

PART 2



Inorganic Division Conference

IC '94

4 - 7 July 1994



Department of Chemistry
University of Western Australia

PROCEEDINGS

An Ab Initio Study Of Novel Tellurium Compounds

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Since the recent discovery of the important role that tellurium plays in a number of biological systems, the largely unconsidered chemistry of tellurium has begun to receive a considerable amount of attention; however, despite the recent efforts of a number of researchers rather little is known of the chemistry of tellurium.

In an effort to increase the understanding of the behaviour of tellurium we have undertaken *ab initio* studies of a number of different tellurium containing molecules. We have completed a study on $\text{Te}(\text{CH}_3)_4$ which was isolated in 1989. In spite of the availability of NMR and IR data the structure of $\text{Te}(\text{CH}_3)_4$ was unable to be elucidated, with the authors suggesting that this molecule may exist as a mixture of the C_{2v} (trigonal bipyramid) and C_{4v} (square pyramidal) structures. We have been able to conclusively determine the structure of this compound.

In addition, our work on tellurium has been extended to include a study of the reaction profiles of homolytic substitution reactions. Many such reactions have been observed to provide an efficient method for synthesising novel compounds of other group 16 elements, and a study of reaction paths for analogous reactions at tellurium will assist in determining whether similar synthetic strategies are likely to prove fruitful and will provide both important mechanistic information as well as structural and kinetic data for these molecules. We hope to be able to begin a synthetic study of organo-tellurium compounds in the coming year.

Ab initio Study of the Cyclic Isomers of N₂S₄

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Abstract

A recent argon-matrix IR study by P. Hassanzadeh and L. Andrews [1], of the products of micro-wave-gas discharge in vapours of nitrogen and sulfur, have revealed the formation of, what appears to be, the previously unknown 1,4-isomer of the cyclic N₂S₄ molecule. Up till now, only the 1,3-isomer of the N₂S₄ has been so far known to exist.

In this study, *ab initio* theory is used to investigate the relative stabilities of the three possible cyclic isomers of the N₂S₄ molecule. Calculations are performed using the SCF, MP2 and QCISD levels of theory, with a DZP-type basis on both the sulfur and nitrogen atoms. Initial geometry optimisations used model potentials [3] on the sulfur atom to reduce size of the calculations. All minimum and transition state geometries together with vibrational frequencies are reported, as well as a discussion of the main features in the potential energy surface of each isomer. At the SCF level of theory, the lowest energy structure for the 1,3-isomer is an asymmetric chair structure, consistent with experimental study [2]. For the 1,4-isomer, two minima are found; a symmetrical chair and a twisted-planar structure. The 1,2-isomer also has two minimum conformations, one, which has twisted-chair geometry and the other, is a symmetrical boat. Although at the SCF level of theory the 1,2-isomer is the lowest energy isomer, the MP2 level of theory does not find a minimum on the potential energy surface. Consequently, as one would suspect from chemical intuition, this isomer does not appear to be stable. Thus, considering, only the 1,3- and 1,4-isomers, the 1,4-twisted-planar structure has the lowest energy, it is 7.6kcal/mol lower than 1,3-isomer and 12kcal/mol lower than 1,4-chair structure.

It was found that at the SCF level of theory the bond lengths and angles calculated with model potentials, differed on average, from the all-electron results, by less than 0.009Å and 0.2°, respectively. At the MP2 level of theory that difference increased to 0.02Å and 0.3°.

The IR spectra of each of the minimum structures of the 1,4-isomer, at the SCF level of theory, is not consistent with the two experimentally found absorption bands for an alleged found N₂S₄ molecule. This indicates that the 1,4-isomer of N₂S₄ is not the structure found experimentally.

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Theoretical Study of the Factors Effecting Water Geometry in Crystalline Hydrates

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Abstract

From a number of surveys [1, 2] done on the, neutron diffraction refined, crystalline hydrates, it has been observed that the internal geometry of the water molecule varies considerably in these hydrates. The O-H bond length occurs in the range from 0.855(29)Å up to 1.04(4)Å and the H-O-H angle varies from 100.9(4)° to 116.1(4)°. The main factors and their exact nature of influence on the water geometry are still ambiguous. This study aims at a systematic investigation of the possible factors which alter water geometry to provide a better understanding of the changes observed in the water geometry. Calculations were done at the MP2 level of theory with a DZP-type basis set on the water molecule and other atoms.

The two major factors, affecting the internal geometry of the water molecule, are, the metal(s) coordinated to the water and the hydrogen bonding to acceptor ions through the water hydrogen atoms. These two factors, were investigated separately. All of the 1st and 2nd row metals, plus 3rd row transition metals were considered. It was found that, the extent, of the metal effect depends on several factors, the coordination type, the metal type, the charge on the metal and the metal-water distance, with the coordination-type having the largest influence in altering the water geometry, followed by the charge on the metal. In case of the hydrogen-bonding effect the study showed that the type of the acceptor ion is moderately important in altering the water geometry; the hydrogen-acceptor (H—A) distance on the other hand has the largest effect. With the water angle changing up to 12° and the O-H bond up to 0.08Å. The hydrogen-bond angle (O-H—A) is also significant in altering the water geometry, however its effect is much more predominant on the H-O-H angle, than the O-H bond length.

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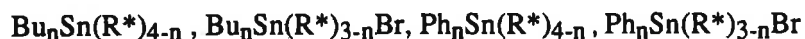
Enantioselective Reagents: Molecular Modelling and Synthesis of Organotin (IV) Compounds Containing Chiral Groups.

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Chiral organotin(IV)hydride compounds have considerable potential as free radical reagents in enantioselective synthesis. We have begun a study to investigate this potential by a program of synthesis and molecular modelling. The initial stages aim to determine whether it is necessary for the tin center itself to be chiral or whether it is sufficient to have chiral substituents at the tin. Reported are the synthesis and characterisation of series of organotin(IV) compounds containing chiral substituents



$\text{R}^* = (-)\text{-menthol}, (-)\text{-menthyl}$

In addition *Ab initio* molecular orbital and molecular mechanics studies have been undertaken on a range of tin hydrides and transition states for hydrogen atom transfer to pro-chiral carbon centred radicals. It is hoped that this work will lead to a simple method of preparing enantiomerically pure compounds of biological interest.

'Atomic Charge' in Diatomic Promolecules and in Promolecular Solids

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Evaluating atomic charges on overlapping *neutral* atoms in a promolecule may appear to be anomalous, but the close relationship between bonding and potential energies makes it physically reasonable to subdivide electron density in proportion to each atom's contribution to the electrostatic potential. Such a partitioning of the promolecule electron density by subdivision in proportion to the constituent atoms' potentials projects that density onto a complete set of atom potential basis functions.

Atomic charges are the differences between atomic numbers and integrals of partitioned electron densities. The promolecule charges evaluated show that cations in diatomic molecules extend their control over electrons at the expense of the anions. For atoms of comparable atomic number the electrostatic potential near but not on an anion nucleus is larger than that for a cation, reflecting the higher effective nuclear charge for the anion's outer core and valence subshells. Electrostatic potentials for cations extend further than those for anions, enabling cations to influence more electrons.

The valence electrons from bonded anions occupy a number of the neutral cation's unfilled states that is larger than the cation valence. A real flow of electrons from the over-filled cation states towards under-occupied anion states polarises the electron distribution, charging cations positively and anions negatively. For most compounds the promolecule charge is slightly larger than the number of valence electrons expected to be involved in spin pairing with neighbouring atoms.

A crystal closely approximates a semi-infinite array of overlapping 'neutral' atoms – the promolecular solid that provides a good first order approximation to lattice energies. That model should also provide approximate values for other physical properties related to the one-electron density, such as atomic charges, which are readily evaluated for crystal structures determined from diffraction measurements. High precision imaging with synchrotron radiation enables the redistribution of electrons in the real crystal, and hence the change in charge due to its formation, to be determined.

Promolecule charges for H atoms are outliers, having positive signs typical of anions, but unlike typical anions state lose much less than one electron in the charge redistribution. Hydrogen's 1s electronic structure and its lack of closed inner subshells limits its electron loss to less than its valence. That mild bias towards cationic behaviour gives a reasonable description of its chemical and physical properties. Hydrogen differs only to a mild degree from the halogens which, although also having one hole in their valence subshell, can potentially 'lose' more than one electron, and thus have promolecule charges larger than unity. But hydrogen differs far more strongly from the alkali metals, which have the negative promolecule charges typical of cations. Inert gas elements, being on the boundary between anions and cations, have small promolecule charges suggesting, perhaps, that the periodic table should be cylindrical!

The Effect of Different d^n s Configurations on Transition Metal Chemistry in Single Ligand Complexes

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Calculations on transition metal complexes with small numbers of ligands are a feasible way to obtain information about the metal-ligand bond, not very reliably understood in the past. In addition, gas-phase experimental data provide tests of the computational results not possible from solid or solution phase chemistry.¹

Results from correlated calculations which use three contracted sets for the metal d -function basis are reported now for the series M^+L and $M^{2+}L$ complexes for $M = \text{Sc}—\text{Zn}$ and $L = \text{H}_2\text{O}$ and OH^- . The results include a number of different excited d -electron configurations for each M^+ and M^{2+} ion and thus allow an answer to questions about the effect to which electrons in different d -orbitals are able to affect the metal-ligand bond.

Compared with the results for adducts formed by the monovalent ions K^+ (d^0) and Cu^+ (d^{10}) the $\text{Sc}^+—\text{Zn}^+$ binding energies display an irregular progression of increasing metal-ligand bond strength for both H_2O and OH^- as ligands, the increments being dependent on the interplay between the increasing effective charge of the cation and the repulsive effect of the d -electrons in the lowest d^n s state. Only in V^+ is the ligand able to change the d configuration from that of the free ion. The bivalent ions $\text{Sc}^{2+}—\text{Zn}^{2+}$, which maintain the same d^n configurations as the corresponding monovalent ions (the $4s$ orbital being unoccupied) behave more simply, producing a smooth increase in binding energy across the series. For both series the $M-\text{OH}_2$ bond strengths cluster much more closely to the values for the end members, $\text{Cu}^+(\text{H}_2\text{O})$ and $\text{Zn}^{2+}(\text{H}_2\text{O})$, than to the d^0 and d^{10} representatives $\text{K}^+(\text{H}_2\text{O})$ and $\text{Ca}^{2+}(\text{H}_2\text{O})$. Inspection of population data show that the d -electron contribution to bonding is small, the major effect being repulsion of the H_2O and OH^- lone pairs. The ordering of the states is consistent with the repulsion sequence which Rosi and Bauschlicher² found for the $M^+(\text{H}_2\text{O})$ adducts, viz. $d\sigma > d\pi > d\delta$.

The deprotonation behaviour for the two series of metal-water adducts is readily predicted: a smooth drop across the $M^{2+}(\text{H}_2\text{O})$ series from Sc^{2+} (5.1 eV) to Zn^{2+} (3.8 eV) paralleling the effect of increasing effective charge. This effect is superimposed on the overall drop in deprotonation energy (DE) shown by all the cations—the DE for the free water molecule being 17.3 eV. The effect of the charge of the monocation is much weaker (mean DE 9.97 eV) and the deprotonation energies across the series reflect, in addition, the repulsive contribution of the filling d shell. The binding and the DEs of water molecules bound to metal ions with other d^n and d^n s configurations are consistent with these results.

The calculations are being extended to combinations of ligands to develop a comprehensive picture of metal-ligand and ligand-ligand interactions in the small, and ultimately, the larger complexes important in transition metal chemistry.

¹ See *Gas-phase metal reactions*, ed A. Fontijn, Elsevier Science Publishers, 1992.

² Rosi, M. and Bauschlicher, C. W., *J. Chem. Phys.*, 1989, **90**, 7264; 1990, **92**, 1876.

**A Study of the Electronic Structure, Metal-Metal Bonding and
Magneto-Structural Correlations in $A_3Mo_2X_9^{3-}$ ($X=Cl, Br, I$)
Complexes from Spin-Restricted and Spin-Unrestricted
Broken-Symmetry X α -SW Calculations**

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The results of spin-restricted X α -SW and spin-unrestricted *broken-symmetry* X α -SW calculations on the face-shared dimer complexes $A_3Mo_2Cl_9$ ($A=K, Rb, Cs, Me_4N$), $A_3Mo_2Br_9$ ($A=Cs, Me_4N$) and $Cs_3Mo_2I_9$ are reported and used to discuss the electronic structure, metal-metal bonding and magneto-structural correlations in these systems. The spin-restricted X α -SW calculations on $Cs_3Mo_2X_9$ ($X=Cl, Br, I$) show that the metal-metal σ and π bonding interactions are significantly reduced for the bromide and especially for the iodide complex relative to $Mo_2Cl_9^{3-}$, consistent with the increased metal-metal bond distances observed for both these complexes. The ground state exchange interaction is shown to be almost entirely the result of direct overlap of magnetic orbitals with negligible contribution from superexchange effects. The *broken-symmetry* X α -SW calculations for the ground state in $Cs_3Mo_2X_9$ ($X=Cl, Br, I$) reveal that the magnetic orbitals involved in the metal-metal π interaction are almost completely localised on the metal ions. The magnetic orbitals involved in the metal-metal σ interaction on the other hand, are partially delocalised between the two metals, but still contribute significantly to the ground state exchange interaction in agreement with earlier spectroscopic and theoretical studies.¹⁻⁵ The calculated exchange coupling constants J_{ab} for the complexes $Cs_3Mo_2X_9$ ($X=Cl, Br, I$) support this conclusion and indicate that the effective maximum spin in the ground state exchange levels lies between 2 and 3. A significant antiferromagnetic contribution arises from ligand \rightarrow metal spin-polarisation effects which accounts for the unusually large $-J_{ab}$ value found for the iodide complex. The magnetostructural correlations observed for the chloride and bromide complexes have been successfully modelled by initially using Mo atomic sphere radii which reproduced the experimental J_{ab} values for $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ and then adjusting the Mo sphere radii for the remaining complexes in proportion to their metal-metal bond distances relative to the Cs salts.

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An Electron Spin Resonance (ESR) And Theoretical Study Of HFCO[•]

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Isolated HFCO[•] was generated in HFCO doped neon matrices at 4 K by X-ray irradiation. The ESR spectra showed the HFCO[•] was rigidly trapped and analysis of the powder ESR spectrum yield the hyperfine tensors for the hydrogen and fluorine nuclei. Synthesis of DFCO[•] confirmed the spectral assignments. The experimental hyperfine tensors are compared with theoretical values predicted by *ab initio* configuration interaction (CI) calculations.

Thermodynamic Modelling of Concentrated Electrolytes with Pitzer's Theory: Application to Systems of Hydrometallurgical Interest

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The Pitzer semi-empirical activity-coefficient model is widely applied to concentrated aqueous electrolytes. It is unique among such models in that its analytical form is identical to that arising in a virial-coefficient expansion of the configurational Gibbs energy. Measurable combinations of ionic virial coefficients are represented empirically as a function of ionic strength, rather than being expressed rigorously in terms of the potential of mean force.

Model-dependent parameters characterizing the strength of binary interactions in single electrolytes and ternary interactions in mixed electrolytes can be obtained from least-squares analysis of appropriate osmotic coefficient data. While the expression for the osmotic coefficient is linear with respect to these parameters, their values depend substantially on the range of molality represented by the data, the magnitudes of experimental errors, and the weighting scheme used (if any). These details have received insufficient attention in the literature. Consequently, published tabulations of Pitzer model parameters contain many serious errors.

In this paper we consider in detail the peculiar difficulties associated with the use of Pitzer's equation in the analysis of osmotic-coefficient data. We also describe qualitatively and quantitatively the agreement of Pitzer's theory for various classes of inorganic electrolytes, with particular reference to those often used as inert background electrolytes in the determination of stability constants.

Finally, we illustrate the application of the Pitzer theory to the modelling of phase- and reaction-equilibrium problems arising in concentrated electrolyte systems of hydrometallurgical interest.

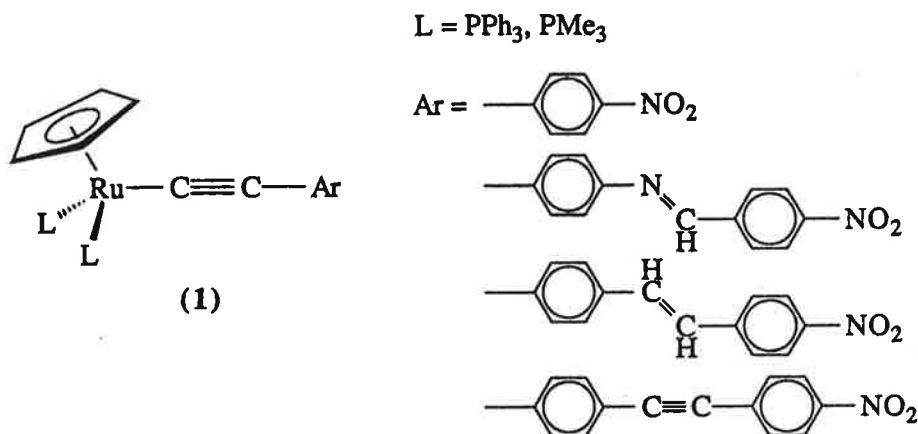
Synthesis and Nonlinear Optical Investigations of Ruthenium Complexes

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There is increasing interest in investigating new materials which have high nonlinear optical efficiencies and in how these efficiencies are related to structure. Nonlinear optical investigations of systematically varied systems will reveal information about structure/property relationships. For this reason, ruthenium acetylides of the type (1) have been prepared and characterized.



These complexes have been shown to have large solvatochromic shifts of up to 65 nm over a range of solvents of differing polarity, suggesting that they may have enhanced nonlinear optical behaviour. Correlations from spectroscopy and cyclic voltammetry can shed light on the electron donating efficiency of the ruthenium centre; these will be presented together with preliminary results from degenerate four wave mixing experiments.

Influence of Metal Ion Characteristics on the Vibrational Spectra of Metal(I) α -Hydroxycarboxylates

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It has frequently been reported that the stretching frequencies of various functional groups are sensitive to metal complexation. In particular, carboxylic acids have been studied because it has been shown that the asymmetric carbonyl stretching frequency is very responsive to various physical properties of the complexing metal such as ionic radius, electronegativity etc.

Attempts to correlate the effect of a metal ion characteristic with the asymmetric carbonyl stretching frequency have not been very conclusive. It is assumed that a combination of effects causes the variations. The present work considers the effect of group 1 and selected transition metal complexation on the asymmetric carbonyl stretching frequency in hydrogen (+)-tartrate, (+)-tartrate and (+)-tartratoarsenate. A very good linear relationship is found between the radius of the group 1 metal ions (as determined from their coordination sphere) and the asymmetric carbonyl stretching frequency of the ligand ($r^2 = 0.981$). Two other metal ions Ag^+ and Tl^+ together with H^+ form another linear relationship ($r^2 = 0.983$). The combined data give a much more unsatisfactory relationship ($r^2 = 0.938$) indicating that whereas the group 1 metals have a very definite constant effect with increasing size, the two transition metals introduce effects other than simply ionic size.

In the case of the metal(I) (+)-tartrate complexes construction of two separate two point lines (H^+ , Na^+) (H^+ , Tl^+) allowed the prediction of the asymmetric carbonyl stretching frequency for potassium (+) tartrate [1593 (pred.), 1591 (obs.)] and silver(I) (+)-tartrate [1607 (pred.), 1606 (obs.)].

For the metal(I) arsenate(III) (+)-tartrate complexes, good agreement of predicted and observed frequencies is obtained in the case of the group 1 metals but only limited agreement is found for the transition metals.

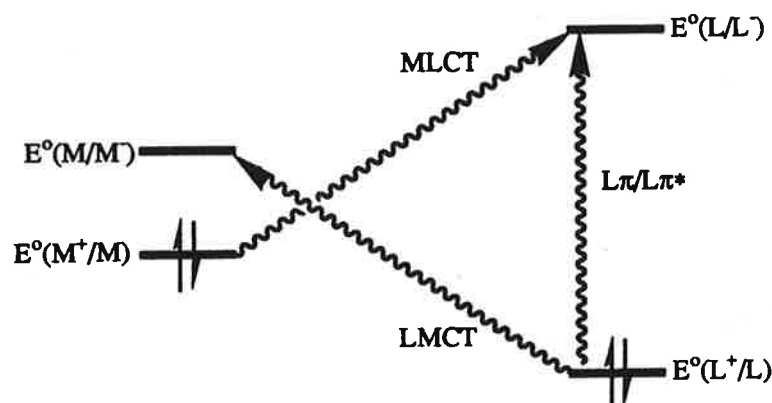
Metal Diketonates: Charge-Transfer Spectra and Electrochemical Data

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If one takes the optimistic view (as we do) that both metal and ligand frontier orbital energies can be mapped from systematic electrode potential data, then testable predictions of the optical charge-transfer band energies for a given complex must follow. The present report combines electrochemical and spectroscopic results with data from SCF-X α -SW calculations to test the validity of this proposition.

