

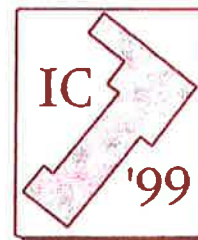
PART 2
Poster abstracts

Joint Meeting
of the Inorganic Division of the

Royal Australian Chemical Institute

and the
Inorganic and Organometallic
Specialist Group
of the

New Zealand Institute of Chemistry



WELLINGTON, NEW ZEALAND

31 January – 4 February 1999

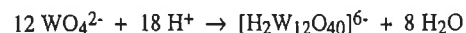
POSTERS

DEFINING THE REDOX STATE OF A POLYOXOANION. THE STRUCTURE OF SIX-ELECTRON REDUCED METATUNGSTATE, [H₂W₁₂O₄₀]⁶⁻: A ¹⁸³W AND ¹H NMR STUDY

Colette Boskovic, Alan M. Bond[†] and Anthony G. Wedd

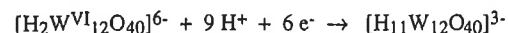
School of Chemistry, University of Melbourne, Parkville, 3052
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Polyoxoanions are formed by the condensation of simple oxoanions in the presence of acid. For example:

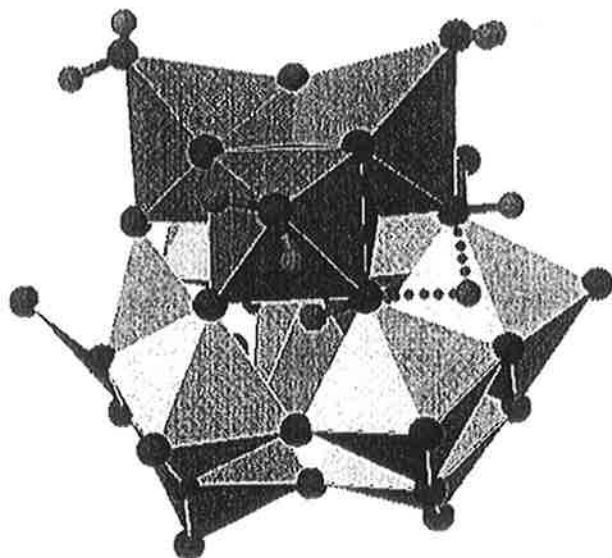


The metatungstate anion has the classic Keggin structure with *T_d* point symmetry. Two protons occupy a central tetrahedral cavity.

Aquo-soluble NH₄⁺ and organo-soluble Bu₄N⁺ salts of a 6-electron reduced form of metatungstate are now available:-



The presence of the two slow-exchanging internal protons makes ¹H NMR a useful characterisation tool. ¹H NMR studies in non-aqueous solvents reveal the presence of the nine external protons on the surface of the anion. Two dimensional ¹H, ¹⁸³W and ¹H-¹⁸³W NMR techniques augmented with H₂O exchange experiments provide a complete assignment of the ¹H and ¹⁸³W resonances and allow a definitive assessment of the sites of protonation.



M1

POSTERS

MOLECULAR ENGINEERING AT THE ACTIVE SITE OF RUBREDOXIN

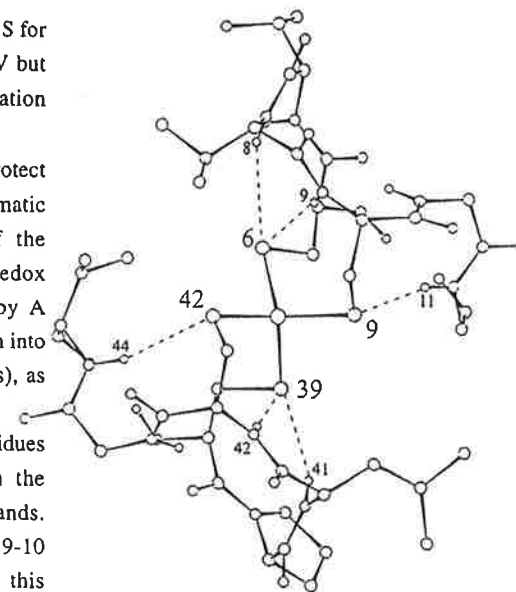
Z. Xiao, M. Lucarelli, A. Gardner, M. Maher,[†] M. Guss[†] and A.G. Wedd

