while the magnetic moments for bimetallics shows that all the metal ions are in a state of high spining and have stronger magnetic-exchange coupling which is one of the typical properties for bimetallic complexes.

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X-RAY STRUCTURE AND PROPERTIES FOR A SERIES OF OXO-CENTERED
HETEROTRINUCLEAR COMPLEXES $[\text{Fe}_2\text{MO}(\mu\text{-CH}_3\text{COO})_6\text{Py}_3] \cdot \text{Py}$ (M=Mn, Co, Ni)

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The series of oxo-centered heterotrinnuclear complexes have been prepared and studied crystallographically as well as spectroscopically. They are $[\text{Fe}_2\text{MO}(\mu\text{-CH}_3\text{COO})_6\text{Py}_3] \cdot \text{Py}$ (I: M=Mn, II: M=Co, III: M=Ni).

Single crystal structures of I, II, III, have been determined by X-ray diffractive method. Their crystallographic parameters are listed in Tab.1. The molecular structure of

all these complexes can be described approximately as three octahedra sharing a common vertex of $\mu\text{-O}$ atom lying in the plane of Fe_2M triangle. Three Py ligands coordinated to the metal ions are nearly parallel to the Fe_2MO plane in I and II but perpendicular in III. Table 2 shows the bond lengths of Fe^{3+} and M^{2+} ion.

Table 1 Crystallographic Parameters

COMP.D.	I	II	III
S.G.	P1	P1	Cc
a(Å)	10.816(3)	10.778(2)	21.996(3)
b(Å)	10.816(3)	10.776(2)	12.479(5)
c(Å)	10.811(2)	10.777(2)	15.924(4)
$\alpha(^{\circ})$	108.96(2)	108.94(1)	116.97(1)
$\beta(^{\circ})$	109.01(2)	108.96(1)	
$\gamma(^{\circ})$	109.03(3)	108.96(1)	
Z	1	1	4
R	0.052	0.050	0.049

Table 2 Ligand Bond Lengths(Å)

	*Fe-Oc	M-Oc	*Fe-N	M-N	*Fe-Oac	*M-Oac
M=Mn	1.907	1.941	2.249	2.212	2.068	2.065
M=Co	1.893	1.938	2.122	2.164	2.058	2.049
M=Ni	1.866	1.938	2.208	2.142	2.036	2.013

* on a bond label denotes average value

characteristic of Fe^{3+} .

That are differ from mixed valence Fe_2FeO complexes^[1]. It can be illustrated by the PKS model expanding to these asymmetric tricentered systems in the first order approximation.

The electronic spectra for the series of complexes have also been examined and well assignment with the ligand field theory. The parameters of ligand field for related metal ions of those compounds have been calculated by the Tanabe-Sugano diagrams. The results are given in Tab.3.

Table 3 Ligand Field Parameters

COMP.D.	I		II		III	
ion	Fe^{3+}	Mn^{2+}	Fe^{3+}	Co^{2+}	Fe^{3+}	Ni^{2+}
B(cm^{-1})	615	719	645	807	664	943
Dq(cm^{-1})	1200	913	1320	850	1450	995

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SPECTRAL STUDIES OF URANYL(VI) COMPLEXES

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ABSTRACT

The Uranyl(VI) complexes of pyridine based pentadentate ligands, derived from 2,6-diacetyl pyridine and semicarbazide (DAPSC) and benzoylhydrazide (DAPBH) have been described and characterized on the basis of spectral studies in addition to elemental analysis and electrical conductance. The spectral IR and electronic studies were done in different solvents and at different pH. The ligands form complexes of the type $[(UO_2)(DAPSC)_x]X$ and $[(UO_2)(DAPBH)_x]X$. The template effect of Uranyl(VI) has been studied in the cyclization of 2,6-diacetylpyridine with carbohydrazide and 2-phenylenediamine. The complexes obtained from 2,6-diacetylpyridine and 2-phenylenediamine represented as $(UO_2Mac_1)_x$, where Mac is a macrocyclic hexadentate (M_6) ligand and complexes obtained by the condensation of 2,6-diacetylpyridine and carbohydrazide has been formulated as $(UO_2)_2(Mac_2)_x$, where Mac_2 is a heptadentate macrocyclic ligand. The formulation of macrocyclic ligand complexes is indicated by the absence of $\nu(C=O)$ of 2,6-diacetylpyridine and formation of azomethine linkage. The intense colour of these complexes also support the formation of macrocyclic ligands.

COORDINATION BEHAVIOUR OF SCHIFF BASES OF SULFADRUGS TOWARDS STANNOUS ION

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Compounds containing the sulphonamide group have long been used as drugs for diseases like cancer, tuberculosis, diabetes, malaria and convulsions. It has now been observed that some of these drugs show increased biological activity when administered in the form of metal complexes [1].

Keeping the above fact in mind, we have synthesized and characterized a number of compounds of tin(II) with Schiff bases derived by the condensation of 2-Hydroxy-1-naphthaldehyde with various sulfadugs viz., sulfathiazole, sulfaphenazole, sulfadiazine, sulfapyridine and sulfaguanidine.

Though, the preparation of pure tin(II) compounds presents difficulties on account of its ease of oxidation in aqueous solution, but it is usually possible to prevent this by carrying out synthesis in a deaerated solution in a non-oxidising atmosphere [2].

The nature of bonding has been further discussed on the basis of the electronic infrared, multinuclear magnetic resonance (^1H , ^{13}C , and ^{119}Sn) and ^{119}Sn Mossbauer spectral studies. The covalent bonding of oxygen and nitrogen to tin and coordinate bond between tin and nitrogen indicate trigonal pyramidal geometry for these derivatives.

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MIXED LIGAND COMPLEXES OF ALKALINE EARTH METALS

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Mixed ligand complexes of the type $[MLL'(H_2O)_2]$ (where M = Mg(II) or Ca(II) and HL is 2-hydroxybenzophenone and HL' is salicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione) have been synthesized by the 1:1:1 molar reactions of metal chlorides with the two different carbonyl compounds. The complexes are yellow solids and have been characterized by elemental analyses, TLC and NMR spectra.

All the mixed ligand complexes show single spots with R_f values being the intermediate of the two corresponding symmetrical bis-complexes. Metal atom is hexacoordinated and the probable geometry may be octahedral. The 1H NMR spectra confirm the structures of these complexes. Binding of the metal atom to the phenolic oxygen of the ligand is confirmed by the disappearance of the OH proton peak which is observed in the spectra of free salicylaldehyde and aromatic ketones. Coordination of the $>C=O$ group of the ligand moiety to the metal atom is supported by the upfield shift of the protons of the CH_3 , CH_2 and CH groups which are in the vicinity of the $>C=O$ group.