In principle, the energy of any electronic charge-transfer transition can be related to the notional orbital electrode potentials of donor and acceptor orbitals as shown in the scheme;



For example: $h\nu_{MLCT}$ (electron volts) $\sim E^\circ(M^+/M) - E^\circ(L/L)$

We have begun with the familiar ruthenium tris-diketonate complexes as a demanding test-case. The spectra (50 000-5000 cm^{-1}) of these and related complexes obtained by spectro-electrogeneration, form a well defined and challenging body of data. Remarkably, the one set of appropriate empirically determined electrode potentials leads to a self-consistent assignment for the u.v./visible spectrum not only of $[\text{Ru}^{\text{III}}(\text{acac})_3]$ (MLCT, LMCT and $L\pi/L\pi^*$ bands), but also of hitherto inaccessible $[\text{Ru}^{\text{IV}}(\text{acac})_3]^+$ and $[\text{Ru}^{\text{II}}(\text{acac})_3]^-$. Most recently, the SCF-X α -SW calculations have been used to map the energy levels within each of the ruthenium tris-diketonate species. This provides further insight into the validity of our apparently simple approach to spectral analysis.

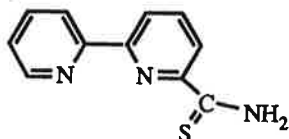
The investigation has been extended to *trans*- $[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]^{1-}$, including spectro-electrochemical measurements and SCF-X α -SW calculations over the same range of ruthenium oxidation states (i.e. Ru ^{II,III,IV}). The spectra of the tris- and *trans*-bis-diketonate complexes look similar and the calculations show that equivalent orbitals are involved in each major transition. The model initially developed for the ruthenium tris-diketonate species continues to give a good representation of the spectra where the π - π^* and charge transfer bands can be sensibly related to known or inferred electrode potentials.

ELECTRONIC PROPERTIES OF Fe(II) COMPLEXES OF 6-SUBSTITUTED BIPYRIDINE SYSTEMS.

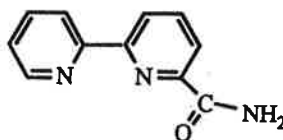
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The electronic properties of Fe(II) complexes of the substituted phenanthroline ligands; 1,10-phenanthroline-2-carbothioamide and 1,10-phenanthroline-2-carboxamide have previously been reported. [1,2,3] It was found that by replacing the sulfur donor atom with an oxygen donor atom there was a marked change in the ligand field strength and hence the electronic properties of the derived complexes. The thioamide complex of the formula $[\text{FeLCl}_2] \cdot \text{H}_2\text{O}$ was of particular interest as it was found to exhibit a singlet - triplet spin transition.[4] It has therefore been the aim of recent work to compare the behaviour of complexes of the bipyridine analogues: 2,2'-bipyridyl-6-thioamide (bpytha) and 2,2'-bipyridyl-6-carboxamide (bpyca), with that of the corresponding phenanthroline derivatives and to examine the effect of the added flexibility inherent in the bipyridine moiety.



bpytha



bpyca

Fe(II) and Ni(II) complexes of the type $[\text{M}(\text{L})_2](\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$ and $[\text{MLCl}_2] \cdot n\text{H}_2\text{O}$ have been isolated for both the thioamide and amide, with the ligands acting as tridentates involving NNS and NNO coordination respectively. The electronic properties of these complexes have been determined by measurement of variable temperature magnetism, electronic and Mossbauer spectra. It has been found that replacement of the thioamide group with the amide group results in a weakening of the ligand field strength and hence differing electronic properties of the central Fe(II) ion. The relative ligand field strengths of bpytha and bpyca have been obtained from the electronic spectra of the Ni(II) complexes.

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Synthesis, structure and physical properties of monovalent oxonickelates

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The thesis that oxygen only stabilizes "high" oxidation states in polynery oxides was regarded as a general guide; examples are KMnO_4 as well as K_2FeO_4 [1] and Cs_2FeO_4 [2]. These and numerous other oxides in more "normal" oxidation states were synthesized by tempering a mixture of binary oxides in sealed metal containers (e.g. Pt, Au, Fe, Co, Ni, Ag). On the other hand a reaction with the container wall normally avoided, presented a new route for a smooth reduction to stabilize "lower" oxidation states, for example K_2NiO_2 [3] and the new ternary oxides $\text{RbNa}_2\text{NiO}_2$, K_3MO_2 ($\text{M} = \text{Fe, Co, Ni}$) [4], producing single crystals grown in situ / "out of the wall".

Spectroscopic data on K_2NiO_2 has been published [5] which provides a useful comparison for some of the properties of these novel compounds which result from the unusual coordination and oxidation state of the transition metal. Therefore further investigations on magnetic, optical and EPR behaviour of K_3NiO_2 and KNa_2NiO_2 are in progress and initial results are presented here.

From the EPR measurments we can confirm that Ni^+ is present, this being isoelectronic with Cu^{2+} . The signal obtained for single crystals is highly anisotropic as we would expect from a linear complex, and the unpaired electron is largely in the d_{z^2} orbital.

Another aspect, for example, is the question why these compounds are of such an intensely dark red colour. This is probably a result of charge transfer bands extending over the visible range, whereas the d-d transitions occur in the infra red region.

Ligand Field calculations on the complex $[\text{O-Ni-O}]^{3-}$ can only simulate the experimental data for both compounds when a strong mixing of the $3d_{z^2}$ with the 4s orbital is considered.

The crystal structures of these two oxides are quite different which has to be taken into account for interpreting the different magnetic behaviour within a cooperative interaction model.

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Crystal Structure and Electronic Spectrum of the Distorted Tetrahedral CuCl_4^{2-} Ion in $(2\text{-aminopyridinium})_2[\text{CuCl}_4]$ and Comparison with the Tetragonally Elongated Octahedral Complex $\text{Cu}(2\text{-aminopyrimidinium})_2\text{Cl}_4$

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Chlorocuprates exhibit a very rich stereochemistry and consequently provide a useful way of correlating spectroscopic properties with molecular geometry. The CuCl_4^{2-} ion is of particular interest in this respect, as the shape of this varies from close to tetrahedral to square planar depending upon the counter-cation, with it being suggested that hydrogen bonding tends to stabilize the latter geometry.¹ The distortion from a regular tetrahedron is accompanied by a pronounced shift in the d-d transition energies, and it has been proposed that the electronic spectrum may therefore be used to predict the shape of the CuCl_4^{2-} ion.²

The electronic reflectance spectrum of $(2\text{-aminopyridinium})_2[\text{CuCl}_4]$, $(2\text{NH}_2\text{PyH})_2[\text{CuCl}_4]$ was recently reported,² and interpreted in terms of the likely metal coordination geometry. To test this prediction, and investigate the relationship between the geometry of the complex and lattice hydrogen bonding interactions, we have determined the crystal structure of $(2\text{NH}_2\text{PyH})_2[\text{CuCl}_4]$. As predicted, the CuCl_4^{2-} ion in the compound adopts a pseudo-tetrahedral geometry, though the distortion away from a regular tetrahedron is rather less than was inferred from the electronic spectrum. The chloride ions are quite strongly hydrogen bonded to the amine groups, showing that such interactions are not limited to planar CuCl_4^{2-} groups. We have also measured the single crystal electronic spectrum at low temperature. The relative intensities of the d-d bands are consistent with the observed geometry of the CuCl_4^{2-} ion, and the transition energies may be interpreted satisfactorily using angular overlap metal-ligand bonding parameters.

For comparison, the optical spectrum of the 6-coordinate complex $(2\text{-aminopyrimidine})_2\text{CuCl}_4$ is reported. Here, planar CuCl_4^{2-} groups occur, but with long axial bonds to nitrogen atoms of the counter-cations completing a tetragonally elongated octahedral geometry. The electronic spectrum is consequently quite different from that of $(2\text{NH}_2\text{PyH})_2[\text{CuCl}_4]$, though it may also be interpreted satisfactorily using chemically reasonable metal-ligand bonding parameters.

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An Investigation of Nitrogen and Thioether Donor Strength from a Low Temperature, Polarised Single-Crystal Absorption Study and Ligand-Field Analysis of the *bis*-Macrocyclic Complexes *trans*-[Ni([9]aneN₂S)₂]²⁺ and *trans*-[Ni([9]aneS₂N)₂]²⁺

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The low-temperature, polarised single-crystal absorption study and ligand-field analysis of the *bis*-macrocyclic Ni(II) complexes [Ni([9]aneN₂S)₂](ClO₄)₂ and [Ni([9]aneS₂N)₂](ClO₄)₂, comprising *trans*-NiN₄S₂ and *trans*-NiN₂S₄ coordination, respectively, is reported along with the crystal structure for the latter complex. Large tetragonal splittings of between 1000 and 3500 cm⁻¹ are observed in both complexes for the parent ³T_{2g}, ³T_{1g}(F) and ³T_{1g}(P) octahedral ligand-field states. Based on the observed spectral bands, the relative σ-donor strengths of the nitrogen and thioether ligands are elucidated from a ligand-field analysis using the *angular-overlap-model* (AOM). The observation of weak, sharp structure at low temperatures associated with the parent ³A_{2g}→¹E_g and ³A_{2g}→¹A_{1g} spin-forbidden transitions, allows the independent determination of both the Racah B and C electron repulsion parameters. From the ligand-field analysis it is concluded that the Racah B and C parameters are significantly lower for the spin-forbidden transitions in comparison with the spin-allowed transitions, implying the presence of a significant *differential nephelauxetic effect* in both complexes.

Investigation of the Differential Nephelauxetic Effect and Spin-Orbit Mixing in Macrocyclic and Encapsulating Complexes of Ni(II) Involving Nitrogen and Thioether Coordination

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The low-temperature (~10 K) absorption spectra of the Ni(II) encapsulating complexes¹ $[\text{Ni}(\text{diAMN}_6\text{sar})]^{2+}$, $[\text{Ni}(\text{AMN}_5\text{Ssar})]^{2+}$, $[\text{Ni}(\text{AMN}_4\text{S}_2\text{sar})]^{2+}$, $[\text{Ni}(\text{AMN}_3\text{S}_3\text{sar})]^{2+}$ and $[\text{Ni}(\text{Me}_2\text{S}_6\text{sar})]^{2+}$, involving nitrogen and thioether coordination, are reported. In almost all cases, the low temperature spectra permitted the observation of the ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ and ${}^3\text{A}_{2g} \rightarrow {}^1\text{A}_{1g}$ spin-forbidden transitions and all three ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ spin-allowed transitions. In general, an asymmetric or double-humped band shape is observed for the lowest energy absorption, corresponding to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ spin-allowed transition, due to the appreciable spin-orbit mixing between the spin-forbidden ${}^1\text{E}_g$ state and the E_g spin-orbit component of the ${}^3\text{T}_{2g}$ state. The relative intensities of the various components contributing to this absorption band were determined for each of the above complexes, and serve to nicely illustrate the effective intensity transfer between the ${}^1\text{E}_g$ and ${}^3\text{T}_{2g}$ ligand-field states. A ligand-field analysis of the above systems using the conventional octahedral model results in progressively lower Racah C/B ratios as the number of thioether donors increases, as well as progressively poorer fits to the spin-forbidden bands. The deviation from the free ion C/B ratio in these complexes is attributed to the *differential nephelauxetic effect* arising from the covalency differences existing between the octahedral t_{2g} and e_g orbitals. To account for this effect, a covalency-adjusted ligand-field model is used which retains the free ion values for the Racah B and C parameters and also the spin-orbit coupling parameter ζ , but introduces the covalency or reduction parameters f_e and f_t associated with the e_g and t_{2g} orbitals, respectively. In this model, the covalency differences between the e_g and t_{2g} orbitals are accounted for by reducing the interelectron repulsion and spin-orbit matrix elements by the f_e and f_t covalency parameters. Application of this model to the above complexes, as well as other Ni(II) complexes involving mixed nitrogen and thioether coordination, results in substantially better fits to the observed positions of both the spin-allowed and spin-forbidden bands. Furthermore, whereas the f_t parameter remains fairly static at around 0.9, the f_e parameter progressively decreases from around 0.87 for N_6 coordination through to ~0.67 for S_6 coordination, highlighting the large nephelauxetic effect of the thioether donor. The model also reveals a covalency correction of $8B(f_e^2 - f_e \cdot f_t)$ for the octahedral ligand-field splitting parameter, 10Dq , based on the energy of the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition. Consequently, the value of 10Dq obtained using the conventional octahedral ligand-field model will be underestimated, particularly for the more covalent ligands.

¹ The $[\text{Ni}(\text{Me}_2\text{S}_6\text{sar})]^{2+}$ complex was kindly supplied by Dr P. Osvath and Prof. A.M. Sargeson.

Iron(II) and Nickel(II) Complexes of 2,6-Bis(pyrazol-1-yl)pyridine and Related Ligands: Structural, Spectral and Magnetic Studies

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The ligands 2,6-bis(pyrazol-1-yl)pyridine and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine have been prepared by reacting 2 moles of the potassium salt of the appropriate pyrazole with 1 mole of 2,6-dibromopyridine¹. Difficulty in purifying the second ligand by recrystallisation techniques was experienced and a purification technique, relying on the superior complexing capacity of the tridentate ligand with respect to the impurities, was developed. Complexes of the formula $[ML_2](anion)_2$, where M = Fe, anion = BF_4 ; M = Ni, anion = ClO_4 , were prepared by reacting the stoichiometric amounts of ligand and metal salt in ethanol for both ligands.

Solid state reflectance and solution spectra of the nickel(II) complexes revealed that the ligands have almost identical field strengths. The iron(II) complex of the methyl-substituted ligand was found to be low-spin at room temperature and heating to 373 K caused no significant spin unpairing. The iron(II) complex of the unsubstituted ligand is high-spin at room temperature and undergoes a precipitous spin-transition at 263 K. The field strength of the methyl-substituted ligand must be significantly greater than that of the unsubstituted ligand. This is in contrast to analogous thiazolyl ligands where substitution adjacent to the donor atom weakens field strength. Clearly, the presence of two methyl groups on each pyrazolyl ring has significantly enhanced the σ -donor capacity of the ligand, outweighing the steric influence.

The structures (RT) of the iron(II) and nickel(II) complexes of the unsubstituted ligand have been determined. The cations have approximately octahedral structure, with metal - donor atom distances typical for high-spin iron(II) and nickel(II), respectively. The structures of the cations will be compared with structures of the iron(II) and nickel(II) complexes of terpyridine and related ligands. The structure of the methyl-substituted ligand has been determined and the molecule, though not completely planar, adopts a *trans-trans* conformation in the solid state, indicating that the repulsions between the nitrogen lone-pairs dominate in determining the conformer.

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AN INVESTIGATION OF THE CRYSTALLINITY OF NATURAL ZIRCONS

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The crystallinity of minerals can significantly affect their chemical reactivity, e.g. rate of dissolution and the preferential leaching of labile ions. X-ray powder diffraction is often used as a means of assessing crystallinity but, as it reflects a bulk property, does not give the detailed information required when dealing with zoned or heterogenous particles. The spatial resolution achievable with Raman spectroscopy makes it an attractive proposition for investigating such materials.

The development of stable high power Near Infra Red lasers, and the consequential reduction in fluorescence problems, along with the introduction of Fourier Transform Raman spectroscopy^{1,2} has greatly enhanced the study of 'real world' samples. Although the spatial resolution of NIR FTRaman spectroscopy (~5 micron) is less than that of UV/Visible Dispersive Raman spectroscopy (1-2 micron), this disadvantage is more than compensated for by the reduction in fluorescence which allows a far wider range of compounds to be investigated.

A range of naturally occurring optically homogeneous zircons, ranging from highly crystalline to amorphous, have been studied by Raman spectroscopy, X-ray powder diffraction and conventional uranium/lead dating techniques.

The uranium content of natural zircons is usually in the range 0-5000 ppm. Thorium is also present, but generally in lower concentrations. Concomitant alpha-decay converts the crystalline zircon to an amorphous metamict phase³, the degree of metamictization being dependant on the alpha particle dose received.

We have found that the position, widths and intensity of peaks in the Raman spectrum is sensitive to the degree of crystallinity, and that different degrees of crystallinity within a zoned single grain can be determined by this method. In particular the internal asymmetric stretching, $\nu_3(B_{1g})$, and the external translatory $E_g(I)$ modes⁴ which occur at 1008 cm^{-1} and 356 cm^{-1} respectively for highly crystalline zircons, progressively broaden and shift to 980 cm^{-1} and 340 cm^{-1} as metamictization increases and may even disappear for highly metamict samples.

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The Benefits of an Inconsistent Thermodynamic Database

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JESS is a new computer package for modelling chemical systems in solution¹. It is designed to solve problems requiring expert knowledge of chemical speciation, where existing programs for simulating metal-ligand interactions in solution are neither general enough, nor easy enough, to use. JESS provides a platform for building large, comprehensive models of chemical speciation in aqueous or non-aqueous environments. It currently comprises over 200 programs, 1800 subroutines and 170,000 lines of Fortran code. The software is highly portable and is implemented under VAX-VMS, Unix, and MS-DOS.

Development of the JESS Thermodynamic database is now well advanced. The system overcomes many problems associated with existing compilations of equilibrium constants. It is fully interactive. Reactions can be expressed in any form. Any number of equilibrium constants, enthalpy, entropy and Gibbs free energy values can be associated with a reaction. Currently, the database contains over 40,000 reactions and over 80,000 equilibrium constants. Thus far, the data span interactions in solution of some 100 metals ions with more than 2,000 ligands. A suite of computer programs exists to facilitate the production of sub-databases and the interchange of data between databases.

Data are stored as they appear in the literature and are only subsequently manipulated by our system to achieve thermodynamic consistency. This means that the data in the database are not converted to conform to a particular pre-determined basis set, unlike most other speciation databases. The advantages of this approach will be highlighted.

Other features of the JESS database include the following.

- Unlike all other major compilations of equilibrium constants, ternary complex formation is naturally represented by the same conventions as our binary reactions. The data can thus be located directly by searching on the metal ion and two ligands involved. The JESS Parent Database is, overwhelmingly, the largest single source of ternary equilibrium constants.

- Chemical substances are indexed by name, by molecular formula and, often by CAS registry number. In general, we have many more variants of chemical names than are provided in alternative sources.

- Every thermodynamic parameter value is individually associated with (i) the conditions under which it was measured, including e.g. the identity of the background electrolyte, the temperature and the ionic strength, (ii) a literature reference and (iii) our current estimation of its reliability, on a scale of 0 - 9. This approach enables the database to be both comprehensive and critical.

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Decomposition and substitution reactions of pentafluoronitrosobenzene and pentafluoronitrobenzene

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Thermal decomposition of monomeric pentafluoronitrosobenzene, prepared from the reaction of pentafluoroaniline with hydrogen peroxide (80%) and formic acid (90%),¹ liberated bis(pentafluorophenyl)diazine N-oxide² and pentafluoronitrobenzene³ as major products. The decomposition of pentafluoronitrosobenzene in presence of phosphine in methylene chloride solvent gave bis(pentafluorophenyl) diazine N-oxide. Reaction of NaN_3 with $\text{C}_6\text{F}_5\text{NO}_2$ in acetonitrile gave $\text{C}_6\text{F}_2(\text{N}_3)_3\text{NO}_2$ as characterized by the mass and ^{19}F NMR spectral data. The mass and ^{19}F NMR spectra of $\text{C}_6\text{F}_5\text{NO}$ and $\text{C}_6\text{F}_5\text{N}(\text{O})\text{NC}_6\text{F}_5$ are described.