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[†]School of Biochemistry, University of Sydney, Sydney, NSW 2006

The engineering of a known protein active site to produce new reactivities is now possible via genetic techniques. The aim here is to induce new properties in rubredoxin, a simple iron-sulfur redox protein, by metal and ligand substitution and by mutations which vary access to the active site. From this simple building block, it appears possible to (i) control redox potential, (ii) activate ligand reactivity and (iii) construct binuclear sites. This enables links to the chemistry of natural enzyme systems to be explored and new chemistries to be created.

Rubredoxin features a single Fe(S-cys)₄ centre (Figure: *D*_{2d} local symmetry). This poster will discuss:-

- (i) Systematic substitution of ligand atom S for O: the potential moves ca. - 200 mV but influences from the second coordination sphere can recover half of this shift;¹
- (ii) The *Pr*ⁱ sidechains of V8 and V44 protect the active site (Figure). Their systematic substitution allows assessment of the influence of solvent access upon redox potential. The substitution of V8 by A effectively converts the present protein into that from another bacterium (*D. gigas*), as predicted theoretically.
- (iii) The small sidechains of conserved residues G10 and G43 allow tight turns in the protein chain carrying the Cys ligands. Substitution of V at G10 causes the 9-10 peptide link to invert. However, this dramatic change still allows retention of the 11NH--S9 bond (Figure) but converts it from a Type II to a Type I hydrogen bond.



¹ Z. Xiao, M.J. Lavery, M. Ayhan, S.D.B. Scrofani, M.C.J. Wilce, J.M. Guss, P. A. Tregloan, G.N. George and A.G. Wedd, *J. Amer. Chem. Soc.* 1998, 120, 4135-4150.

M2

SUPRAMOLECULAR MOTIFS FOR INORGANIC AND ORGANOMETALLIC MOLECULES

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We are exploring the supramolecular motifs adopted by inorganic and organometallic molecules. This is done by investigation of the regularly occurring patterns of molecular association in crystal structures. These supramolecular motifs involve only intermolecular attractions: we exclude supermolecules based on metal coordination linkages.

While hydrogen bonding is well-known and valuable as a supramolecular synthon, we are concentrating on other motifs. In this poster we summarise — by pictorial collage — the main supramolecular motifs already recognised.

- Multiple phenyl embraces: the main types have 4, 6, 8 or 12 phenyl groups involved in a concert of edge-to-face or offset-face-to-face phenyl••phenyl interactions. There are various subsets with different geometries, and an inverted sixfold aryl embrace involving anthracenyl groups.
- Multiple aryl embraces by heterocyclic ligands: familiar complexes $[M(\text{bipy})_3]^2$ and $[M(\text{terpy})_2]^2$ form concerted embraces using the heterocyclic rings. These cationic complexes form 1-D and 2-D nets.
- Molecules $X\text{Ph}_4$, especially Ph_4P^+ , can form more than one multiple phenyl embrace, and so form 1-D, 2-D and 3-D nets.
- The cation MePh_3P^+ forms diamondoid lattices, which function like host lattices for associated anions: other RXP_3 with threefold symmetry form similar nets.
- Cl, O and Br atoms, and CH_3 groups, on the surfaces of molecules can substitute for phenyl groups in multiple phenyl embraces, and also form sets of $\text{C}\cdots\text{H}\cdots\text{X}$ interactions.

A fundamental characteristic of these motifs is that they involve concerted local intermolecular interactions, and possess a directionality which is determined also by intramolecular conformations of surface functionalities.

We will present our estimates of the attractive energies of these supramolecular motifs.

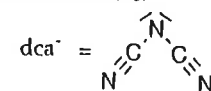
MOLECULE-BASED FERROMAGNETS AND SPIN-CANTED ANTIFERROMAGNETS IN THE METAL-DICYANAMIDE (dca) COORDINATION POLYMERS, $M(\text{dca})_2$, WHERE $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$

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Coordination polymers and supramolecular arrays involving open-shell d-block ions can display new and fascinating examples of molecule-based ferromagnetism and antiferromagnetism. Such materials display long-range magnetic order below a critical temperature with magnetisation and hysteresis features characteristic of the spin-coupling throughout the bulk lattice. We have recently discovered that an old class of metal dicyanamide compounds, $M(\text{dca})_2$, displays a rich and varied array of magnetic features.^{1,2} All are members of a rutile-like extended single-net structures (α -isomer) containing 6-connecting (octahedral) M cations and 3-connecting dca anions, $\alpha\text{-Cu}(\text{dca})_2$ having Jahn-Teller lengthened Cu-N(amide) axial bonds. The latter example is a near paramagnet while the Co(II) and Ni(II) compounds are ferromagnets. Surprisingly, the Mn(II) and Fe(II) are spin-canted antiferromagnets!

$\text{Zn}(\text{dca})_2$ forms a β -structure with tetrahedrally coordinated metal ions and bidentate dca ligands bonded via nitrile nitrogen atoms only. This structure is also adopted by $\text{Co}(\text{dca})_2$ when it is prepared by desolvation of $\text{Co}(\text{dca})_2(\text{pyridine})_2$. This structural isomer of Co(II) is also a molecular magnet but quite different in detail to $\alpha\text{-Co}(\text{dca})_2$. The structures and magnetic properties of the α - and β -phases will be described together with those of a fascinating series of chain, layer and square-grid $M(\text{dca})_2(\text{L})_n$ derivatives (L = pyridine, H_2O , DMF, ROH, 4,4'-bipyridine, pyrazine) some of which possess interpenetrating double-net lattice structures.



Interest in metal dicyanamide compounds has been kindled elsewhere with related reports of structure and magnetism beginning to appear.^{3,4}

This work is supported by the Australian Research Council (Large) Grants Scheme.

1. S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray and R. Robson, *Chem. Commun.* 1998, 439.
2. K.S. Murray, S.R. Batten, B. Moubaraki, D.J. Price and R. Robson, *Mol. Cryst. Liq. Cryst.*, in press.
3. M. Kurmoo and C.J. Kepert, *New J. Chem.* 1998, in press.
4. J.L. Manson, C.R. Kmetz, Q.-Z. Huang, J.W. Lynn, G.M. Bendele, S. Pagola, P.W. Stephens, C.M. Liable-Sands, A.L. Rheingold, A.J. Epstein and J.S. Miller, *Chem. Mater.* 1998, 10, 2552.

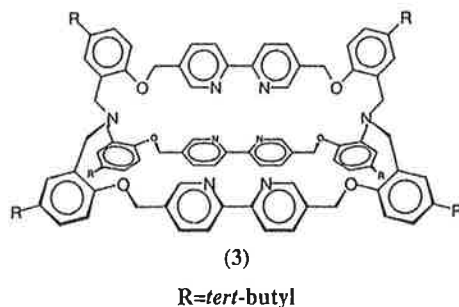
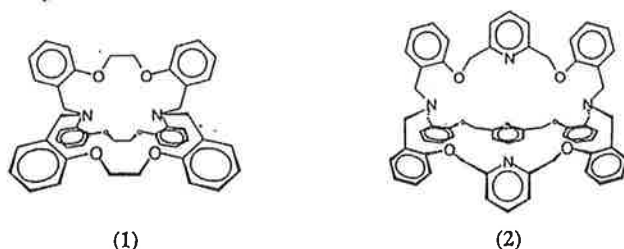
CONTAINING, MOLECULAR CAGE AND ITS METAL ION COMPLEXES.

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^a School of Chemistry University of Sydney, Sydney, NSW., Australia, 2006

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Recently we have been interested in the construction of new cage molecules for the selective binding of both small molecules and metal ions. Typical examples are given by (1) and (2). We have now extended this work to include the supra-cage (3) containing three bipyridine moieties. This product was obtained by a related synthetic procedure to that for (2) in which the pyridine moiety was replaced by a 2,2'-bipyridyl moiety.