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SOME CHEMISTRY OF THE ALL-CARBON LIGAND C₄

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There is a growing interest in transition metal complexes containing unsaturated all-carbon ligands, as these compounds are potential precursors to polymeric materials with useful non-linear optical properties.¹ However, metallocumulenes ($[M]=(C)_n=CR_2$) and metal polyacetylide ($[M]-(C_2)_n-R$) also present an exciting opportunity to extend the chemistry that has been developed for vinylidene and acetylide complexes.²

The carbon centres in these extended chains are expected to show alternating electrophilic and nucleophilic character similar to that observed in the vinylidene and acetylide complexes. This behaviour may allow for the synthesis of novel organic molecules, and the literature contains several examples of complexes with unusual ligands presumed to be derived from additions to metallocumulenes generated *in situ*.³

Unlike the vinylidene and acetylide complexes, a general synthetic method to give metallocumulenes and metal polyacetylides has not yet been reported.³ Our attempts to generate these complexes from reactions of LiC_4R , HC_2C_2R , and $Me_3SiC_2C_2R$ ($R = H$, $SiMe_3$, Ph) with suitable transition metal substrates such as $RuCl(PPh_3)_2Cp$, $FeCl(CO)_2Cp$, $NiBr(PPh_3)Cp$ and $WCl(CO)_3Cp$ will be described. The reactions of these compounds with a range of electrophiles and nucleophiles will be reported, as will their use to construct novel heterometallic systems.

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Reactions of Diynes with Clusters of Ruthenium and Osmium

Anja Werth and Michael I. Bruce

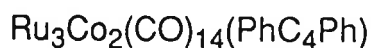
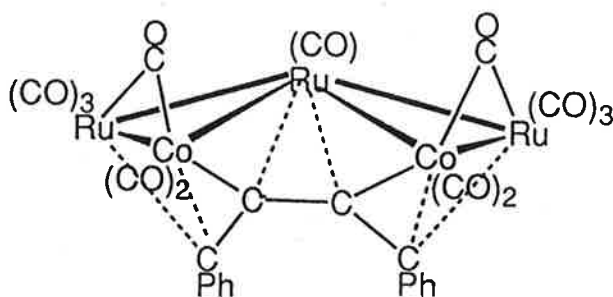
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While alkyne complexes of transition metal clusters are well known similar compounds from diynes have only recently been reported.

The two triple bonds have the possibility of reacting independently which may afford complexes with two or more different metal-ligand systems.

We have commenced an investigation of the reactions of ruthenium cluster complexes like $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$, $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ and $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$ with a variety of diynes $\text{RC}_2\text{C}_2\text{R}'$ ($\text{R}=\text{R}'=\text{H}, \text{SiMe}_3$; $\text{R}=\text{Ph}, \text{SiMe}_3, \text{tBu}$; $\text{R}'=\text{H}, \text{Ph}$).

The resulting hydrido- or alkyne cluster complexes containing a free triple bond can react with further metal substrates like $\text{Co}_2(\text{CO})_8$ to form heterometallic systems.



95 %

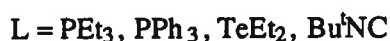
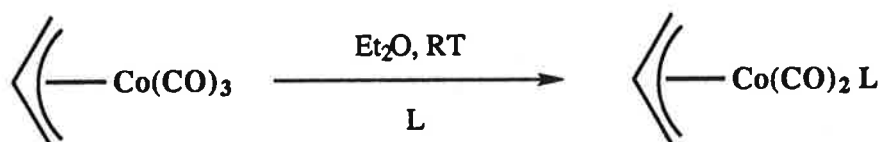
ASSESSMENT OF ALLYL COBALT CARBONYL COMPLEXES FOR METAL ORGANIC CHEMICAL VAPOUR DEPOSITION (MOCVD) STUDIES

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Previously, $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ has been used as a source compound, together with GaEt_3 , to deposit thin films of CoGa in an MOCVD reactor.¹ In this work we are assessing the suitability of allyl-cobalt systems for doping Co into II-VI and III-V semiconductors. Vapour pressures of the complexes $[\text{Co}(\eta^3\text{-allyl})(\text{CO})_3]$ (allyl = C_3H_5 **1**, 2-Me C_3H_4 , 1,1-Me $_2\text{C}_3\text{H}_3$) have been measured and at 20°C the values are found to be in the range 1.0 - 4.0mmHg. Thus these complexes are deemed to be too volatile for low level doping.

Substitution of one carbonyl ligand for another ligand L (L = PEt_3 **2**, PPh_3 **3**, TeEt_2 **4**, Bu^tNC **5**) in the complex $[\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_3]$ **1** decreases the vapour pressure of the substituted products by two orders of magnitude relative to **1**. Therefore complexes **2-5** are more suitable for MOCVD dopant studies and the vapour pressures and thermal decomposition behaviour of these complexes will be reported.



The possible use of $[\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{TeEt}_2]$ **4** as a single source precursor for the production of CoTe layers will also be discussed.

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The Assessment of Organometallic Precursors for the Chemical Vapour Deposition of Thin Metal Films

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There is a need to expand the range of chemicals that can be used in the chemical vapour deposition of thin films of metals and metal alloys. In particular, volatile chemicals of relatively low thermal stability are required so that low temperature ($< 250^{\circ}\text{C}$) growth of doped II-VI semiconductors can be achieved using conventional metal organic chemical vapour deposition (MOCVD) techniques. The further development of alternative deposition techniques brings with it the requirement for chemicals with a somewhat different set of physical properties. Suitable photo-sensitive chemicals are required for photo-enhanced CVD which can sometimes be accomplished without the need to extrinsically heat the substrate. Deposition of metals from organometallic chemicals of relatively low volatility can be achieved by CVD under high vacuum conditions in a process known as chemical beam epitaxy (CBE). The degradation pathway is different under MOCVD and CBE conditions, and so different chemical precursors may be appropriate.

We have assessed a range of organometallic chemicals for CVD applications, and some recent results will be described. The discussion will focus on two areas.

- (i) *The laser induced deposition of antimony films from tetraethyldistibine and tetramethyldistibine.* The deposition of antimony films on GaAs has been achieved using a XeCl excimer laser operating parallel to the substrate. Antimony films were obtained from as little as one pulse of the laser. Analysis of the deposits by XPS indicates no incorporation of carbon from Me_4Sb_2 , but there is a significant amount of carbon from Et_4Sb_2 .
- (ii) *The assessment of some single source compounds containing antimony-tellurium and transition metal-tellurium bonds.* Data on the physical properties and thermal degradation characteristics of compounds with Sb-Te, Mn-Te, Co-Te, and Fe-P bonds will be presented, and preliminary studies on the CVD of selected compounds will be discussed.

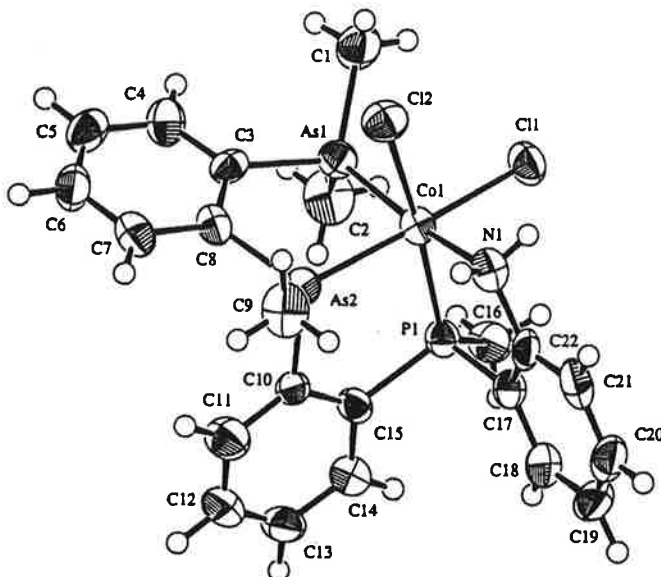
Completely Stereoselective Synthesis of a Chiral Quadridentate Ligand with As₂NP Donors

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The asymmetric bidentate (\pm)-(2-aminophenyl)(2-chlorophenyl)methylphosphine, (\pm)-1, has been prepared in four relatively high yielding steps from (2-aminophenyl)-diphenylphosphine and resolved by the separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing (\pm)-1 and an ortho-metalated (R)-dimethyl[1-(1-ethyl)naphthyl]amine. The absolute configuration of the S enantiomer of the ligand has been assigned by an X-ray crystal structure determination of the least soluble diastereomeric palladium(II) complex [(R),(R)]-(-)-589-[(2-aminophenyl)(2-chlorophenyl)methylphosphine-N,P][1-[1-(dimethylamino)ethyl]naphthyl-C²,N]palladium(II) hexafluorophosphate. Reaction of (\pm)-1 with sodium (2-dimethylarsinophenyl)methylarsenide is completely stereoselective giving (R*,S*)-1-[(2-dimethylarsinophenyl)methylarsino]-2-[(2-aminophenyl)methylphosphino]-benzene, (R*,S*)-2; as confirmed by a crystal structure determination of *cis*-[CoCl₂{(R*,S*)-2}]Cl.2H₂O (the molecular structure of the Δ -(R_{As},S_P) cation is depicted below). The optically active bidentate (S)-1 [or (R)-1] should again react with sodium (2-dimethylarsinophenyl)methylarsenide in a completely stereoselective manner to give (R,S)-2 [or (S,R)-2] the cobalt(III) complex of which is to be used as a potential chiral auxiliary in enantioselective synthesis.



Separation and Structural Characterisation of Diastereoisomeric Forms of Ligand-Bridged Dimetallic Species

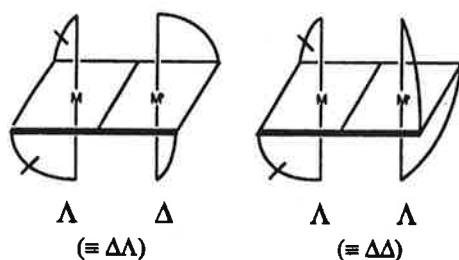
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There is considerable current interest in polymetallic supramolecular assemblies to achieve conversion of light energy to chemical fuels: however, one feature that is uncertain is the influence the stereochemistries of the various metal centres will exert on intramolecular electron- and energy-transfer processes. In addressing this problem, we¹ and others² have studied stereoisomerism in dinuclear species.

We have developed a synthetic methodology for ligand-bridged dinuclear species of the type $[(pp)(pp')Ru(BL)Ru(pp'')(pp''')]\text{4}^+$ by reaction of monomeric species $[Ru(pp)(pp')(BL)]\text{2}^+$ with $[Ru(pp'')(pp''')(CO)_2]\text{2}^+$ under decarbonylation conditions (pp, pp' etc. are bidentate polypyridyl ligands; BL is a bridging ligand).

There are two diastereoisomeric forms of such dinuclear species (shown for the simple case where $pp = pp'$ and $pp'' = pp'''$), each comprising an enantiomeric pair.



There is a significant difference in the relative ligand orientations: the terminal polypyridyl ligands "above" and "below" the plane of the bridging ligand are approximately parallel in the $\Delta\Delta/\Lambda\Lambda$ form, whereas they are perpendicular in the $\Delta\Lambda/\Lambda\Delta$ stereoisomer. We have separated the two diastereoisomeric pairs for a range of such dinuclear complexes by cation-exchange chromatography, and assigned the stereochemistry of the separated diastereoisomers by high field ^1H NMR studies (e.g. decoupling experiments, with connectivity confirmed by HMBC and HMQC 2D NMR techniques).

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The Development of a Chiral Iron Polymer-Supported Stationary Phase for Asymmetric Synthesis and Chromatography

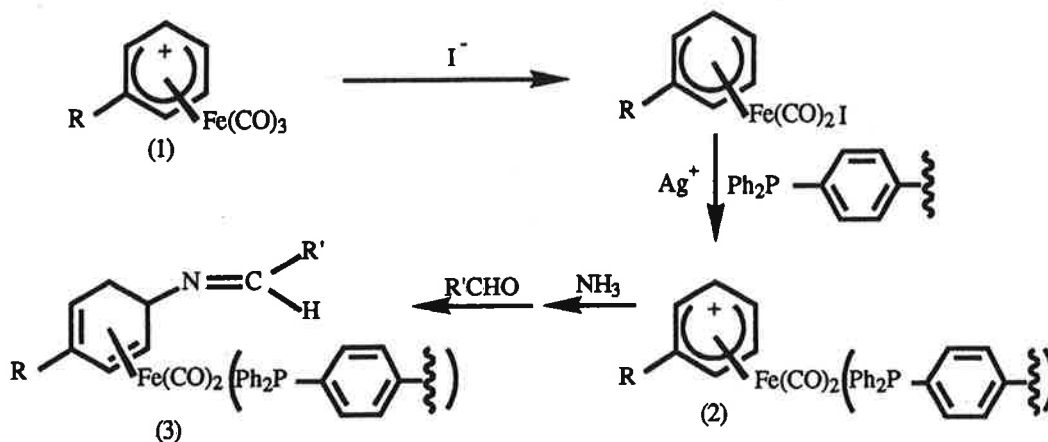
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Asymmetric organic synthesis is particularly important in the pharmaceutical industry. Due to the markedly different biological activities often shown by two enantiomers of the same molecule, the optically pure drug is in increasingly high demand.¹ In the drug market today, 44% of the synthetic drugs are chiral and 88% of these are sold in racemic form.² The administered racemic drugs can cause very serious side effects (*e.g.* thalidomide). Therefore it is necessary to develop new and efficient methods to produce pharmaceuticals in optically pure form.

This project is exploring the use of chiral organometallic iron compounds as novel reagents for the asymmetric synthesis of drugs and drug precursors. In addition, by attachment of such iron compounds to polymer surfaces we hope to develop new chiral stationary phases for the chromatographic separation of racemic chiral compounds of pharmaceutical interest.

Previous studies by other workers in our laboratory have shown that chiral dienyl complexes of the type (1) are powerful new reagents for the asymmetric synthesis of amines. In this project, we have now developed a method for the attachment of these chiral iron compounds to polystyrene by the replacement of one of the CO ligands by polystyrene supported triphenyl phosphine (Scheme 1). The chemistry of these new chiral materials (2) is being investigated, in particular their reactions sequentially with NH_3 and aldehydes, to give imine adducts (3). Subsequent addition of nucleophiles to imines (3) to provide chiral amines will be explored to determine the degree of asymmetric induction.



Scheme 1

1. E. Polastro, *Chimicaoggi*, Nov.1992, p23;
2. E. J. Ariens, *Chem. & Eng. News*, March 19, 1990, p40.

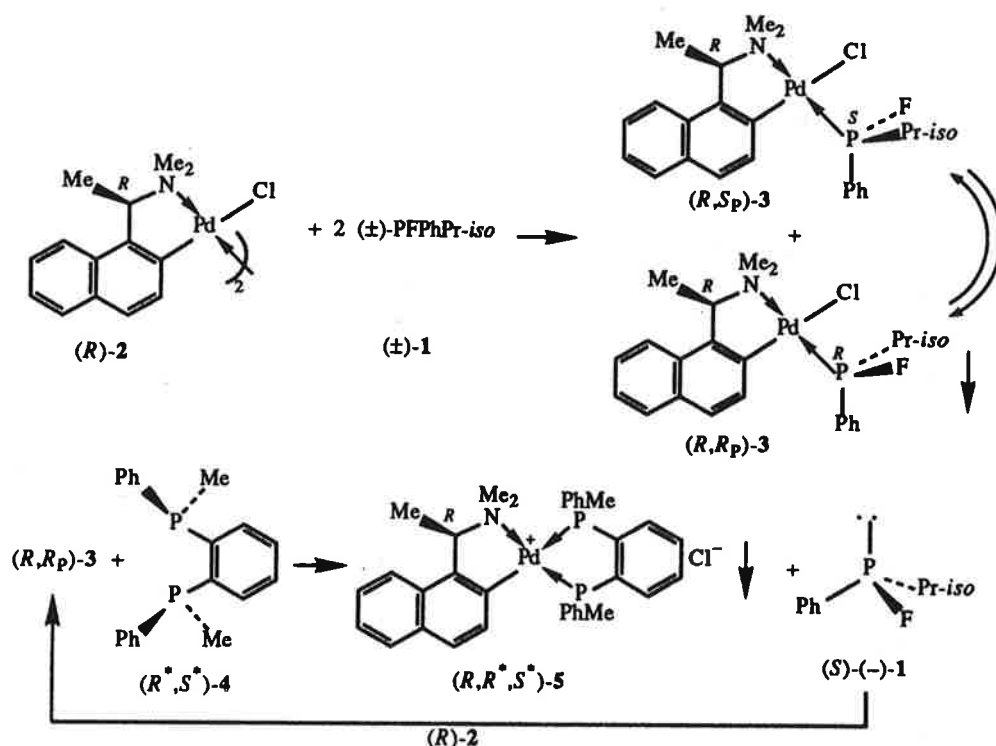
First Resolution of a Fluorophosphine Chiral at Phosphorus

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Chiral halophosphines of the type PXR^1R^2 when resolved into their enantiomers are potentially valuable intermediates for the synthesis of other optically active phosphorus compounds by substitution of the halogen atom.

(±)-Fluorophenylisopropylphosphine (±)-1 has been synthesized in good yield from the corresponding chlorophosphine by reaction with sodium fluoride in sulfolane. Upon treatment of (±)-1 with (*R*)-2 in dichloromethane diastereoisomer (*R,R*p)-3 (crystal structure) crystallized in 64% yield by second-order asymmetric transformation.

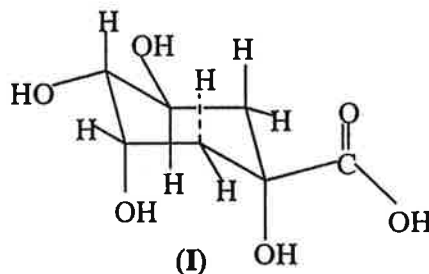


The liberation of optically pure (*S*)-(-)-**1** from (*R,R*)-**3** with (*R*^{*},*S*^{*})-**1,2**-C₆H₄(PMePh)₂ proceeds with retention of the configuration at phosphorus as verified by reparation of (*R,R*)-**3** from the free phosphine and (*R*)-**2**. The stereochemistry of reactions of optically active **1** in both coordinated and free form will be discussed.

NOVEL MIXED VALENCE V(V)-V(IV)-V(V) TRIMER WITH QUINIC ACID - A VERSATILE LIGAND

Rachel Codd, Peter A. Lay and Trevor W. Hambley
Inorganic Chemistry Division, University of Sydney, N.S.W., 2006

Quinic acid, 1-*L*-1,3,4,5-tetrahydroxycyclohexanecarboxylic acid (I), is a naturally occurring optically active α -hydroxyacid found in coffee and apples. The ligand offers several potential chelation sites via the hydroxy acid moiety and the triol groups. Quinic acid is a good model for α -hydroxyacids found *in vivo*, such as lactic and citric acid and the poly-hydroxy substituted cyclohexane ring also serves as a model for sugars. The ligand is therefore useful in synthesizing transition metal complexes which may mimic complexes formed *in vivo* hence furthering understanding of the roles played by such metals in biological processes.



We have isolated and structurally characterised an unusual mixed valence V(V)-V(IV)-V(V) trimer $(\text{NH}_4)_2\{[\text{V}^{\text{V}}(\text{O}_2)]_2[\text{V}^{\text{IV}}(\text{O})](\text{quinato}(3-))_2\} \cdot \text{H}_2\text{O}$ with quinic acid acting as a tridentate ligand. The mixed valence V(V)/V(IV) trimer, shows a distorted trigonal bipyramidal vanadium coordination environment comprised of entirely oxygen donors. The epr spectrum of the complex suggests that the electron is trapped at the vanadyl centre.¹

The ligand also stabilizes the relatively unstable Cr(V) centre as determined by epr spectroscopy. The mode of chelation here, is identical to that found in Cr(V)- α -hydroxyacid complexes of known structure such as $\text{Na}[\text{Cr}(\text{2-hydroxy-2-methylbutanoato}(2-))_2\text{O}]$.² The optically active Cr(V)-quinic acid complex synthesized here is being used to better understand the mechanisms of chromate induced carcinogenesis, in which Cr(V) species have been implicated.³

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Why is the Chromium Oxidation State Important in the Promotion of Chromium-Induced Cancers?

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Chromates are human carcinogens. This was recognised over forty years ago following epidemiological evidence indicating an increased incidence of lung cancer in workers employed in chromate industries. Carcinogenicity is further supported by animal testing as well as mutagenic activity in mammalian and bacterial cells. The majority of tests indicate that Cr(VI) complexes are carcinogenic and mutagenic whilst Cr(III) complexes are not. Interestingly, electron paramagnetic resonance spectroscopy of chromate-treated cells detected the production of Cr(V) *in vivo*. Subsequently, gel electrophoresis studies of DNA products indicated that incubation with Cr(V) resulted in significant DNA damage. The work described pursues these issues by focusing on the membrane permeability, toxicity and mutagenicity of Cr(III), Cr(V) and Cr(VI) complexes.