Molecular modelling indicates that the new species will interact with a single octahedral metal ion such that a helical twist extending about 26 Å along the axial length of the system will occur. Such behaviour is unusual relative to other helical structures recently reported¹⁻³ in which multiple metal ion coordination is required to induce a helical twist along the length of the system.

A preliminary study indicates that (3) forms a highly coloured metal ion complex with iron(II).

1. Constable, E. C., *Tetrahedron* 1992, 48, 10013 and references cited therein.
2. Kramer, R., Lehn, J.-M., De Cian, A., Fischer, J., *Angew. Chem. Int. Ed. Eng.* 1993, 32, 5, 703.
3. Lehn, J.-M., Rigault, A., *Angew. Chem. Int. Ed. Eng.* 1988, 27, 8, 1095.

M5

POSTERS

A NEW AZA-OXYGEN MACROCYCLE INCORPORATING A PENDANT PYRIDYL GROUP

Jy D. Chartres,^{*} Grover W. Everett,[#] Xue Kui Ji,[†] Anthony J. Leong,^{*} Leonard F. Lindoy,[†] Owen A. Matthews,^{*} George V. Meehan,^{*} Brian W. Skelton,^{*} Gang Wei[†] and Allan H. White^{*}

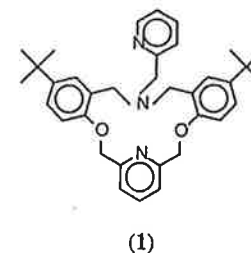
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As part of an investigation of new reagents for heavy metal ion discrimination, the 14-membered diazadioxamacrocyclic (1) incorporating a pendant pyridyl group has been synthesised. The metal ion binding properties of this species towards cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II) and silver(I) have been investigated in both the solid state and in solution. In each case 1:1 (metal:ligand) complexes were observed. The X-ray structure of the copper complex, [Cu(1)NO₃]⁺, shows that all donors of the ligand coordinate to the copper. The latter has a distorted octahedral geometry in which the remaining coordination site is occupied by a monodentate nitrate ligand.



The lead complex, [Pb(1)(NO₃)(ClO₄)], is eight coordinate and incorporates bidentate nitrate and monodentate perchlorate ligands. All donors of (1) are coordinated to the metal with the latter occupying a position above the central macrocyclic cavity.

Potentiometric log *K* determinations in 95% methanol reveal that the above ligand yields a stability order for its metal complexes of silver(I)~copper(II)>nickel(II)>lead(II).