To date unicellular detection of chromium using electron microscopy has been unsuccessful due to the sensitivity limitations imposed by the electron beam. Consequently, incorporation of chromium into cells has only been assessed using radioactive ⁵¹Cr isotopes and atomic absorption spectroscopy, both of which are bulk techniques. In contrast, we have employed microprobe PIXE analysis to combine the features of high resolution and greater sensitivity to study chromium-treated hamster lung cells. We have been able to detect traces of intracellular chromium that provides information concerning the kinetics of chromium permeability, its distribution within the cell and most importantly, permeability differences associated with the oxidation state of the chromium complex. The complexes studied included; Cr₂O₇²⁻, [CrO(ehba)₂]⁻ (ehba = 2-ethyl-2-hydroxybutanoato(2-) acid), [CrO(mampa-dcb)]⁻ (mampa = macrocyclic tetraamide complex), [Cr(en)₃]³⁺ (en = 1,2-ethanediamine) and [Cr(phen)₂(H₂O)₂]³⁺ (phen = 1,10-phenanthroline). The toxicity levels and the mutagenic properties of these complexes utilising the same cell-line have also been investigated and these results will be discussed in relevance to microprobe PIXE analyses.

And Then There Was a Positron - The Tale of ^{45}Ti

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2234

Radionuclides that are positron-emitting are isotopes that are proton-rich. They may be prepared by high energy proton bombardment using a linear accelerator or a cyclotron. A positron (positive electron) is released from the nucleus which then loses its energy by collision with a nearby electron, resulting in annihilation. This collision results in the production of electromagnetic radiation.

The aim of this research is to investigate the production of a range of positron-emitting titanium coordination compounds that may be suitable for use as diagnostic and or therapeutic radiopharmaceuticals.

The radioisotope ^{45}Ti is a useful element in the field of nuclear medicine. Titanium-45 is prepared by the $^{45}\text{Sc}(p,n)^{45}\text{Ti}$ reaction and has a relatively short half life ($t_{1/2} = 3.08$ h). The work presented here represents the first production of ^{45}Ti on the southern hemisphere. The isotope decays primarily by positron emission ($>85\%$, $E_{\beta+\text{max}} = 1.02$ MeV), with γ -emissions of less than 1%, to give the stable isotope ^{45}Sc . This leads to the possibility of producing compounds that are suitable for use in Positron Emission Tomography (PET), one of the most sophisticated, non-invasive tools available for medical imaging. It can be used in the diagnosis and treatment of some of the leading causes of death and disability such as heart disease, cancer, and brain disorders.

To date, a number of preliminary investigations¹ have been carried out on several radiolabelled titanium coordination compounds for use as tracers or therapeutic agents. These coordination compounds have mainly involved ligands such as EDTA, DTPA and citric acid. However, a major problem to be overcome is the ease with which the complexes themselves hydrolyse. This has not been addressed in these earlier studies. Thus the concern in the production of any compounds during this research is that they be stable in an aqueous environment, since the radiolabelled drug is to be injected into the aqueous environment of the human body.

Chelation studies carried out so far have shown some interesting results using various commercial ligating molecules and further work is still to be completed. Work on the synthesis of novel ligating molecules is also being carried out with the aid of molecular modelling.

This poster will describe the tales and trails travelled thus far.

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Study of the Interaction of Fluoroquinolone Antimicrobial Drugs with Metal Ions

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The fluoroquinolones (FQs) are a new class of antimicrobial drugs which have excellent activity against many Gram-positive and Gram-negative bacterial pathogens.^{1,2} The mechanism of antibacterial action of these drugs is proposed to be the inhibition of DNA gyrase (Topoisomerase II) the enzyme responsible for coiling the long DNA molecule into the bacterial cell.^{1,2} FQs such as ciprofloxacin have provided a new approach to antimicrobial chemotherapy because difficult and dangerous pathogens such as *Pseudomonas spp.* can be effectively treated without the need for intravenous administration of antibiotics in hospital.

Over-the-counter pharmaceutical preparations containing iron, zinc and copper, or aluminium and magnesium in antacids, have been shown to inhibit the oral absorption of the FQ ciprofloxacin.³ For example, a 30 mL dose of the antacid Maalox given prior to ciprofloxacin (750 mg) reduced the amount of ciprofloxacin absorbed by 85%.⁴ With the increasing use of FQs in general medicine there is serious concern that interactions of this type may result in therapeutic failure.

Despite the increasing numbers of published reports on the detrimental effects of metal ions on FQ absorption, the pharmaceutical chemistry of the FQ's in the presence of metals is largely unknown, although some aspects of the chemistry have been reported.⁵⁻⁷ This paper will report studies concerned with the interaction of the FQs ciprofloxacin and norfloxacin with various metal ions.

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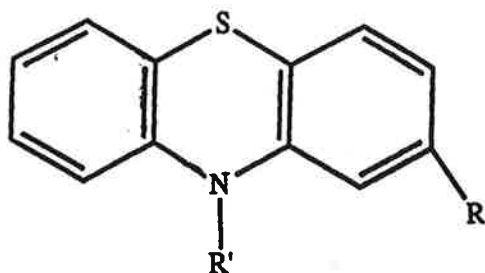
Coordination Complexes of Some Phenothiazine Based Pharmaceuticals and their Antiplasmid Action.

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Phenothiazine based pharmaceuticals have a wide variety of medical uses, such as an antihistamine, an anticholinergic or as a psychotropic drug. These drugs are known to produce toxic side effects after extended use. The drugs have also been shown to exhibit bacteriostatic effects both *in vitro*¹ and *in vivo*². Their mode of action is understood to be related to the endocyclic sulfur and the conformation of the nitrogen side chain. It is obvious that the sulfur (and possibly the nitrogen side chain) is capable of binding to a metal ion and this may be a reason for some of the drugs side effects.



R = H or Cl

R' = H, (CH₂)₃N(CH₃)₂ (A) or

CH₂CHCH₃N(CH₃)₂ (B)

X-ray crystallographic studies³ of Pd(II) chlorpromazine (A), Pd(II) and Hg(II) promazine (B) complexes have confirmed that these ligands act as monodentates, binding at the endocyclic sulfur.

Our study involves the isolation and characterisation of a number of metal complexes of these tricyclic drugs with the view to studying their effects *in vivo* and *in vitro*. Since the pharmaceuticals have been shown to eliminate the antibiotic resistance of bacteria, it was determined to study if the metal complexes had the same or similar effect on bacteria. This paper will present preliminary results concerning the isolation and characterisation of some of these metal complexes and their antiplasmid activity.

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Biomimetic Complexes with Asymmetric Coordination Sites

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Biomimetic chemistry continues to contribute many model complexes aimed to further our understanding of structural, spectroscopic and functional aspects of metal containing proteins. To date several workers^{1,2} have contributed to the range of 'binuclear' model complexes, however these complexes have typically been characterised by similar ('symmetric') coordination environments about each metal ion. This is in direct contrast to the structure of many metalloenzyme 'active sites' in which the coordination environment is often significantly distorted thus providing the protein with unusual physical and chemical characteristics not observed in simple model complexes.

Our approach has been to design, synthesise and characterise multinuclear model complexes that contain dissimilar coordination sites. These complexes then impart differing electronic and structural influences on the metal ions due to the 'asymmetric' nature of the coordinating ligand.

Specific metalloproteins that we have targeted are Ascorbate Oxidase and Superoxide Dismutase. In Ascorbate Oxidase the trinuclear 'active site' contains three copper atoms but sub-site differentiation is observed. For the Superoxide Dismutase metal ion selectivity (eg. Cu and Zn incorporation) is observed in a binuclear coordination site. These two enzymes comprise ideal examples for our 'asymmetric' ligands.

The synthesis, spectroscopic and redox characterisation of our asymmetric multinuclear model complexes will be presented together with a discussion on their relevance as biomimetic models for metalloprotein 'active sites' eg. Ascorbate Oxidase and Superoxide Dismutase.

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Evaluation of the Solvent-Dependence of Redox Standards

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The sensitivities of the redox potentials of various $\text{Fc}^{+/0}$ couples and $\text{C}_{60}^{0/-}$ to the nature of the solvent have been evaluated. From a variety of considerations, it has been concluded that the decamethylferricenium/decamethylferrocene ($\text{Me}_{10}\text{Fc}^{+/0}$) couple is the best redox standard of those studied. Factors that have been considered include the solubility, stability, heterogeneous electron transfer rate constants and sensitivity of the redox standards to the nature of the solvent.

While the large sizes of the fullerenes are expected to minimize differences in solvation within the two members of the redox couple (and hence the solvent dependence of the redox potential), solubility and reactivity problems probably limit their general applicability as redox standards. They also appear to have important π -stacking contributions to the redox couples.

$\text{Me}_{10}\text{Fc}^{+/0}$ has sufficient solubility in all solvents (including water) to obtain reversible redox couples. The steric effects of the methyl groups of the complexes both shield the Fe charge centre from significant interactions with the solvent and prevent distortion of the structure in order to allow the solvent to interact in the axial interactions. This couple is far superior than the IUPAC standard $\text{Fc}^{+/0}$ in these respects and this is reflected in the solvent dependences of the couples.

The conclusions drawn on the solvent dependences of the redox couples are supported by a variety of spectroscopic and other experiments.

Electrochemical Synthesis of Gold(I) Phosphine Complexes

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Electrochemical synthetic techniques offer the potential of simple and efficient methods of preparing gold(I) phosphine complexes. A number of complexes have been prepared by the anodic dissolution of gold into an acetonitrile solution containing phosphine ligand and mineral acid. These presently include LAuX complexes such as pmesAuCl, pmesAuBr, and pmesAuI where pmes represents the substituted triphenyl phosphine ligand *tris*(2,4,6-trimethylphenyl)phosphine. Use of the basic ligand, *tris*(2,4,6-trimethoxyphenyl)phosphine (tmpp) resulted in the synthesis of tmppAuCl and tmppAuBr, and [Htmpp][AuBr₂]. The electrochemical preparation of gold phosphine complexes with bidentate ligands such as 1,2-*bis*(diphenylphosphino)ethane (dppe) have been followed by ³¹P NMR solution spectroscopy.

These complexes have been investigated with stationary and rotating ring disk cyclic voltammetry, solution and solid multinuclear (³¹P, ¹³C) FT-NMR, FT-IR spectroscopy, solid and surface enhanced FT-Raman spectroscopy, and single crystal X-ray diffraction studies.

The effectiveness of these electrochemical synthesis procedures is limited by decomposition of ligands under certain experimental conditions and the region of electrochemical stability. This region of stability for the ligands has been investigated using cyclic voltammetry.

Since the role of the halide anions in the anodic dissolution of gold is important, it is being investigated in detail. Anodic dissolution of gold with mineral acids other than hydrohalide acids is also important and the mechanism of dissolution with these acids is also being investigated as is the influence of the phosphine ligand and the solvent.

The Electronic Properties of Triple-Halide Bridged Diruthenium Complexes, $[(AsR_3)_3Ru(\mu-X)_3Ru(AsR_3)_3]^n+$

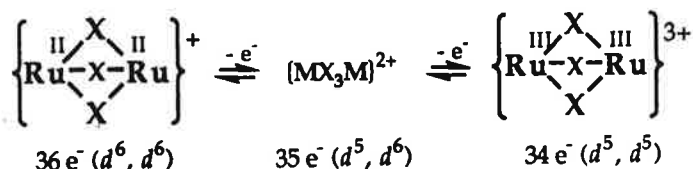
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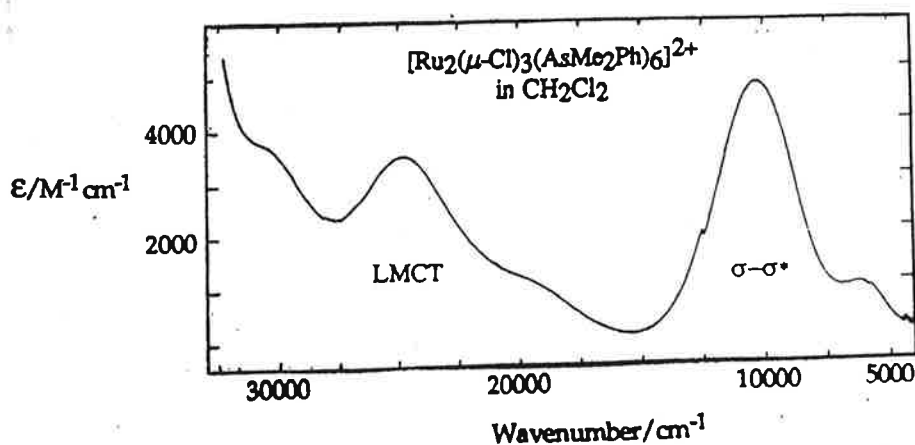
A range of triple-halide bridged binuclear species, $[Ru_2(\mu-X)_3(AsR_3)_6]^+$ ($X=Cl, Br$; $AsR_3=AsMe_3, AsMe_2Ph, AsMePh_2$), have been prepared:



These complexes, isolated in the $\{Ru_2^{II,II}\}^+$ state, exhibit two reversible one-electron oxidations corresponding to progressive oxidation of the binuclear RuX_3Ru core;



The solution electronic spectra ($45000 - 4000 \text{ cm}^{-1}$) of each dimer in successive oxidation states have been recorded in an optically transparent thin-layer electrode (OTTLE) cell at -50°C . The major features of the visible and near-ir regions of the mixed valence $\{Ru_2^{II,III}\}^{2+}$ species can be assigned to transitions within the molecular orbital manifold for binuclear D_{3h} systems. The wide range of analogous PR_3 complexes studied, $[Ru_2(\mu-X)_3(PR_3)_6]^{2+}$, have strikingly different properties from the corresponding ruthenium 'blues' $[Ru_2(\mu-X)_3(NH_3)_6]^{2+}$. In contrast the 35-electron AsR_3 complexes behave like the classical 'blues' (see visible/near-ir spectrum below), and this provides a key to understanding the range of behaviour we encounter.



The Ionic Product of Water in Highly-Concentrated Aqueous Electrolyte Solutions

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The ionic product of water, $K_w = [H^+][OH^-] = 10^{-pK_w}$, has been determined in aqueous NaCl (0.5 - 5.0 M), KCl (3.0 M), NaNO₃ (3.0 and 5.0 M) and KNO₃ (2.5 M) at 25°C from high-precision potentiometric titrations carried out in cells with liquid junction using either glass or hydrogen electrodes. Measurements of K_w provide a set of self-consistent data that can be used in the estimation of activity-coefficient changes and liquid junction potentials in the study of extremely concentrated electrolyte solutions. Where comparison is possible, results obtained by hydrogen electrode measurements are in excellent agreement ($ca \pm 0.005$ in pK_w) with other reliable experimental values and the predictions of the Pitzer activity-coefficient model. The glass electrode results are, as expected, routinely lower (by 0.03 - 0.05 pK_w units), owing to interference by Na⁺ ions. This effect virtually disappears in solutions of potassium salts. Comparison of the experimental results with the Pitzer predictions shows that knowledge of the ternary interaction parameters is essential to account for specific ionic effects in the concentration-dependence of pK_w .

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Decomposition of Monazite by Mechanical Milling with Sodium Hydroxide

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In this study, the mechanical milling method has been used successfully on a laboratory scale to replace the most difficult part of the industrial alkali method for decomposing monazite. It has been found that during milling, the monazite mineral was effectively decomposed by solid sodium hydroxide in about 10 hours, under an inert argon atmosphere with a 15:1 ball/powder ratio. The reaction products were rare earth element (REE) hydroxides and sodium phosphate, similar to those obtained in the industrial process. The sodium phosphate was readily removed by water leach.

In the industrial process for decomposing monazite with sodium hydroxide, the monazite mineral needs to be ground to a fine powder before reaction, which usually requires heating and elevated pressure. The products are a slurry and difficult to handle.¹ In the mechanical milling method used in this study, pre-grinding was not required, and the milling was carried out at ambient temperature and pressure. The products were dry fine powders, and easy to transfer in the subsequent processing stages, such as water leach. Mechanical milling, therefore, has apparent advantages over the conventional method of decomposing monazite.

Both beach sand monazite and carbonatite laterite monazite, two typical monazites of Western Australia, have been decomposed by the mechanical milling method. The decomposition products were basically same, except that the thorium, present in the beach sand monazite, was contained in a mixed REE/Th hydroxide, which might be a solid solution. After the sodium phosphate has been removed by water leach from the decomposition products of beach sand monazite, subsequent purification processes are like those used in industry, for the separation of the REE from thorium and other impurities, such as zircon. For the decomposition of carbonatite laterite monazite, the relatively pure REE hydroxide was obtained after the sodium phosphate was removed. Since the thorium content in this monazite is already very low (0.51% ThO₂), it appears that the REE/thorium separation may not be necessary. The water-leached products may be used directly for the individual REE separation after dissolution in acid.

When the milling products were left in air at room temperature for some time, the interplanar d-spacing of REE hydroxide has been found to decrease with the time. It is proposed that some of the Ce³⁺ in the hydroxide may have been oxidised to Ce⁴⁺, giving rise to a contraction in the unit cell. The unit cell parameters for the REE hydroxide solid solution before and after the oxidation have been derived from the Rietveld refinement of powder X-ray diffraction data. The crystal structure of the REE trihydroxide seems not to have changed with the Ce³⁺ oxidation, and the Ce⁴⁺ may still be in the REE site.

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Synthesis and characterisation of rare earth doped Bi_2O_3 and CeO_2 solid electrolyte materials.

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A number of metal oxides have been found to have applications as solid electrolyte materials. One such system which exhibits mainly ionic conduction, is Bi_2O_3 . The structure at room temperature is monoclinic and it exhibits electronic conduction, but at $\sim 730^\circ\text{C}$ it undergoes a structural transformation to the cubic fluorite phase, which exhibits high ionic conductivity. The cubic phase can be stabilised at room temperature by doping with rare earth or alkaline earth oxides, which leads to high ionic conduction at room temperature.

In this study mechanical alloying (ball milling) was used as an alternative synthetic route to calcination and coprecipitation to prepare new phases comprising Bi_2O_3 doped with Sm_2O_3 and CeO_2 respectively, as well as CeO_2 doped with Sm_2O_3 . The nature of the ball milling process promotes solid state chemical reaction between reactant powders as a result of repeated fracture and welding of the powder particles. The products of ball milling were characterised by Scanning Electron Microscopy, Energy Dispersive Spectrometry and Powder X-ray Diffraction (PXRD).

In carrying out the PXRD characterisation analyses, it was found that the new oxide phases yielded peaks very close to each other, sometimes overlapping, making identification difficult. This necessitated the use of Rietveld full profile methods to deconvolute the PXRD patterns, allowing for better identification and the determination, quantitatively, of the amounts of synthesised phases.

Characterisation of Gibbsite and Bayerite by Microscopy

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The rate of gibbsite crystallisation from solution is an extremely slow process and is not well understood. By studying crystallisation on different synthetic gibbsite crystal faces, a detailed understanding of the mechanism and rate of crystal growth from solution may be obtained. This work concentrates on the initial characterisation of polymorphs of aluminium trihydroxide (ATH) crystals produced from aluminate solutions.

Crystallisation from sodium or potassium aluminate solution results in the formation of gibbsite and/or bayerite. The ATH crystals were prepared by a number of methods including homogeneous and heterogeneous nucleation, slow de-supersaturation of the aluminate solution with addition of acid or by bubbling CO₂ through the solution.

At 70°C, crystallisation from potassium aluminate solution resulted in the formation of single crystals of gibbsite in the form of hexagonal needles, while agglomerates of hexagonal discs were formed from sodium aluminate solutions. Bayerite was the predominant species formed from sodium aluminate solution at room temperature.

The gibbsite and bayerite crystals were characterised by scanning electron microscopy and energy dispersive spectrometry to determine the morphology, composition and purity. X-ray diffraction was used to identify the major phase present. Transmission electron microscopy was used to determine the Miller indices of the crystal faces.

Gold and Silver Selective Anion Exchange Resins II

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The economic viability of selective anion exchange resins compared to activated carbon for precious metal recovery from cyanidated pulp has been recently demonstrated at MINTEK in South Africa [1, 2]. A strong base, sterically hindered resin, MINIX, has been successfully trialled on a scale of 100, 000 tonnes pulp/month [3].

In this work several gold and silver selective anion exchange resins are reported based on quaternary ammonium derivatives of free, blocked and macrobicyclic forms of tri-n-alkanolamines and tris(n-alkanethiol)amines. Several resin matrices were compared for their suitability for derivatisation.

In tests using synthetic and industrial leachates, some of the resins have shown outstanding selectivity for gold and silver cyanide complex abstraction. The loading of these outstandingly performing resins was observed under various conditions of temperature, pH and ionic strength and compared to industrial activated carbon and commercial resins. Various kinetics models were applied to the data in order to predict the loading characteristics. The elution and regeneration of these resins was observed and modelled using various stripping techniques [4]. Several of the resins were also independently tested and their performance compared to activated carbon and other selective resins.

References:

- [1]. Johns, M. W., *Proc. Randol Gold Forum '93*, Beaver Creek, Colorado, 1993, p. 293.
- [2]. Johns, M. W., *Proc. Randol Gold Forum '91*, Cairns, Qld., 1991.
- [3]. Kotze, M. H., Green, B. R., and Steinbach, G., in *Hydrometallurgy-Fundamentals, Technology and Innovations*, 1993, Hiskey, B. and Warren, G. Ed., AIME.
- [4]. Lawson, P. J., Dicinoski, G. W., and Rideout, J. A., *Proc. Randol Gold Forum '93*, Beaver Creek, Colorado, 1993, p. 301.

Degradation of organophosphates by metal oxide surfaces

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The presence of organophosphates which degrade to form inorganic phosphate in natural water systems is a factor in the formation of algal blooms. Understanding of the pathways leading to the degradation of organophosphate compounds could assist in the management of water resources to prevent these blooms from occurring.

The main pathway for degradation of organophosphates in natural water systems is thought to have been through the action of exoenzymes excreted by microorganisms.¹ Our work has shown that another pathway exists in which metal oxides, commonly found in the environment, promote hydrolysis of a model organophosphate, nitrophenylphosphate. The metal oxides studied include goethite (FeOOH), hematite (Fe₂O₃), titania (anatase and rutile), aluminium oxide and manganese dioxide. Several other insoluble compounds tested include two clays, kaolinite and bentonite, silica and barium sulfate. The metal oxides all showed activity. The clays, silica and barium sulfate exhibited no effect on the rate of hydrolysis.

Hydrolysis of the substrate, nitrophenylphosphate (2×10^{-6} M), by a metal oxide suspension in water (0.05g/250mL) at a pH~ 6 was complete within approximately 10 days by all of the metal oxides tested except titania and a manganese dioxide sample. The manganese dioxide sample completed the hydrolysis reaction in less than 24 hours. The hydrolysis reaction using the titania sample, however, did not go to completion. Its reaction rate showed evidence of product inhibition which was later established to be caused by phosphate adsorption.

Initial studies show that the hydrolysis reaction appears to be dependent upon the adsorption of the substrate onto the metal oxide surface. This is a pH dependent factor as adsorption of the negatively charged substrate only occurs when the pH of the suspension is below the point of zero charge, when the surface of the solid is positively charged. Other factors which may affect the rate of reaction include the types and numbers of active sites on the metal oxide surface as well as the surface area.

¹ Muir, D.C.G., Yarecheweski, A.L. and Grift, N.P.; *Toxicology and Environmental Chemistry*, 1989, **18**, 269-286.

Manganese Dioxide - The Role of a Surprisingly Complex 'Simple' Inorganic Compound in Batteries

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Although in principle a simple metal oxide, the simple formula of manganese dioxide belies a great complexity; there are a range of structural forms of MnO_2 , and in few is the formula strictly correct, non-stoichiometry being the norm. Manganese dioxide is one of the most widely used materials for primary batteries, and in particular electrolytic manganese dioxide (EMD) is an excellent depolarising material for alkaline batteries. EMD is produced in Newcastle at the Australian Manganese Company Limited plant, who supply approximately 20% of the world market for EMD for alkaline batteries.

EMD is not a single compound, but rather a family of closely related compounds whose properties vary according to the conditions of electrodeposition. The simplest physical picture of EMD is that of an intergrowth of two crystal forms. The battery activity of EMD is primarily related to the ability of the proton-electron pair, formed during discharge, to diffuse away from the EMD surface to the interior of the material. The rate at which the proton-electron pair diffuses is limited by the ability of the proton to move through the solid and is a function of the structural, chemical, physical and electrochemical properties of the EMD. Some results relating to how the conditions of its electrochemical deposition direct properties and eventually battery performance will be presented. In commercial alkaline batteries, the EMD is present as a paste with graphite and strong potassium hydroxide solutions with the role of the graphite being primarily to improve electrical conductance. Optimisation of the mixture for battery activity is of some concern, and some limited results relating to this commercial study will be outlined.

Although its use in primary batteries is well known, in terms of secondary (rechargeable) batteries, development is less advanced. Manganese dioxide is rechargeable only under conditions of shallow depth of discharge not exceeding a fraction of the one electron capacity. Even under these conditions only some 50 - 100 cycles can be obtained, related to structural changes in the discharge-charge cycles which are not fully reversible. However, there is evidence that some chemically-modified manganese dioxides have a greatly enhanced rechargeability, approaching 80 - 95% of the theoretical two electron capacity in each cycle with extended cycle life. The manganese dioxide phase that exhibits these properties is the birnessite group, a form of manganese dioxide prepared chemically (CMD), suitably doped with foreign metal ions. The excellent rechargeability has been interpreted in terms of the structural stabilisation of reduction intermediates due to the presence of the foreign metal ions. Notably, doped EMD also exhibits enhanced rechargeability under certain doping conditions, possibly due to the formation of an intermediate birnessite species during cycling. Results pertaining to our study of the properties of the intermediate stages formed during the reduction of an undoped birnessite material will be presented, along with some preliminary results of improvements resulting from doping with foreign metal ions.

Mechanochemical Transmetalation Reactions

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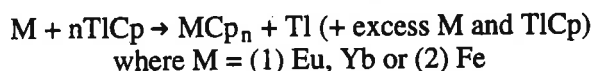
^CResearch Centre for Advanced Mineral and Materials Processing, Department of
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Mechanochemical alloying (ball milling) has been found to be a useful technique for encouraging otherwise difficult or unachievable chemical reactions to take place.^{1,2} The process simply involves milling the reagents at room temperature, in the solid state, in a sealed high energy ball mill vial, where repeated fracture and welding of the powder particles promotes the transmetalation reaction.

The reactions undertaken were of two types:

- (1) those known to occur in solution, in order to study reaction times versus yields, and
- (2) those known not to occur in solution.

The reactions performed were



After milling, the solid product mixture was characterised by X-ray diffraction, and the remainder was separated and isolated by solution techniques in order to determine the yield. Detection of Ti establishes that reaction occurs under ball milling conditions, rather than exclusively on workup.

Results indicate that, generally, a shorter milling time (minutes versus hours) is best, and that a larger excess of metal (for M = Yb) gives a better yield.

References:

1. G.B. Shaffer and P.G. McCormick, Materials Forum, 1992, **16**, 91.
2. N.G. Danielian, S.K. Janazian and V.V. Melnichenko, Modern Physics Letters B, 1991, **5**(20), 1355.

Lithium-doped Silica and Aluminosilicate Gels: Thin Film Production

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Electrochromic windows offer the possibility of substantial energy savings in terms of air-conditioning loads in large buildings with large window area. An integral component in an electrochromic window, based on substances that change colour with change in oxidation state, is a transparent ionically-conducting layer. Lithium-doped silica gels produced via the sol-gel process¹ are candidates for incorporation in electrochromic windows². Conditions for the optimisation of production of thin-films of lithium-doped silica and aluminosilicate gels have been investigated. Parameters that have been varied include gel composition, lithium source, dipping speed, drying regime, firing temperature and cooling rate. Problems that have been experienced include cracking of the films and film translucency. Spectra (Vis-NIR) and atomic force microscopy images will be presented to compare the transparency and integrity of the films obtained under different conditions and from various lithium precursors.

References

1. Hench, L.L. and West, J.K., *Chem. Rev.*, 1990, **90**, 33.
2. Klein, L.C., *Solid State Ionics*, 1989, **32/33**, 639.

Application of Volatile Acetylacetonates for Production of Zinc Oxide from Roasted Zinc Ore

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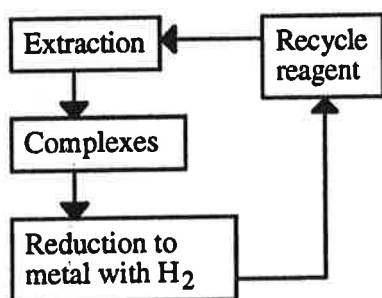
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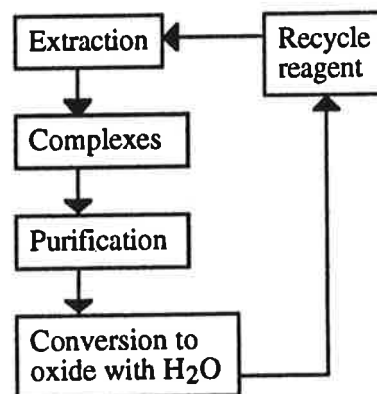
^C Pasmenco Research Centre, Newcastle, Australia

Preliminary studies of the potential application of volatile metal complexes for the winning of a range of metals from ores have been reported¹, as illustrated in Scheme 1 for volatile tetradentate Schiff base ligands as reagents. We have been developing this approach further to include studies of selective extraction of zinc from roasted ore ("calcine") to give a zinc oxide product which may be chemical grade ZnO. Scheme 2 illustrates this procedure. A less pure ZnO product, containing some ferric iron, could also be useful as a relatively clean neutralising agent in the electrolytic zinc plant in order to lower the heavy metal content of precipitated iron wastes.

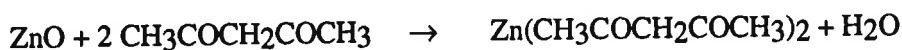
The reagent of choice for the potential process of Scheme 2 has been acetylacetone (Hacac) which reacts with a range of metal oxide and related materials as illustrated in Equation 1 for ZnO. Recent results indicate that the zinc acetylacetonate complex can be volatilised and subsequently hydrolysed with steam with negligible losses of the organic reagent.



Scheme 1 (from ref 1, simplified)



Scheme 2



Equation 1

Reference

¹Barr, D.W., Cox, M., Flett, D.S., Holt, G., "Extraction of nickel from low-grade ores by volatile organic reagents", IMM, London, pp 27-43 (1989)

A Synchrotron X-ray Study of the Electron Density in YFeO_3

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Ionic solids are often depicted as inter-penetrating arrays of negatively charged anions and positively charged cations. Accurate diffraction imaging of the electron density in compounds with anion structural symmetry lower than those approximated by the cation lattice tests the reliability of that model.

The rare earth orthoferrites RFeO_3 , where R is a rare earth element, belong to the perovskite-type (CaTiO_3) series of compounds. The small R cation radius distorts the ideal cubic perovskite structure forming an orthorhombic unit cell, while the environment of the Fe atoms remains essentially octahedral. The degree of distortion decreases with increasing R radius. Yttrium orthoferrite, YFeO_3 , is an important antiferromagnetic material with weak ferromagnetism. In assessing the nature of the magnetic interactions, YFeO_3 is a comparatively simple reference standard. The Y cation is diamagnetic and magnetic susceptibility is due to the Fe cation interactions. The magnetic arrangement can be described by two pseudo-cubic interpenetrating sublattices in which each Fe cation is surrounded by six nearest-neighbour antiferromagnetic Fe cations.

Structure factors for synthetic YFeO_3 have been measured for two small crystals using focused $\lambda = 0.75 \text{ \AA}$ synchrotron and Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) tube X-radiation. The structure factors from the two data sets are consistent. Space group $Pbnm$, orthorhombic, $M_r = 192.76$, $a = 5.5877(3) \text{ \AA}$, $b = 7.5951(4) \text{ \AA}$, $c = 5.2743(2) \text{ \AA}$, $V = 223.84(2) \text{ \AA}^3$, $Z = 4$, $D_x = 5.719 \text{ Mg m}^{-3}$, $\mu_{0.75} = 30.08 \text{ mm}^{-1}$, $F(000) = 356$, $T = 293 \text{ K}$, $R = 0.021$, $wR = 0.023$, $S = 4.22$ for 1039 unique reflections in the synchrotron data set.

Approximate high symmetry in the concordant deformation electron densities ($\Delta\rho$) indicates that the cations deform the electron density more strongly than the oxygen atoms. Overlapping atomic electron densities are deformed mainly by interactions involving cations, notably those between second nearest neighbours. Electron density overlapping with closed inner subshells of heavy cations is transferred by exchange to regions of lower electrostatic potentials further from the nuclei. In that process anions can 'acquire' negative charges, but the extent of that charge transfer is questionable because the transferred density retains the cations' symmetry. By penetrating the diffuse cation valence electron clouds the neutral anions are exposed to inner shell electrons. Point charge representations of the phenomenon are misleading.

However, the $\Delta\rho$ map symmetry is lower than that expected from Fe cation interactions alone. The map's symmetry is reduced by the effect of neighbouring Y cations, but not by neighbouring O anions. This confirms that the dominant effect on the $\Delta\rho$ density is by the cations. This may contribute to a better understanding of the magnetic interactions in the rare earth orthoferrites.

The Structural Variation Within the Rare Earth Orthoferrites and Aluminates

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In an exhaustive structural investigation of the rare earth orthoferrites (RFeO_3) Marezio Remeika and Dernier¹ related mean lattice parameter for each of those orthorhombic perovskite structures to the orientation of the FeO_6 octahedra and to the rare earth coordination geometry, attributing systematic variation with atomic number to the lanthanoid contraction. It is more difficult to explain the lattice parameter variation in detail in terms of simple models that represent bonded lanthanide atoms by spherical ions. The aspherical lanthanide coordination geometries that characterise the reduction in coordination number from twelve in the ideal perovskite structure to eight in the orthorhombically distorted perovskite retain two approximate 3-fold axes, related by a mirror plane. The rotations of the FeO_6 octahedra from the ideal orientation, and the displacement of R atoms from the ideal site reflect the development of R-O bonds of markedly different strengths. That effect is most obvious in the coordination polyhedra for the two crystallographically independent O atoms in the orthorhombic structure.

Additional information on the structure-distorting torques has been obtained from precise synchrotron radiation studies of the Gd and Ho members of the isomorphous RAlO_3 series, studied previously by several authors^{2,3}. With the improved precision small distortions of the AlO_6 octahedra due to the differential strengths of the R-O interactions that distort the structure can be identified.

The conclusions are reinforced by rigid body analysis of the vibrational motions of the corner connected AlO_6 octahedra that make up the framework for the structure. The analysis confirms that the O atom vibrations are well represented by the rigid body model. The rigid body librations for the AlO_6 group have an obvious relationship to the differences in strengths of R-O interactions. The amplitude of libration about the approximate three fold axis is restricted by three strong trigonally oriented R-O bonds.

Their effect of those strong R-O interactions on the deformation density in the structure is also evident near the R atoms, but not near the O atoms. The approximate symmetry of the deformation density near the Al atom is also higher than that expected if the perturbation of the electron density by bonding was predominantly due to interaction between Al and O atoms. It is far more consistent with a model in which interactions between the R and Al atoms perturb the electron density more strongly than the R-O or Al-O interactions.

The results are generally consistent with a structural model in which the extended electron densities for the cations influence the structural geometry, vibration amplitudes and the deformation densities for these perovskite structures.

¹ Marezio M., Remeika, J.P. and Dernier, P.D. (1970). *Acta Cryst.* B26, 2008-2022.

² Geller, S. and Bala, V.B. (1956). *Acta Cryst.* 9, 10-19.

³ Marezio M., Remeika, J.P. and Dernier, P.D. (1972). *J. Sol. Stat. Chem.*, 4, 11-19.

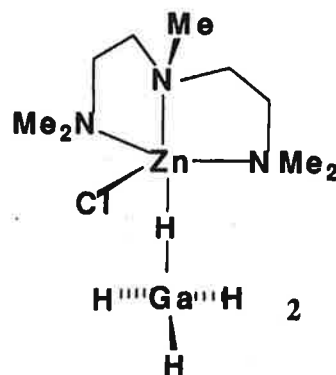
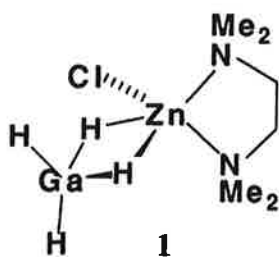
Hetero-bi-metallic Gallium/Zinc Hydrido Species

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Nathan, Brisbane, Queensland, 4111, Australia

As an extension of our systematic studies on the chemistry of gallane¹ we have embarked on developing hetero-bi-metallic species based on gallium hydride and a transition metal. Such compounds have potential application in generating binary alloys using CVD technology, and as selective reducing reagents in organic synthesis. We find that treatment of $\text{ZnCl}_2(\text{TMEDA})$ with LiGaH_4 gives compound **1** which has a novel doubly bridged $\text{Zn}(\mu\text{-H})_2\text{Ga}$ moiety. The corresponding PMDETA species, compound **2**, has been similarly prepared. However, here there is a single hydride bridge between the two metal centres. In general zinc hydride species tend to be insoluble and are reluctant to form coordination complexes.



1. G. A. Koutsantonis, C. Jones, and C. L. Raston, *Polyhedron*, 1993, **12**, 1829.

The Unusual Stevens Type Rearrangement of Some Dialkyl Sulfides on a Rh-Rh Bond.

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The range of organic transformations induced by metal complexes will be expanded through use of polynuclear metal-metal bonded species because the latter offer considerable scope for different types of metal-ligand bonding, including bridge bonding. Our previous studies¹ with the dirhodium complex $\text{Cp}_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ (**1**) have revealed an incredible variety of reaction types in which bridging groups have been implicated. Our investigation of the reactions of some dialkyl sulfides with (**1**) have added to that variety. When (**1**) is treated with excess Me_2S , the coordinative addition product $\text{Cp}_2\text{Rh}_2(\text{CO})(\text{Me}_2\text{S})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ (**2**) is formed initially, but in solution it converts to $\text{Cp}_2\text{Rh}_2(\mu\text{-SEt})\{\mu\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{H}\}$ (**3**). The structure of (**3**) has been confirmed by an X-ray crystal structure determination. This interesting conversion of a terminal Me_2S ligand to a bridging EtS group occurs under remarkably mild conditions (room temp., 3-4 hours). It can be classified as a Stevens rearrangement.

Similar reactions with other dialkyl sulfides have been explored. With Et_2S , the addition product $\text{Cp}_2\text{Rh}_2(\text{CO})(\text{Et}_2\text{S})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ (**4**) is formed initially, but it converts in solution to two bridging sulfido complexes $\text{Cp}_2\text{Rh}_2(\mu\text{-SEt})\{\mu\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{H}\}$ (**3**) and $\text{Cp}_2\text{Rh}_2(\mu\text{-SCHMeEt})\{\mu\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{H}\}$ (**5**). The conversion of (**4**) to (**3**) presumably involves elimination of ethene, whereas the formation of (**5**) from (**3**) is another Stevens rearrangement. Two stereoisomers of (**5**) have been detected by NMR spectroscopy. Each of the μ -sulfido complexes can also be formed by treatment of (**1**) with the appropriate thiol RSH. The reaction between (**1**) and Pr_2S yields the initial addition product but there is no evidence of rearrangement when this complex is left in solution. No reaction occurs when Pr^i_2S is added to (**1**).

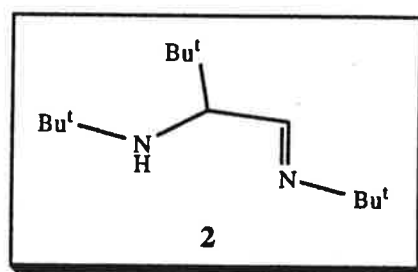
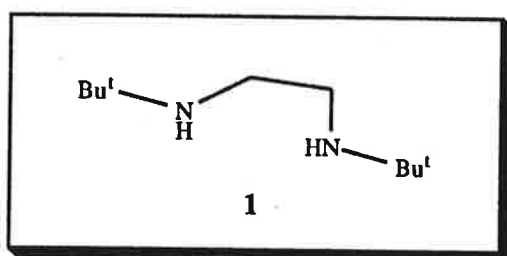
(1). R.S. Dickson, Polyhedron Report Number 39, Polyhedron, **10** (1991) 1995. 94

A Study of the Reactivity of Trimethylamine Alane with Selected Bulky Amines.