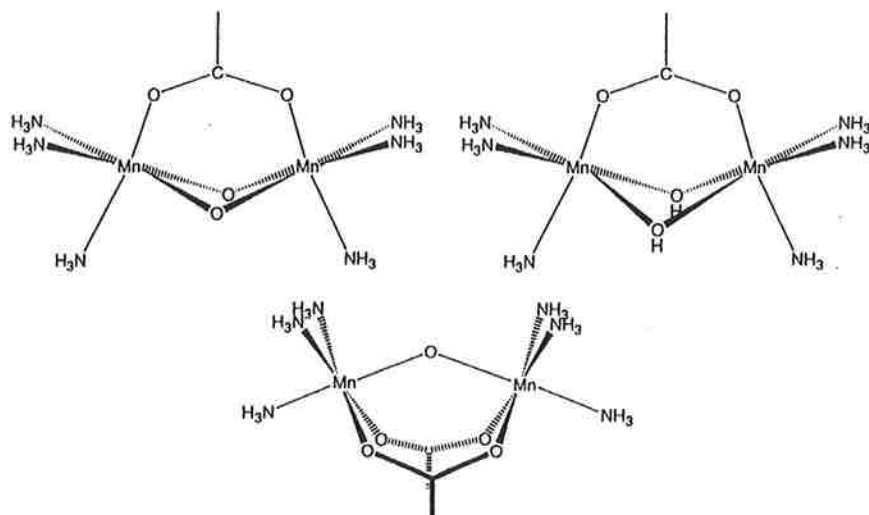
M6

A DFT INVESTIGATION INTO THE MAGNETIC AND ELECTRONIC PROPERTIES OF OXOMANGANESE DIMERS

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In recent years a great deal of effort has been spent investigating the electronic structure and magneto-structural correlations of transition metal dimers using the Broken Symmetry approach in Density Functional Theory (DFT)[1,2] and the formalism described by Noodleman[3] to extract magnetic exchange constants. We have performed a series of calculations using DFT on a series of oxo, hydroxo and carboxylato tri-bridged manganese dimers. Various oxidation states of the manganese ions are possible but only the biologically relevant III-III, III-IV and IV-IV redox states are considered. Particular attention is paid to trends in the magnetic properties and geometry as the bridging ligands and oxidation state of the manganese ions are changed. The results of these calculations can be related to the magnetic properties of manganese dimers in bioinorganic systems, such as manganese catalase and the oxygen evolving center of photosystem II.



[1] Tom Ziegler, *Chem. Rev.* (1991), 91, 651

[2] L Noodleman and D. A. Case, *Adv. Inorg. Chem.* (1992), 38, 423

[3] L Noodleman, *J. Chem. Phys.* (1981), 74, 5737

XSophe, a Computer simulation software suite for the analysis of Electron Paramagnetic Spectra.

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Department of Mathematics and ^bCentre for Magnetic Resonance, The University of Queensland, St Lucia, Brisbane, QLD, 4072, Australia.

XSophe-Sophe provides scientists with an easy to use research tool for the analysis of Isotropic, Randomly Orientated and Single Crystal Continuous Wave Electron Paramagnetic Resonance Spectra. *Sophe* is a sophisticated computer simulation software suite, written in C++ using the most advanced techniques, including: the SOPHE partition and interpolation schemes^{1,2} and field segmentation algorithm^{1,2} and homotopy.³ Homotopy, a method which traces the eigenvalues and eigenvectors across the surface of one or more octants allows computer simulations for any magnetically isolated or coupled spin system to be performed in frequency space.

XSophe provides an X Windows Interface for *Sophe* allowing; the creation of multiple input files for *Sophe*, and the display of sophe.log and input files. *XSophe* allows transparent transfer of EPR spectra and spectral parameters between *XSophe*, *Sophe* and *Xepr*, using state of the art platform independent Corba libraries. This interactivity allows *XSophe* to run and interact with *Sophe* on the same computer or on remote hosts. The functionality of *Sophe* is shown below:

Experiments

- Energy level Diagrams, Transition Surfaces, Continuous Wave EPR Spectra.

Spin Systems

- Isolated and Magnetically Coupled spin systems. An unlimited number of electron and nuclear spins is supported with nuclei having multiple isotopes.

Continuous Wave EPR Spectra

- Solution Spectra, Randomly Orientated Spectra and Single Crystal Spectra.
- Symmetries: Isotropic, Axial, Orthorhombic, Monoclinic and Triclinic
- Variable Temperature and Frequency spectra. Simulation of Single crystal spectra in a plane.

Methods

- Matrix Diagonalisation, Sophe Interpolation and Homotopy. 1st Order Perturbation theory can be chosen for superhyperfine interactions.

Optimisation (Direct Methods)

- Hooke and Jeeves, Simplex, Quadratic and Simulated Annealing.
- Spectral Comparison: Raw Data and Fourier Transform.

1. Wang, D.M.; Hanson, G.R.; *J. Magn. Reson. A*, 1995, 117, 1.
2. Wang, D.; Hanson, G. R.; *Appl. Magn. Reson.*, 1996, 11, 401.
3. Gates, K.E.; Griffin, M.; Hanson, G.R.; Burrage, K., *J. Magn. Reson.*, 1998, In Press.