Michael Gardiner, Stacey Lawrence*, Colin Raston.

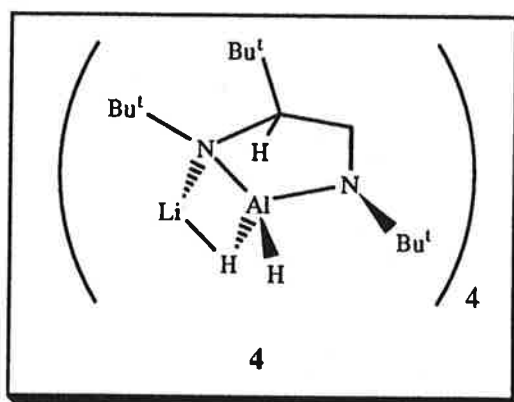
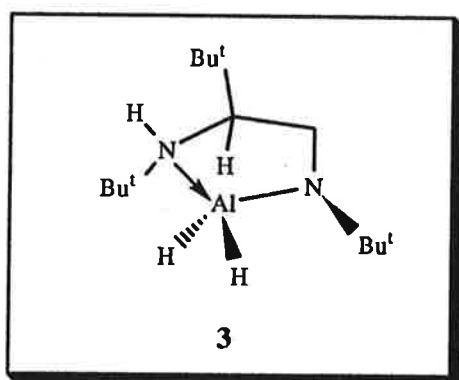
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Nathan, Brisbane, Queensland, 4111.

As part of a systematic investigation on amido-alane complexes, we have embarked on a study of the reaction of trimethylamine alane with selected bulky amines, in particular,



Results thus far include the treatment of **1** with $n\text{AlH}_3\text{NMe}_3$ in diethyl ether which affords a dimeric species when $n=1$ and a novel monomeric species when $n=2$.¹ In addition, compound **3** has been isolated from the reaction of **2** with $n\text{AlH}_3\text{NMe}_3$ ($n=0.5, 1, 2$) as an exclusive product.

Interestingly, the analogous reaction of AlH_3NMe_3 with the Li complex of **2** yields a tetrameric species, **4**.



(1) Atwood, J.L.; Lawrence, S.M.; Raston, C.L. *J. Chem. Soc., Chem Commun.*, 1994, 73.

A Ball and Socket Nano-Structure:

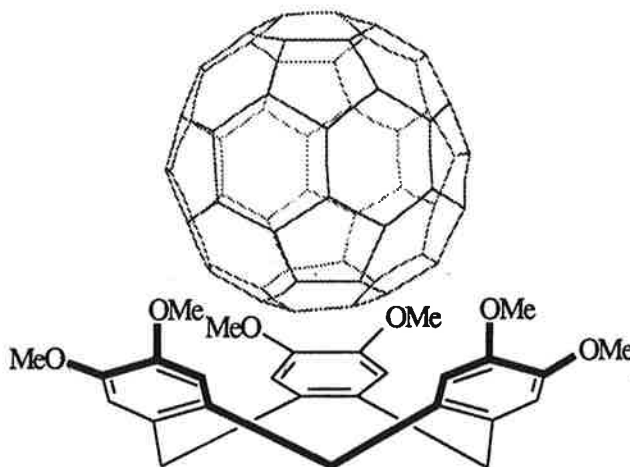
Fullerene-60.Cyclotrimeratrylene

Jerry L. Atwood^a and Peter C. Junk^a, Michael J. Barnes^{b,*} and Colin L. Raston^b

^a Department of Chemistry, University of Alabama, Tuscaloosa Alabama, 35487 USA

^b Faculty of Science and Technology, Griffith University, Nathan, Brisbane 4111 Australia

Complexation of cup-shaped cyclotrimeratrylene (=CTV) with fullerenes was examined as a route into direct retrieval of fullerenes from fullerite, and in the construction of ball and socket nano-structures. CTV forms a discrete 1:1 complex with C₆₀, **1**, which co-crystallises with free C₆₀. Excess CTV selectively precipitates C₆₀ and C₇₀ (> 67%) from toluene solutions of crude fullerenes. Addition of methylene chloride or chloroform to the precipitate, and to the C₆₀ complex, results in degradation of the CTV complexes, and precipitation of the fullerenes. The C₆₀ in **1** is arranged symmetrically in the CTV cavity such that three C-5 rings of the fullerene reside over the aromatic rings of the CTV, the intermolecular distance being commensurate with charge transfer interactions.



The Synthesis and Characterisation of Calcium/Lead Phosphate and Arsenate Fluorapatites

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Unsatisfactory current methods for the disposal of toxic heavy metal byproducts of industry have led to the development of a new technology for safer waste management. Known as 'XTALTITE', the process involves conversion of waste streams into synthetic analogues of natural minerals, which are highly stable and suitable for direct land burial. One mineral suited for this purpose is apatite, which can accommodate numerous substitutions covering the entire spectrum of heavy metals.

Mineral-like fluorapatites of phosphate and arsenate were synthesised on a laboratory scale, using a two stage hydrometallurgical and pyrometallurgical process. The effect of substituting lead into the calcium phosphate and arsenate fluorapatites was examined, by characterisation of the Ca-Pb solid solutions using Powder X-Ray Diffraction, quantitative profile refinement and Scanning Electron Microscopy.

Lattice parameters of the complete solid solutions were found to increase linearly with increasing lead content for the arsenate series, but with possible discontinuities and deviations for the lead-substituted phosphate apatites. Evidence of ordering of calcium and lead around the 20% Pb-substitution composition was found for both arsenate and phosphate fluorapatites.

Preliminary accelerated leach testing of the arsenate apatite series, conducted in boiling water, showed, initially, high leach rates for As, which decreased dramatically upon further leaching. The resulting low leach rate for arsenic provides a high level of confidence in the long term durability of such apatite heavy metal waste forms.

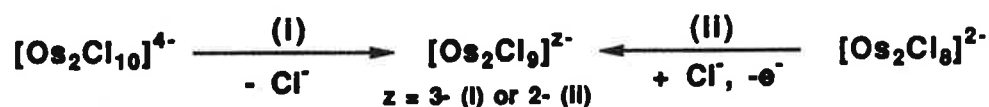
Transformation of Directly Metal-Metal Bonded $[\text{Os}_2\text{Cl}_8]^{2-}$ to Triply Chloride-Bridged $[\text{Os}_2\text{Cl}_9]^{3-}$.

Stephen F. Gheller * and Graham A. Heath

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The face-sharing $[\text{Os}_2\text{X}_9]^{z-}$ species were first identified in 1990.¹ The bioctahedral structure has since been confirmed crystallographically for $\text{Rb}_3[\text{Os}_2\text{Br}_9]$.² The $[\text{Os}_2\text{Cl}_9]^{3-}$ species were previously identified only in solution by reductive chloride expulsion of edge-shared bioctahedral $[\text{Os}_2\text{Cl}_{10}]^{4-}$. $\text{A}_x[\text{Os}_2\text{Cl}_9]$ salts ($\text{A}=\text{cation}$, $x=2,3$), have now been prepared by a radically different pathway: namely, oxidative addition to triply bonded $[\text{Os}_2^{\text{III,IV}}\text{Cl}_8]^{2-}$, initially forming $[\text{Os}_2^{\text{III,IV}}\text{Cl}_9]^{2-}$. The reaction can be performed either electrochemically, or chemically using suitable oxidants eg. NOPF_6 .



Newly isolated $(\text{Et}_4\text{N})_3[\text{Os}_2\text{Cl}_9]$ is characterised in the solid state by its far-ir spectrum, (326, 248 cm^{-1}). In solution the $[\text{Os}_2\text{Cl}_9]^{3-}$ anion exhibits electronic absorption band maxima at 28 600, 32 400 and 49 000 cm^{-1} , and, a highly structured near-ir band at 5800 cm^{-1} . The 28 600 cm^{-1} band is assigned to the metal-metal bonding $\sigma\text{-}\sigma^*$ transition which is strongly influenced by electron correlation. E^0 for the $[\text{Os}_2\text{Cl}_9]^{2-/3-}$ couple is equal to 0.20V vs Ag/AgCl. In solution mixed-valence $[\text{Os}_2\text{Cl}_9]^{2-}$ has a uv/visible manifold centred on 25 000 cm^{-1} , in addition to a broadened band at 5000 cm^{-1} . $[\text{Os}_2\text{Cl}_9]^{2-}$ can be further oxidised to $[\text{Os}_2\text{Cl}_9]^{1-}$ which has been optically characterised in solution. The spectral data for $[\text{Os}_2\text{Cl}_9]^{z-}$ and $[\text{Os}_2\text{Br}_9]^{z-}$ enable explicit comparisons of M - M bond strength with the isostructural $[\text{Ru}_2\text{X}_9]^{z-}$ complexes ($\text{X}=\text{Cl}, \text{Br}$).

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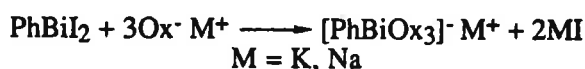
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Unusual Phenomena Observed in the Synthesis of 8-Quinolinolatosphenylbismuth(III) Derivatives

Katharine A. Smith, Glen B. Deacon and W. Roy Jackson

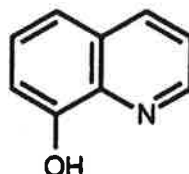
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We have been interested in the preparation of soluble arylbismuth(III) compounds for evaluation in cancer therapy.^{1,2} 8-Quinolinolatosphenylbismuth(III) derivatives were prepared by reacting phenylbismuth(III) halides or bismuth(III) trihalides with salts of 8-quinolinol* in ethanol. Some of the results indicated disproportionation of the product had occurred, which was shown by ¹H n.m.r. spectroscopy. Examples of the reactions attempted include:



Evidence will also be presented for retention of sodium chloride or bromide in PhBiOx₂ even after copious aqueous washings of the product. These include changes in the chemical shifts in the ¹H n.m.r. spectra and results from electrospray and FAB mass spectroscopy.

* 8-quinolinol = 8-hydroxyquinoline = oxine = OxH =



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LEWIS ACIDITY OF DIORGANOTIN CENTRES

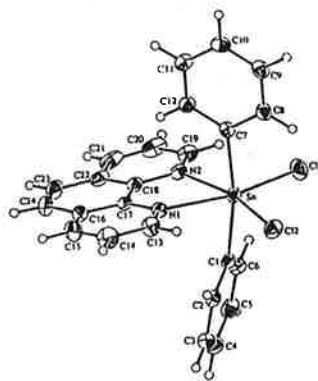
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Recent reviews of the coordination chemistry of organotin carboxylates ¹ and thiolates ² have revealed that there exists a rich structural diversity for these compounds. Seemingly closely related compounds may give rise to very different structures in which the geometry of the tin atom may vary, as the mode of coordination of the carboxylate (or thiolate) ligands are altered. The reason(s) for the large range of structural types remains uncertain. A possible cause is the different Lewis acidity of the diorganotin centres.

The above mentioned structural diversity does not seem to pertain in the bidentate aromatic amine (N \cap N) adducts of the diorganotin dichlorides. Hence, a systematic study of the molecular structures of a number of these compounds may give an indication as to the relative Lewis acidity of diorganotin centres. Added impetus to this work is found in the reported anti-tumour activity of these and related organotin systems. A structure/activity relationship for these tin compounds has been proposed.³ Derivatives in which the Sn-N bond distance is less than 2.39 Å are inactive and by contrast, those with Sn-N greater than 2.39 Å are generally active.

A series of crystal structures have been determined for R₂SnCl₂(N \cap N) compounds where R = alkyl or aryl and N \cap N = 2,2'-bipyridyl, 1,10-phenanthroline and other related Lewis bases. An example, namely that of Ph₂SnCl₂(1,10-phenanthroline) is shown below:



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Small Ferromagnetic Clusters as Possible Building Blocks for Molecular Magnetic Materials

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In two recent books on magnetochemistry, methods have been described for synthesizing molecular materials possibly suitable as molecular-based magnets.^{1,2} One such method is to obtain small, well characterized, ferromagnetically-coupled clusters which can subsequently be stitched together into three-dimensional arrays. The latter requirement is the difficult part of the strategy. In this paper we describe the structure and magnetism of a hexanuclear copper(II)-bipyridine complex, $[\text{Cu}_6\text{bipy}_{10}(\text{CO}_3)_2(\text{OH})_2](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$. Low temperature magnetisation studies have proven particularly useful in defining the $S' = 6/2$ ground-state which arises from ferromagnetic coupling of the species via μ -hydroxo and μ -carbonato pathways. Swapping the anion in this hexanuclear complex to PF_6^- has also led to a novel tetranuclear framework being obtained, $[\text{Cu}_4\text{bipy}_4(\text{PO}_4)_2]^{2+}$, which contains bridging phosphate groups formed by hydrolysis of PF_6^- , but which displays weak net antiferromagnetism.

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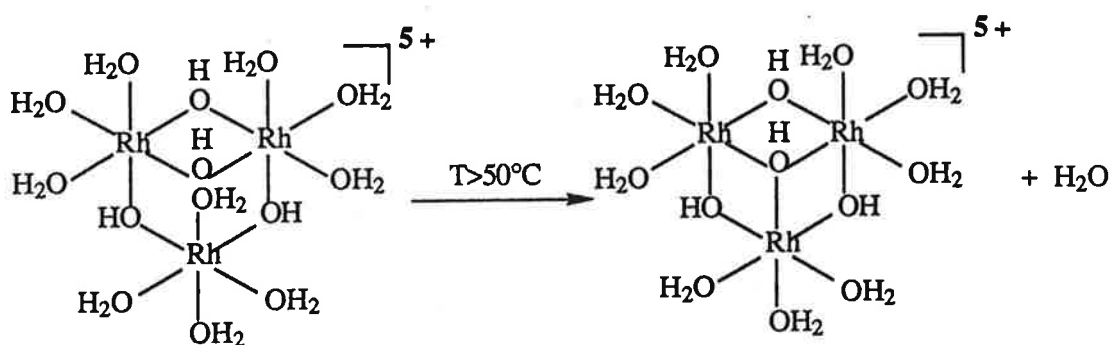
Synthesis And Solution Characterization of Open and Closed Forms of the Rh(III) Hydrolytic Trimer

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Recent studies into the early stages of the hydrolytic polymerization of Rh^{3+} have shown that small Rh(III) oligomers are formed in alkaline solutions of $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ and can be separated by ion-exchange chromatography¹. Solution characterization techniques such as UV-vis spectroscopy, charge/Rh determinations, elution behaviour with oligomers of known charge and ^{17}O and ^{103}Rh NMR² have been used to characterize these oligomers. The Rh(III) trimer is one oligomer which has been characterized in detail but some uncertainty remains about its structure. Our recent investigations have shown that two forms of trimer exist whose properties are consistent with the structures given in the scheme. The open form of the trimer can be converted to the closed form by heating solutions of the open form at temperatures above 50°C for several hours.

A major kinetic study has been carried out to follow the conversion of the open form of the Rh(III) trimer to the closed form. The reaction rate was found to increase significantly with pH. This is probably due to deprotonation of the trimer which results in labilization of the remaining H_2O molecules coordinated to the Rh(III) centre. A mechanism consistent with the kinetic data has been developed.



Scheme

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Inorganic Chemistry in the Raw: Reactions of Naked Metal Ions with Lonely Sulfur Molecules Producing Some Unusual Progeny.

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Gas phase reactions of metal ions with molecules may be viewed as a measure of the fundamental reactivity of the ions, devoid of the complicating effects of solvation and counter ions. We are investigating gas phase coordination chemistry, through the reactions of metal cations with various ligands, including thiols and H_2S . In this study we examine the reactions of naked metal ions with sulfur, $\text{S}_8(\text{g})$. Being an elemental ligand this has fundamental significance: further, there are multiple coordination sites with the same type of donor atom, avoiding some of the variability of coordination site as occurs with thiols. Metal polysulfides are well known in solution and in crystals.

Naked monocationic metal ions are generated using laser ablation (LA), and trapped in a vapour of sulfur inside the ion-trap of a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The FTICR/MS works best at low pressures ($<1 \times 10^{-7}$ mbar) and so reactions can be studied only in a limited pressure range. The ion trapping is efficient, but reactions cannot be studied for reaction times longer than 100s: however in most cases these conditions are sufficient for complete reaction of the naked metal ion.

An outline of the method will be presented with emphasis on the processes occurring in the LA/FTICR/MS experiment.

The results of reactions of M^+ ions for many metals over the periodic table will be presented. The products frequently contain an even number of S atoms, and range up to $[\text{CuS}_{16}]^+$. Probable structures for selected products will be presented.

Previously only one system only has been extensively studied: Frieser¹ et al studied the reaction of Fe^+ with sulfur vapor and produced the ions $[\text{FeS}_n]^+$ where $n=1-10$. These ions were shown to undergo sequential collisional dissociation by loss of S_2 species.

This technique examines only the monocationic state of the metal, which is not the usual oxidation state for the coordination chemistry of most metals in condensed phases. Further, laser irradiation of metals or metal compounds often produces metal ions in electronically excited states, and so care must be taken in the design of the LA/FTICR experiment to make sure ground state ion properties are being studied and compared.

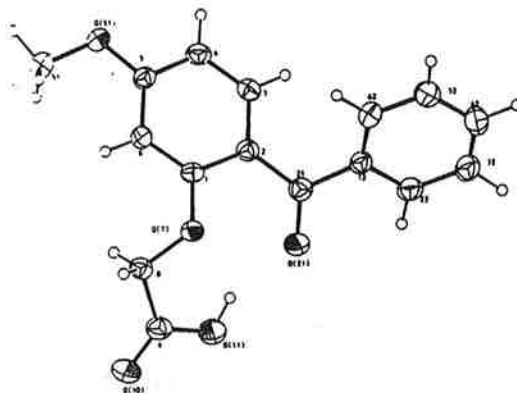
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**Some Complex Chemistry of the Tridentate Substituted
Phenoxyalkanoic Acid, (2-Benzoyl-5-methoxyphenoxy)acetic Acid**

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A new potentially tridentate carboxylic acid, the substituted phenoxyalkanoic acid (2-benzoyl-5-methoxyphenoxy)acetic acid, LH, (1), has been synthesized and some of its coordination chemistry investigated.

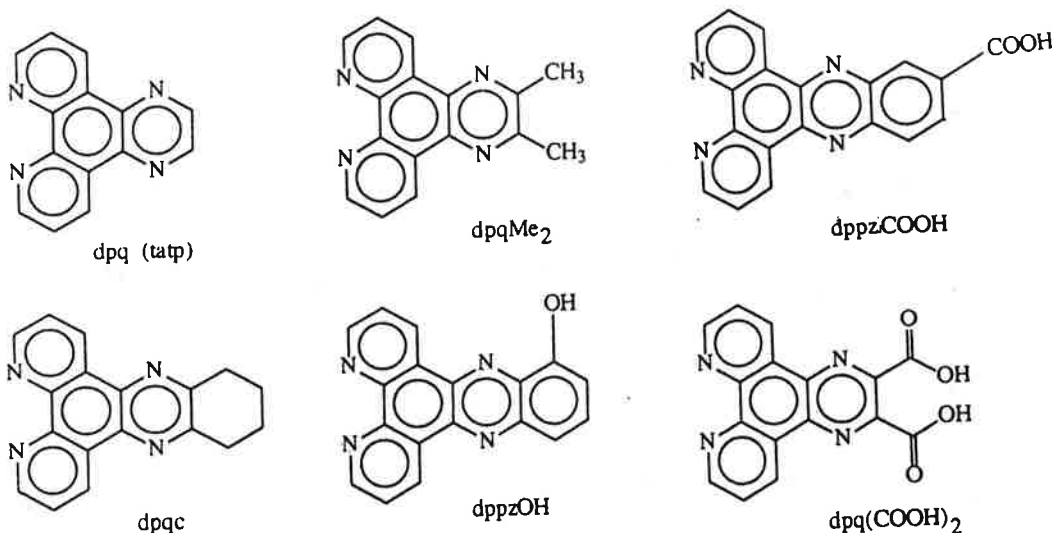


The Synthesis of Phen-Based N₂-Bidentates and Their d⁶ Metal Complexes

Ivan Greguric* and Janice R. Aldrich-Wright¹

Department of Chemistry, University of Western Sydney, New South Wales 2560, Australia

Initial computer simulation^{2,3} of the Δ and Λ -[Ru(phen)₃]²⁺ cations incorporated into various nucleotide base sequences indicated comparatively little allowed overlap of the phenanthroline ligand. The ambiguity^{4,8} concerning the enantiomeric selectivity of this simple DNA probe Δ and Λ -[Ru(phen)₃]²⁺, may be due, indirectly, to the inadequacy of this overlap. If metal complexes like [M(diimine)_m]ⁿ⁺ are intended to bind by intercalation the ligand must be enhanced by the extension of the available aromatic area and the resulting complexes' solubility improved. Elementary changes to the molecular size of the parent diimine, *phen*, produced compounds such as dipyrdo[3,2-d:2'3'-f]quinoxaline (*dpq*), dipyrdo[3,2-a:2'3'-c]phenazine (*dppz*) and 7,8-dimethyldipyrdo[3,2-a:2'3'-c]phenazine (*dppzMe*)⁹. In this work the effect of further variation such as the addition of an unsaturated ring, and aldose or a functional group on the added ring are being explored. These are illustrated below. The development of new molecules that bind strongly and selectively to nucleic acids is hoped to expand the range of drug, probes and visualizing agents that can be used for molecular biology.