S.M. Moussa,¹ R.R. Fenton,¹ B.A. Hunter,² B.J. Kennedy¹ and R.O. Piltz.²¹ School of Chemistry, University of Sydney, N.S.W., 2006, Australia² ANSTO, PMB 1 Menai, N.S.W., 2234, Australia

This work is part of the ongoing investigations into the structures and hydrogen-bonding networks of divalent metal(II) amino-acidato complexes. Studies of these types of complexes are of considerable interest due to their significant roles in many biological systems and in the possibility that they may enhance our understanding of the more complicated metalloproteins.

The structure of *cis*-bis(L-alaninato)copper(II) (*cis*-[Cu(L-ala)₂]) was determined using single crystal neutron diffraction techniques at both low (7 K) and ambient temperature. The cell is orthorhombic, space group P2₁2₁2₁. The unit cell parameters obtained at ambient temperature were *a* = 11.645(4) Å, *b* = 8.772(3) Å and *c* = 8.444(2) Å, *V* = 862.6(5) Å³ while at low temperature *a* = 11.564(4) Å, *b* = 8.709(3) Å and *c* = 8.406(3) Å, *V* = 846.6(5) Å³. The final measures of fit were, *R*₁ = 2.3% and *wR*₂ = 4.2% for 982 unique reflections and GOF 1.1; *R*₁ = 2.2% and *wR*₂ = 4.5% for 1145 unique reflections and GOF 1.2 using the ambient and low temperature data set respectively.

At both temperatures the coordination sphere around the copper atom is best described as square pyramidal, where the fifth position is occupied by a weakly bonded carbonyl oxygen from an adjacent alanine unit. The alanine ligands coordinate to the divalent copper atom in an approximately square planar *cis*-arrangement. The significant difference between the two structure determinations is the contraction of the apical carbonyl oxygen - copper bond distance from 2.372(4) Å to 2.326(2) Å upon cooling.

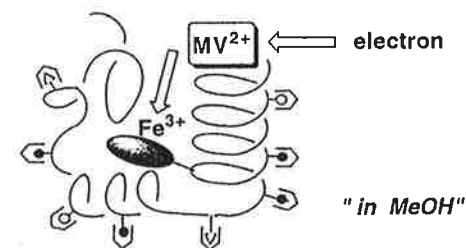
The structure was also refined using powder neutron diffraction techniques. During refinement of the structure a second phase was detected and was subsequently included. The cell parameters obtained were *a* = 11.6273(5) Å, *b* = 8.7580(4) Å and *c* = 8.4358(4) Å and final measures of fit were *R*_p = 1.27 %, *R*_{wp} = 1.55 %, *R*_{exp} = 0.93 % and *R*_{bragg} = 0.92 % and GOF = 2.75.

REDOX ACTIVE BEHAVIORS OF CYTOCHROME C - CROWN ETHER COMPLEX IN METHANOL

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Cytochrome c is a heme protein, widely distributed in living organisms, and mediates electron transfer in the mitochondrial respiratory chain. This also act as a biocatalyst especially in the oxidation of organosulfides and aromatic hydrocarbons. Although several chemical modifications have been performed to improve the catalytic activity of the cytochrome c in organic solvents, they included laborious exercises and complexed procedures.¹⁾

We report that some crown ethers solubilized the cytochrome c into the methanol. Interestingly, the resulting cytochrome c complex with crown ether had a redox active structure even in the methanol solution, and exhibited characteristic reduction potential more close to biological one than chemically modified ones. Thus, crown ethers can modify the solubility and reactivity of the protein.²⁾



- 1) R. Tinoco *et al.*, *Enzyme Microb. Technol.*, **22**, 8 (1998).
- 2) H. Tsukube, *Coord. Chem. Rev.*, **148**, 1 (1996)

USE OF THE ORGANOMERCURY DERIVATIVE $\text{Hg}(\text{C}_6\text{H}_4\text{PPh}_2)_2$ IN THE SYNTHESIS OF CYCLOMETALLATED COMPOUNDS

Martin A. Bennett, María Contel and Rhodri Ll. Thomas

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Organomercury derivatives have been widely used as transfer reagents in the chemistry of transition metals.¹ They are usually employed when organomagnesium and/or organolithium derivatives fail as a result of reduction to lower oxidation states or to metal, especially with Pd(II).