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Synthesis and Reactions of a Cyclic Platinum(II) Thiolate Complex

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Brian K. Nicholson,^B and David R. Russell^A

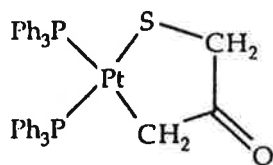
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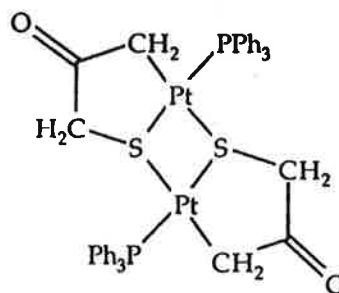
The thiolate ligand, RS^- , is a fundamental class of ligand, and one which shows a very strong preference to binding to soft, late transition-metal centres. In recent years there has been a resurgence of interest in the chemistry of metal-thiolate complexes, spurred in part by the occurrence of metal-thiolates in biological systems and inorganic pharmaceuticals.

Reaction of the readily prepared chloro-acetyl complex *cis*- $[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ with an excess of Na_2S yields the cyclic thiolate complex **1** in high yield. Ligand substitution reactions of **1** with phosphines, phosphites and alkyl isocyanides (L) results in mixtures of isomers of the monosubstituted complexes $[Pt\{SCH_2C(O)CH_2\}(PPh_3)L]$.

The reactions of **1** with a range of carbon and metal electrophiles have been studied. With alkyl halides RX , alkylation of the sulfur occurs with loss of a PPh_3 ligand (as Ph_3PMe^+) giving in high yield the cyclic thioether complexes $[Pt\{RSCH_2C(O)CH_2\}(PPh_3)X]$, whereas with mercury(II) halides the dimeric thiolate-bridged heterobimetallic Pt-Hg complexes $[Pt\{SCH_2C(O)CH_2\}(PPh_3)_2 \cdot HgX_2]_2$ are formed, and crystallographic data will be presented on the $HgBr_2$ adduct. In contrast, reaction of **1** with the labile Rh complex $[(OC)_2Rh(\mu-Cl)_2Rh(CO)_2]$ results in PPh_3 abstraction, giving the dimeric thiolate-bridged complex **2**, characterised by an X-ray study.



1



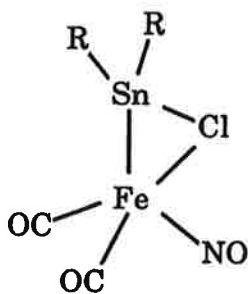
2

Some Chemistry of Compounds with Group 14 to Transition Metal Bonds.

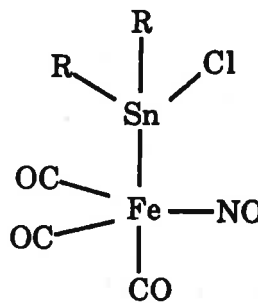
Brian K. Nicholson, Mayson Kay and Scott McIndoe.

School of Science and Technology, University of Waikato, Hamilton, New Zealand.

The chemistry of compounds formed in reactions of $\text{Na}[\text{Fe}(\text{CO})_3(\text{NO})]$ with germanium and tin polyhalides has been re-investigated. Previous reports suggested halide-bridged species of type 1 were formed, based on spectroscopic evidence¹. However, we have now shown that these are "normal" derivatives such as 2 on the basis of X-ray structures of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\text{NO})$ and $\text{Ph}_2\text{ClSnFe}(\text{CO})_3(\text{NO})$. The complicated infrared spectra in the $\nu(\text{CO})$ region has been interpreted as providing indirect evidence for $d\pi-d\pi$ bonding in the Sn-Fe bond.



(1)



(2)

It has been shown recently² that $\text{H}_3\text{Si-O-SiH}_3$ reacts with $\text{Co}_2(\text{CO})_8$ to give, *inter alia*, $\text{Si}[\text{Co}_2(\text{CO})_7]_2$, which is the usual product of SiH_4 with cobalt carbonyl. This involves cleavage of the very strong Si-O bond under reducing conditions, presumably via disproportionation processes. To examine simpler systems we have now characterised species from the reactions of $\text{HPh}_2\text{Si-E-SiPh}_2\text{H}$ with $\text{Co}_2(\text{CO})_8$ ($\text{E} = \text{O}, \text{S}$) to assess the properties of Co-Si-O and Co-Si-S linkages.

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Copper Complexes of Asymmetrical N₂S₂ Ligands

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Recently we have investigated the changes in structure and properties that arise when the co-ordinated thioethers are displaced from a copper(I) N₂S₂ complex replacing them with a second diimine moiety from additional ligand.¹ The ligand in this case was symmetrical with two imine type nitrogen donors and two thioether type sulphur donors.

In continuation of our research into the characteristics of copper-N₂S₂ entities, which are of biological importance, our efforts have been directed towards producing asymmetrical N₂S₂ ligands which possess both thioether and thiolate sulphur donors. These types of ligands are of even further relevance in view of the donor sets found in some copper containing proteins.²

This has led us into an investigation of ligands containing various protecting groups for sulphur, and also into the conditions necessary to remove these groups prior to, or concomitantly with, metal encapsulation. One such group that has been employed previously for this purpose is tertiary-butyl.³

Detailed here will be an investigation of two closely related ligands containing tertiary-butyl thioether and their corresponding copper chemistry. X-ray structural determination, along with ¹³C NMR spectroscopy, have shown the copper(I) complexes of these ligands to retain the tertiary-butyl thioether linkages under conditions reported to result in facile elimination of this group (for example Fig. 1).

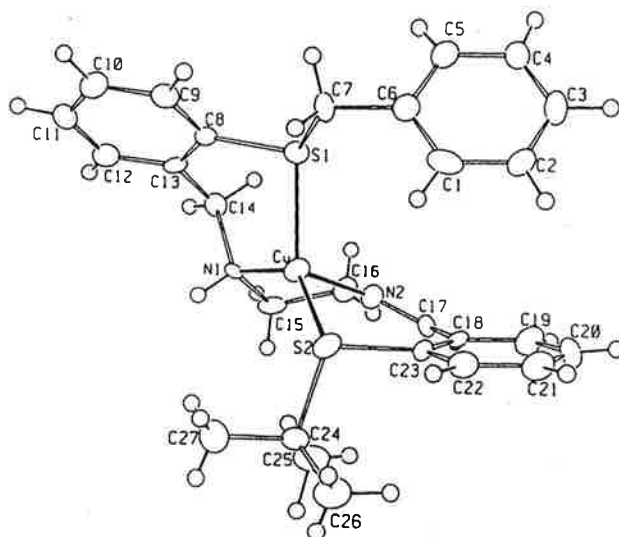


Fig. 1 [Cu(L1)]⁺ cation as determined by x-ray crystallography.

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Metal Complexes of Sterically Active Ligands

Anthony T. Baker* and Jeffrey K. Crass

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A number of bis(HET)alkane ligands were synthesised, where HET = pyridin-2-yl, pyrazol-1-yl, 2-imidazolin-2-yl, benzimidazol-2-yl, benzothiazol-2-yl and benzoxazol-2-yl, to map the coordinating ability of these potentially chelating bidentate ligands. A range of ligands was proposed in order to provide variation in coordinating capacity and fine control of steric activity. The bis(HET)alkane ligands, where HET = benzimidazol-2-yl, benzothiazol-2-yl and benzoxazol-2-yl were obtained through the polyphosphoric acid catalysed condensation of dicarboxylic acids with *o*-phenylenediamine, *o*-aminobenzenethiol and *o*-aminophenol¹ respectively. The bis(pyrazol-1-yl)alkanes were prepared by reaction of the appropriate pyrazole with dibromoalkanes². First row transition metal, palladium and platinum complexes of these ligands, of the general formula $[M(\text{ligand})X_2]$, (where X = halide) were prepared as part of the program of characterising the ligands. The effect of variation in the connecting chain and substitution of the functional group (HET = benzimidazol-2-yl, benzothiazol-2-yl and benzoxazol-2-yl) on the spectroscopic properties (diffuse reflectance UV/Vis/NIR) will be presented.

Bis(1,2-bis(2-imidazolin-2-yl)ethane-N,N') nickel(II) bromide dihydrate is square planar with the two heterocycles on the same side of the coordination plane and tilted at angles approaching the perpendicular. This complex has a similar structure to [(1,2-bis(6-methylpyridin-2-yl)ethane-N,N')(malonato, O,O')palladium(II)] trihydrate³. The complexes *cis*-aquadichloro(1,2-bis(3,5-dimethylpyrazol-1-yl)ethane-N)copper(II) and tris(*trans*-dichloro (μ -(1,2-bis(3,5-dimethylpyrazol-1-yl)ethane-N,N'))palladium(II)) are also square planar but the ligand acted as a monodentate in the former complex and as a bridging bidentate in the latter trimer. In the crystal structures of [bis(acetato-O,O') (1,3-bis(benzimidazol-2-yl)propane-N,N')cobalt(II)] dihydrate ethanol solvate and [(1,2-bis(benzimidazol-2-yl)ethane-N,N')(ethanato-O)(nitrate-O)(nitrate-O,O')nickel(II)] the metal ions are in distorted octahedral environments. Some of the important structural features will be presented and the implications discussed.

An interesting feature of a number of the structures is the intramolecular approach of hydrogens to the metal centre. The hydrogen atoms of the methylene groups of the ligands were often found to closely approach the metal atom. Agostic intramolecular interactions of the kind C-H...M had been reported in a number of structures⁴; those representing a 'strong' interaction having M...H distances under 2 Å, whereas the 'weaker' interactions were considered from 2 Å to the sum of the Van der Waals radii⁵. In certain cases, agostic intramolecular interactions of the kind C-H...M were found, whereas in other cases the interaction represented 'close packing' of atoms and these results will also be presented.

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Metal Complexes of Pyrazolyl Ligands

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Oligopyridines have been shown to yield metal complexes of unusual topology. In the ligands reported here oligopyridine analogues have been prepared by replacing some of the pyridinyl rings with pyrazolyl groups. A number of new bidentate, tridentate and quinquedentate ligands have been prepared. Several complexes have been prepared and structurally characterised. Metal complexes of the quinequepyridine analogues are of unusual structure, of a type not reported for quinequepyridine.

The bidentate ligands 3-(pyridin-2-yl)pyrazole (pp), 5-methyl-3-(pyridin-2-yl)pyrazole (mpp) and tridentate ligands 2,6-bis(pyrazol-3-yl)pyridine (bpp) 2,6-bis(5-methylpyrazol-3-yl)pyridine (bmpp) were prepared using Lin and Lang syntheses of pyrazoles¹. The potentially-quinquedentate ligands, 2,6-bis[1-(pyridin-2-yl)pyrazol-3-yl]pyridine (1bppp), 2,6-bis[5-methyl-1-(pyridin-2-yl)pyrazol-3-yl]pyridine (1bmppp) and 2,6-bis[3-(pyridin-2-yl)pyrazol-1-yl]pyridine (3bppp) and 2,6-bis[5-methyl-3-(pyridin-2-yl)pyrazol-1-yl]pyridine (3bmppp), were prepared using the above-mentioned bidentate and tridentate ligands as starting materials. The pyrazoles were reacted with potassium to yield a salt which was reacted in an inert solvent with an appropriate bromo compound to produce the desired compound. Another tridentate which was prepared in a similar manner was 1,3-bis(pyridin-2-yl)pyrazole (bpypz).

A copper(II) and two cobalt(II) complexes of 1bppp have been characterised by single crystal X-ray diffraction which shows the copper complex and one of the cobalt complexes to contain the $[M_2(1bppp)(\mu^3-OH)(O_2C_2H_3)_2]^+$ cation. In each case, the cation dimerises through the triply-bridging hydroxo ligand. In these complexes, one metal centre is six-coordinate and the other is five-coordinate. The other cobalt complex, $[Co(1bppp)]Cl_2$ has trigonal bipyramidal geometry with a 1:1 metal:ligand ratio. Only the central three heterocycles are coordinated to the metal atom. The cations of $[Ni(bmpp)_2][ClO_4]_2$ and $[Fe(bpypz)_2][PF_6]_2$ are both of approximately octahedral geometry. There is a remarkable difference in the Fe - N_{central} and Fe - N_{distal} bond lengths for the tridentate ligand that has a central five-membered heterocycle.

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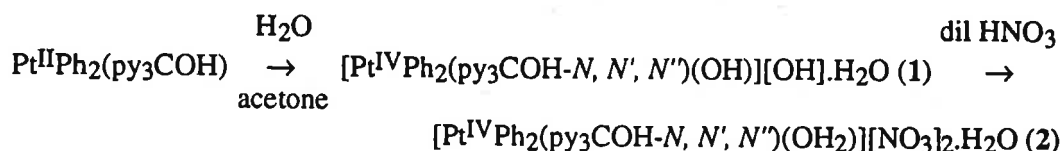
Oxidation of σ -Bonded Organometallic Compounds by Water

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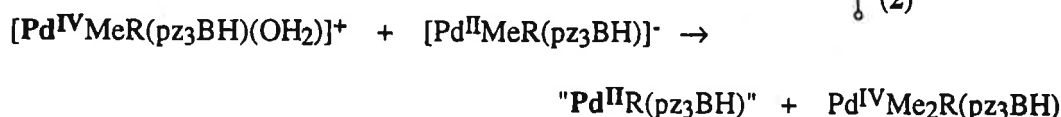
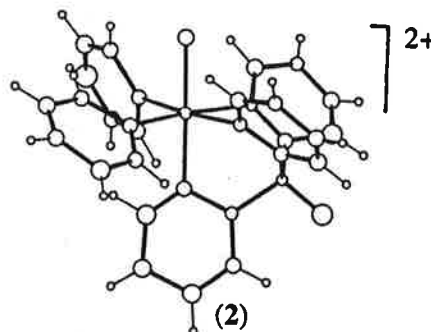
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Few accounts of the oxidation of σ -bonded organometallic complexes by water are available, and none involve structural characterization of products.¹ The oxidations result in the formation of hydrides, and in most cases the hydrides are unstable in water and are hydrolysed to form hydroxo complexes. We present here an example of this reaction type for Pt(II) oxidised to Pt(IV), structural characterization of the Pt(IV) complexes of tris(pyridin-2-yl)methanol (1) and (2), and the first report that water will oxidize Pd(II) in remarkable reactions involving conversion of diorganopalladium(II) to monoorganopalladium(II) and triorganopalladium(IV) species.² The monoorganopalladium(II) products are characterizable as PPh₃ derivatives PdR(pz₃BH)(PPh₃), and structural studies have been completed for PdPh(pz₃BH)(PPh₃) and PdMe₃(pz₃BH).



For the palladium chemistry it is proposed that oxidation analogous to that for Pt(II) occurs to form undetected Pd^{IV}MeR(pz₃BH)(OH) in equilibrium with [Pd^{IV}MeR(pz₃BH)(OH₂)]⁺, followed by transfer of a methyl group from the Pd(IV) cation to the highly nucleophilic Pd(II) reagent [PdMeR(pz₃BH)]⁻ to form the Pd(II) product and Pd^{IV}Me₂R(pz₃BH), respectively.



Alkyl transfer from Pd(IV) to Pd(II) is known to occur via nucleophilic attack by Pd(II) reagents on an alkyl group at cationic Pd(IV) centres.³

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Development of a Mass Sensitive Device for the Detection of Metal Ions in Aqueous Solution

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The piezoelectric crystal microbalance consists of a thin circular quartz crystal with circular gold electrodes placed centrosymmetrically on opposite faces.¹⁻⁵ Application of an alternating electric field across the electrodes results in vibration of the crystal at its resonance frequency (the converse piezoelectric effect). The frequency of the crystal is decreased by deposition of mass (Δm) on its surface.⁵ These devices are radially sensitive; the surface of the central gold electrode has the highest sensitivity, the quartz surface is not sensitive to mass deposited.⁶ In the gas phase the change in frequency for a quartz crystal is related to Δm by the Sauerbrey equation,

$$\Delta F = -2.3 \times 10^{-6} F^2 (\Delta m / A),$$

where ΔF (Hz) represents the change in frequency due to added mass, F (MHz) is the resonance frequency of the crystal, Δm is the mass (g) deposited and A (cm²) is the area over which the mass was deposited.⁷ For a 5 MHz crystal, a 1 Hz change in frequency corresponds to a change in mass of the order of 10^{-8} g/cm². Circuits capable of permitting oscillation of a fully immersed crystal have been reported,⁸ and the relationship between the change in frequency of a crystal immersed in solution to the mass loading has been explored.⁹

In an effort to utilise the converse piezoelectric effect for the detection of metal ions in solution, we have sought ways to deposit metal ion receptor sites on the gold electrodes of the piezoelectric crystals. This has been achieved by the initial deposition of a layer of a polysiloxane adhesive followed by deposition of spherical particles of 5 μ silica gel, derivatised with appropriate ligands. Ligands employed include macrocyclic species and aminopolycarboxylate ligands. This paper will report the synthesis of the derivatised silicas, their application to the surface of the quartz crystal, and the effect of complexation on the piezoelectric properties of the device.

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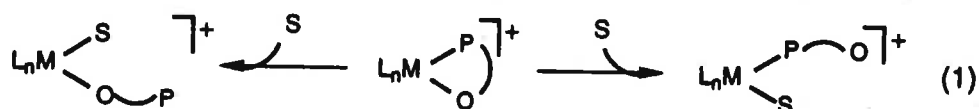
Hemilabile Ligands in Palladium Catalysed C-C Linkages: Codimerization of Ethylene and Styrene and Cooligomerization of Ethylene and CO

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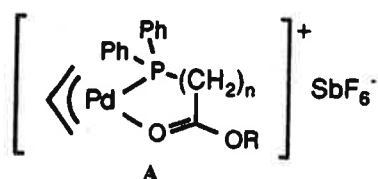
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Bidentate P,O-ligands, combining a hard and a soft donor atom, show interesting properties in coordination chemistry and catalysis.¹ Depending on the strenght of the P-metal or O-metal bonds the equilibria shown in eqn. (1) can exist, in which the ligand bite opens up.

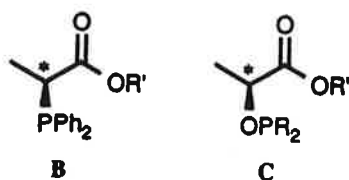


This opening of the chelate bite can be initiated by other ligands or solvent molecules S and has been termed *hemilabile*.²

We have prepared novel cationic palladium allyl complexes of type A with ω -(diphenylphosphino)carboxylic acid esters as ligands³ and investigated their catalytic properties for the C-C linkage of ethylene with styrene and carbon monoxide.⁴



The main product of the codimerization of styrene and ethylene, 3-Phenyl-1-butene is chiral. In order to induce chirality novel ligands of type B and C were prepared and their enantioselectivity in catalysis was tested.



The synthesis of other hemilabile systems with N,O- or S,O-ligands and their application in homogeneous catalysis are under current investigation.⁵

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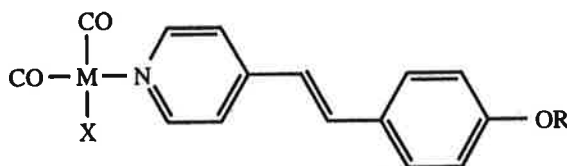
The Pyroelectric and Potential Non-Linear Optical Activity of Langmuir-Blodgett films of Rhodium (I) and Iridium (I) Stilbazole Complexes

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Metal complexes of the type shown below are known to exhibit large molecular hyperpolarisabilities¹ (first order non-linear optical effects).



M = Rh, Ir.

X = Cl, Br.

R = -CH₂*CH(CH₃)CH₂CH₃, -(CH₂)_nCH₃ n = 5 - 12.

However, introduction of a chiral alkyl group to induce a noncentrosymmetric crystalline form (which is necessary in order for this molecular property to be expressed by the bulk material), did not result in a large macroscopic effect.

When the group R is a straight alkyl chain, it has been found that the complexes form high quality, ordered, Y-type Langmuir-Blodgett films². Noncentrosymmetric, alternate layer films have been formed with these complexes and tricosanoic acid. The non-linear optical activity of these films is under investigation.

It has also been found that such alternate layer films possess a large temperature dependent pyroelectric coefficient.

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Some 2,2':6',2"-Terpyridine Complexes of Group II Salts

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Reports of 2,2':6',2"-terpyridine (terpy) complexes of alkaline earth halides or pseudohalides are scarce, with only four complexes having been described. These are $\text{Mg}(\text{NO}_3)_2 \cdot \text{terpy} \cdot \text{H}_2\text{O}$, $\text{M}(\text{SCN})_2 \cdot \text{terpy}_2 \cdot \text{H}_2\text{O}$, $\text{M} = \text{Ca}, \text{Ba}$, and $\text{Mg}(\text{ClO}_4)_2 \cdot \text{terpy}_2 \cdot \text{H}_2\text{O}$.¹⁻⁴ Of these, only the complex $\text{Mg}(\text{ClO}_4)_2 \cdot \text{terpy}_2 \cdot \text{H}_2\text{O}$ has been characterised by a single crystal x-ray structure determination.⁴ The Mg atoms are coordinated by six N atoms from two terpy ligands, each acting as a tridentate ligand, resulting in distorted octahedral geometry about the Mg atom.

The array of Group II salt complexes with terpy is here extended to include the complexes $[\text{Mg}(\text{terpy})(\text{MeOH})(\text{H}_2\text{O})_2]\text{Cl}_2$, $[\text{Mg}(\text{terpy})_2][\text{Mg}(\text{terpy})(\text{OH}_2)_3]\text{Br}_4 \cdot \text{i-propanol}$, $[\text{CaCl}_2(\text{dmf})(\text{terpy})]_2$, $[\text{Ba}(\text{terpy})_2\text{I}_2]$, $[\text{Ba}(\text{terpy})_2(\text{ClO}_4)_2]$, $[\text{Ca}(\text{terpy})_3]\text{I}_2 \cdot x\text{MeOH}$, $[\text{Sr}(\text{terpy})_3]\text{Br}_2 \cdot x\text{MeOH}$, and $[\text{Sr}(\text{terpy})_3]\text{I}_2 \cdot x\text{MeOH}$, (I to VIII respectively). Each of the Mg complexes contain the metal in distorted octahedral environments as MgN_6 or MgN_3O_3 arrays. The complex $[\text{CaCl}_2(\text{dmf})(\text{terpy})]_2$ contains Ca in a seven coordinate, $\text{CaCl}_3\text{N}_3\text{O}$ environment. The $[\text{Ba}(\text{terpy})_2\text{L}_2]$, $\text{L} = \text{I}$ or ClO_4 , complexes contain Ba atoms coordinated by two terpy ligands each acting as a tridentate ligand and by either monodentate I or bidentate ClO_4 ligands. If each bidentate ClO_4 ligand is considered as a single ligand, then the BaN_6L_2 arrays each have distorted dodecahedral geometry. The three remaining complexes form an (almost) isomorphous set where each complex contains the metal atom in a nine-coordinate environment with distorted tricapped trigonal prismatic geometry.

Cell parameters are I triclinic, $P\bar{1}$ (C_i^1 , No. 2), a 14.049(7), b 8.354(4), c 8.301(2), α 74.25(3), β 73.05(3), γ 80.37(4); II triclinic, $P\bar{1}$ (C_i^1 , No. 2), a 19.352(6), b 12.852(5), c 11.463(3), α 110.95(3), β 99.04(2), γ 98.81(3); III monoclinic, $C2/c$ (C_{2h}^6 , No. 15), a 23.27(2), b 11.225(6), c 16.517(8), β 109.56(5); IV monoclinic, $P2_1/c$ (C_{2h}^5 , No. 14), a 10.812(4), b 16.740(5), c 17.458(4), β 109.39(2); V triclinic, $P\bar{1}$ (C_i^1 , No. 2), a 14.220(4), b 11.212(2), c 10.511(2), α 65.66(2), β 87.32(2), γ 88.92(2); VI, VII, VIII trigonal, $\sim 13^\circ$, $\sim 13^\circ$, $\sim 15.3^\circ$.

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Some Monodentate N-Base Complexes of Group II Salts

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The only Group II halide complex with MeCN to have been characterised by a single crystal X-ray diffraction study is $\text{BeCl}_2 \cdot 2\text{MeCN}$, which contains Be in a distorted tetrahedral environment, being coordinated by two chloride ions and two nitrogen atoms.¹ Three anhydrous complexes with pyridine (py) have been characterised by a single crystal X-ray diffraction study, $\text{MgCl}_2 \cdot 4\text{py}$, $\text{MgBr}_2 \cdot 6\text{py}$ and $\text{Mg}(\text{SCN})_2 \cdot 4\text{py}$.^{2,3,4} This limited array of Group II halide monodentate N-bases complexes is here extended to include a diffraction study characterisation of $\text{MgBr}_2 \cdot 3\text{MeCN}$, $\text{CaBr}_2 \cdot 2\text{MeCN}$, $\text{CaI}_2 \cdot 5\text{MeCN}$, $\text{SrI}_2 \cdot 5\text{MeCN}$, $\text{SrBr}_2 \cdot 5\text{py}$ and $\text{BaI}_2 \cdot 6\text{py}$.

Synthesis of these complexes was achieved by dissolution of the salt in dry ligand with the addition of a few drops of MeOH or H_2O to clarify the mixtures if necessary. (1) $[\text{Mg}(\text{MeCN})_6][\text{MgBr}_4]$ Triclinic, $P\bar{1}$ (C_i^1 , No. 2) a 19.129(1), b 16.870(8), c 8.737(7) Å, α 83.96(3), β 87.93(4), γ 65.24(2)°. (2) $[\text{Ca}(\text{MeCN})_2\text{Br}_2]_\infty$ Orthorhombic, $Pbam$ (D_{2h}^9 , No. 55) a 14.252(3), b 8.539(2), c 4.2088(6) Å, V 512.2(2) Å³. (3) $[\text{Ca}(\text{MeCN})_5\text{I}_2]$ Orthorhombic, $Pcab$ (variant of D_{2h}^{15} , No. 61) a 18.248(7), b 14.57(1), c 14.22(1) Å, V 3781(4) Å³. (4) (isomorphous to (3)) $[\text{Sr}(\text{MeCN})_5\text{I}_2]$ a 18.481(6), b 14.752(8), c 14.473(4) Å, V 3945(3) Å³. (5) $[\text{Sr}(\text{py})_5\text{Br}_2]$ Orthorhombic, $Pbca$ (D_{2h}^{15} , No. 61) a 18.611(5), b 17.768(7), c 17.411(7) Å, V 5757.5. (6) $[\text{Ba}(\text{py})_6\text{I}_2]$ Monoclinic, $C2/c$ (C_{2h}^6 , No. 15) a 18.311(2), b 9.960(3), c 18.856(8) Å, β = 99.28(3), V 3781(4)

Microanalytical results indicate that the $\text{MgBr}_2 \cdot \text{MeCN}$ solvate contains $\text{MgBr}_2 \cdot \text{MeCN}$ in the ratio 1:3. Results of a single crystal X-ray diffraction study show the complex to be ionic $[\text{Mg}(\text{MeCN})_6][\text{MgBr}_4]$ containing tetrahedral $[\text{MgBr}_4]^{2-}$ and octahedral $[\text{Mg}(\text{MeCN})_6]^{2+}$. The CaBr_2 complex was found to be a polymer with the calcium ions being bridged by pairs of bromide ions with the remaining two coordination sites occupied by MeCN ligands. The CaI_2 and SrI_2 complexes are isomorphous with an unusual structure, with seven-coordinate *trans*- MX_2Y_5 forming a pentagonal bipyramidal array; a similar structure is found for $\text{SrBr}_2 \cdot 5\text{py}$. $\text{BaI}_2 \cdot 6\text{py}$ contains Ba atoms coordinated by two I ions and six py ligands forming distorted dodecahedral geometry.

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ZEOLITES-A AND ZEOLITE-X FROM PADDY RICE HUSK WASTE

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In order to overcome the environmental problem concerning paddy husk waste, this material has been evaluated for the production, by synthesis, of various zeolites. The paddy husk was fired at 700 °C and the resulting ash melted by using sodium hydroxide. It was then diluted with deionized water in order to produce a sodium silicate solution. The sodium aluminate solution was slowly added to the sodium silicate solution and the mixture stirred thoroughly until an homogeneous creamy white gel was formed. Crystalization of zeolite was achieved by heating the paste in an oven at 80-90 °C for 8-10 hours.

The resulting zeolites were characterized by infrared spectroscopy, x-ray diffraction, solid-state NMR, chemical analysis for Si, Al, Na and thermal gravimetric analysis (TGA) for H₂O. It was concluded that the synthetic zeolite contains three different zeolite structures: zeolite-A, zeolite-X and sodalite. The chemical formula of the zeolites are Na₅[(AlO₂)₂(SiO₂)₃] 8 H₂O, Na₄[(AlO₂)₅(SiO₂)₅] 12 H₂O, Na₄[(AlO₂)₂(SiO₂)₂] 4 H₂O. The structures and the relative amounts of the zeolites produced were influenced by the mole ratio of silicate and aluminate solution.

Supercritical Fluid Chromatography (SFC) of Picrate complexes of the Lanthanide series.

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The use of Supercritical Fluids in the separation of rare earth picrate complexes with the general formula $M(\text{picrate})_3 \cdot 12(\text{H}_2\text{O})$ has been studied. The optimal conditions for separation of mixtures have been determined using supercritical fluid chromatography (SFC) as a precursor to the selective extraction and separation by supercritical fluid extraction (SFE).

A Hewlett-Packard G1205A Supercritical Fluid Chromatograph equipped with a UV diode array detector was used. This allowed simultaneous scanning of up to 5 wavelengths to monitor separation efficiencies. The mobile phase used was carbon dioxide modified with up to 10 % methanol (by volume). A reversed phase ODS-Hypersil HPLC column was used for all experiments.

Initially, individual picrate complexes were studied over a range of mobile phase densities and compositions. These studies were then used to define conditions that allow resolution of all picrates from the lanthanide series.

Application of Supercritical Fluids to the separation of Calixarene Complexes.

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Calixarenes are large cage like chelates to which various functionalities can be added. They are of interest as chelating agents for the separation of rare earth complexes and they have been identified as a means of processing nuclear waste. In this study, the separation of the Calixarenes using Supercritical Fluid Chromatography (SFC) has been investigated.

A Hewlett Packard Supercritical Fluid Chromatograph (SFC) with a UV diode array detector, ECD and NPD was used for the measurements. An ODS-Hypersil HPLC column was used together with carbon dioxide modified with ethanol or dichloromethane as the mobile phase.

The Calixarenes were initially investigated in the absence of rare earths to study the effects of functionality on their solubility in Supercritical Fluids. The effect of incorporation of rare earth metal ions will be investigated in a future study.

X-ray and Neutron Diffraction by Molecular Ionic Crystals

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Computer routines have been (and are being) developed which enable the calculation of X-ray scattering factors and Neutron flipping ratios for diffraction by molecular ionic crystals. The crystals are assumed to be perfect, with the molecular ionic fragments non-interacting. The molecular orbitals are computed using Gaussian basis sets. Fourier transforms of Gaussian pairs are calculated using formulae developed by Chandler and Spackman ¹. Experimental thermal tensors are used in temperature factor formulae ² to incorporate thermal motion. A crystal space group routine ³ is used to generate all the molecular positions of the cell, and to generate the corresponding matrices that are used to rotate the scattering vector.

Calculations of X-ray structure factors on $(ND_4)_2Cu(SO_4)_2 \cdot 6H_2O$ using a good basis set produced good agreement with experiment: $R = 1.30\%$. Plots of $\sin\theta/\lambda$ versus R reveal that the prime discrepancy between experiment and the model is at low angle (the valence region). Attempts are being made to incorporate CI into the model.

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Structural Characterisation of Some Bis(triphenylphosphine) Copper (I) Fluoroacetates

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The bis(triphenylphosphine)copper(I) cation is a soft acceptor ion which can accommodate a wide range of coordinating anions to form complexes of the type $[(\text{Ph}_3\text{P})_2\text{CuX}]$. The donor properties of the anion and the steric interactions between the anion and the cation have been shown to be a significant factor in determining the P_2CuX core geometries.¹⁻⁴

The data on the formate and acetate complexes show formate coordinates as a symmetrical bidentate ligand and acetate coordinates unsymmetrically.^{5,6} The fluoro substituted acetate complexes $[(\text{PPh}_3)_2\text{Cu}(\text{O}_2\text{CCF}_{3-n}\text{H}_n)]$ ($n = 1-3$) provide the potential to examine a series of complexes in which the donor properties of the anion can be changed whilst keeping the steric profile essentially constant.

The $[(\text{PPh}_3)_2\text{Cu}(\text{O}_2\text{CCF}_{3-n}\text{H}_n)]$ ($n = 1-3$) complexes are isomorphous, with the acetate complex crystallising in $P2_1/a$ with cell dimensions $a \approx 18$, $b \approx 11$, $c \approx 19.3 \text{ \AA}$, $\beta \approx 120^\circ$. The most prominent feature of this series of compounds is the effect of the increasing base strength on the co-ordination of the anion. As the pK_a decreases from 4.78 to 0.50, i.e. with increasing fluoro substitution, the anion coordinates more unsymmetrically, resulting in Cu-O(1) decreasing slightly and Cu-O(2) increasing from 2.257(5) Å to 2.545(5) Å; this is consistent with increasing double bond character of the C-O(2) bond and localisation of the anion charge on O(1) as the co-ordination becomes increasingly monodentate in nature.

Recrystallisation of the complexes with $n = 2, 3$ from ethanol results in the complexes crystallising with coordinated ethanol and the fluoroacetate anion coordinating as a monodentate ligand, giving the complexes $[(\text{PPh}_3)_2\text{Cu}(\text{O}_2\text{CCF}_{3-n}\text{H}_n)(\text{EtOH})]$ ($n = 2, 3$). This provides the first structural characterisation, to our knowledge, of any copper(I) complex with co-ordinated ethanol.

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Synthesis and Structural Characterisation of Some Triphenylphosphine Copper(I) and Silver(I) Halide Adducts with Bidentate Nitrogen Base Ligands

Effendy, Robert D. Hart* and Allan H. White,

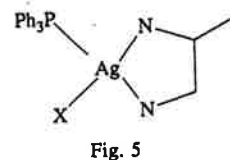
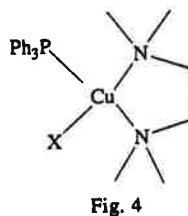
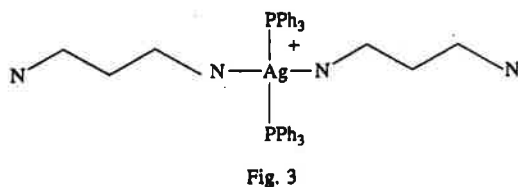
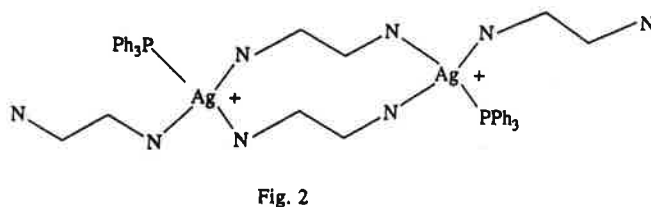
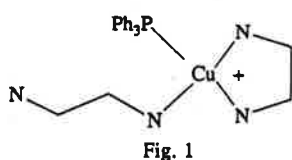
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The crystallisation of copper(I) and silver(I) halides with triphenylphosphine from a range of potentially bidentate nitrogen bases has yielded adducts which have been characterised by single crystal X-ray structure determinations.

The adducts of $(\text{Ph}_3\text{P})\text{CuX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) obtained from ethylenediamine (en) are $[(\text{Ph}_3\text{P})\text{Cu}(\text{en})_2]^+\text{X}^-$ with the four-coordinate CuPN_3 environment comprising both bidentate and monodentate en (Fig. 1). A similar crystallisation of AgCl and PPh_3 from en yields the centrosymmetric binuclear adduct $[(\text{Ph}_3\text{P})(\text{en})\text{Ag}(\text{en})_2\text{Ag}(\text{en})(\text{PPh}_3)]\text{Cl}_2$ in which the four coordinate AgPN_3 environment contains monodentate en and a pair of nitrogen atoms from bridging en ligands (Fig. 2).

The adducts of AgX ($\text{X} = \text{Cl}, \text{Br}$) obtained with PPh_3 from 1,3-diaminopropane (1,3-dap) take the ionic form $[(\text{Ph}_3\text{P})_2\text{Ag}(1,3\text{-dap})_2][(\text{Ph}_3\text{P})_2\text{AgX}_2]$ with four coordinate P_2AgN_2^+ and P_2AgX_2^- for the cation and anion respectively; the 1,3-dap ligand in the cation is monodentate (Fig. 3).

The adducts of $(\text{Ph}_3\text{P})\text{CuX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) obtained from $\text{N}, \text{N}', \text{N}', \text{N}'$ -tetramethylethylenediamine (tmeda) are monomeric $[(\text{Ph}_3\text{P})\text{Cu}(\text{tmeda})\text{X}]$ with copper in a distorted tetrahedral PCuN_2X environment in which the tmeda ligand is bidentate (Fig. 4). This is similar to the silver adducts $(\text{Ph}_3\text{P})\text{AgX}$ ($\text{X} = \text{Cl}, \text{Br}$) with 1,2-diaminopropane (1,2-dap) which form the complexes $[(\text{Ph}_3\text{P})\text{Ag}(1,2\text{-dap})\text{X}]$ (Fig. 5).



The Reactions of Electrogenenerated $[\text{Ni}(\text{sacsac})_2]^-$

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The electrochemical reduction of $[\text{Ni}(\text{sacsac})_2]$ ($\text{sacsac}^- = \text{C}_5\text{H}_7\text{S}_2^-$ = dithioacetylacetonate) has been investigated by cyclic voltammetry and coulometry at a glassy carbon electrode in acetone/ Bu_4NBF_4 (0.1M). The reactions of the reduction product(s) with CO, CO_2 , MeI, $\text{C}_{12}\text{H}_{25}\text{SH}$, light and water have been examined.

At a scan rate of 100 mV s^{-1} , $[\text{Ni}(\text{sacsac})_2]$ (0.005M) undergoes a reversible one-electron reduction ($\Delta E_p = 88 \text{ mV}$) at -0.543 V (vs $\text{Fc}/\text{Fc}^{+/0}$) and an irreversible four-electron oxidation at $+1.635 \text{ V}$. The oxidation generates the 3,5-dimethyl-1,2-dithiolium cation, as evidenced by the observation of the (known) reduction of this cation at $+0.160 \text{ V}$. The product of the reduction of $[\text{Ni}(\text{sacsac})_2]$ reacts with light, water, CO, CO_2 , MeI and $\text{C}_{12}\text{H}_{25}\text{SH}$.

Thus, for example, under CO at a scan rate of 100 mV s^{-1} , the reduction of $[\text{Ni}(\text{sacsac})_2]$ is observed as an irreversible process at -0.410 V . These and other reactions will be reported.

Decaphenylferrocene

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Decaphenylferrocene was obtained as an extremely insoluble, pale purple microcrystalline solid by heating $[(\eta^5\text{-C}_5\text{Ph}_5)((\eta^6\text{-C}_5\text{H}_5)\text{C}_5\text{Ph}_4)\text{Fe}]$ and was characterised by ^{57}Fe Moessbauer spectroscopy, X-ray photo-electron spectroscopy, mass, electronic and vibrational spectroscopy, solid state ^{13}C NMR spectroscopy and high resolution X-ray powder diffraction, which showed it to be isostructural with decaphenylnickelocene.

MacLab in Chemistry

Paul A. Duckworth

AD Instruments

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