The aim in our research group has concentrated lately in the preparation of mono and bis-cyclometallated palladium (II) compounds containing the phosphine $\text{C}_6\text{H}_4\text{PPh}_2$ (Fig 1). Although Lahuerta² *et al* reported on the preparation of mono-cyclometallated palladium compounds containing the same phosphine, the bis-cyclometallated palladium complex has not yet been synthesized. We believe these kind of complexes, especially the latter, can behave as good catalysts for the Heck reaction.³

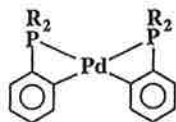


Fig 1. Cis and trans isomers

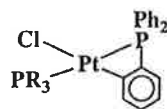


Fig 2.

In this paper we report on the reactions of the compound $\text{Hg}(\text{C}_6\text{H}_4\text{PPh}_2)_2$ and platinum and palladium substrates that have led to cyclometallated complexes. In the case of platinum⁴ the mono-cyclometallated compounds with chloride (Fig 2) have been obtained in a clean way starting from the mono-hydride derivatives. Some interesting intermediates and side-products will also be presented.

References

1. Davies G.A. and Wardell J.L. in 'Comprehensive Organometallic Chemistry'. (Ed. Abel, E.W., Stone, F.G.A. and Wilkinson G.), Pergamon Press, 1995, 3, chap 3.
2. Aarif A.M., Estevan F., García-Bernabé A., Lahuerta P., Sanaú M. and Úbeda M.A., *Inorg. Chem.*, 1997, 36, 6472.
3. Shaw, B.L., *New J. Chem.*, 1998, 77
4. Bennet M.A., Contel M., Hockless D.C.R. and Welling L.L., *Chem. Commun.*, in press.

Titanium Organoimido Complexes From Imido Exchange

Reactions and Their Olefin Polymerisation Ability

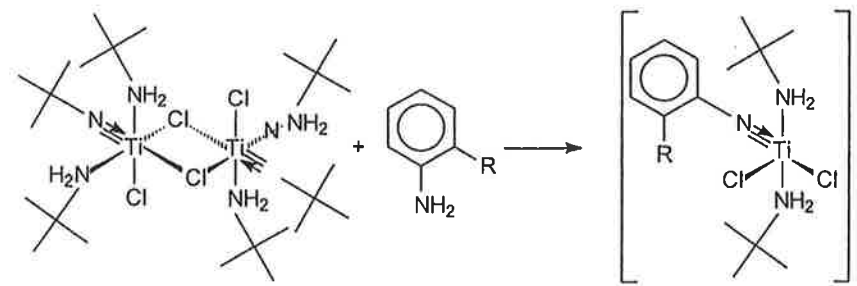
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The addition of *tert*-butylamine (6 equiv.) to a solution of titanium tetrachloride in dichloromethane results in the formation of the now structurally characterised complex $[\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{NH}_2^t\text{Bu})_2]_2$ (1).

In a manner similar to that of $\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_2$, 1 undergoes imido exchange reactions with arylamines to form arylimido compounds, $[\text{Ti}(\text{NAr})\text{Cl}_2(\text{NH}_2^t\text{Bu})_2]_x$ ($\text{Ar} = \text{C}_6\text{H}_4^t\text{Bu}-2$, $\text{C}_6\text{H}_4\text{-Ph}-2$, $\text{C}_6\text{H}_4\text{-Me}-2$ and naphthyl) with the concomitant loss of *tert*-butylamine.



Addition of donor ligands such as pyridine and tetramethylethylenediamine (tmeda) result in the formation of compounds such as $\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_2$ or $[\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_2]_2$ depending on reaction conditions and $\text{Ti}(\text{NAr})\text{Cl}_2(\text{tmeda})$ or $[\text{Ti}(\text{NAr})\text{Cl}_2(\text{tmeda})]_2$ depending on imido identity. Preliminary results for ethene and propene polymerisation by this type of catalyst, activated by methylaluminoxane (MAO) are reported.

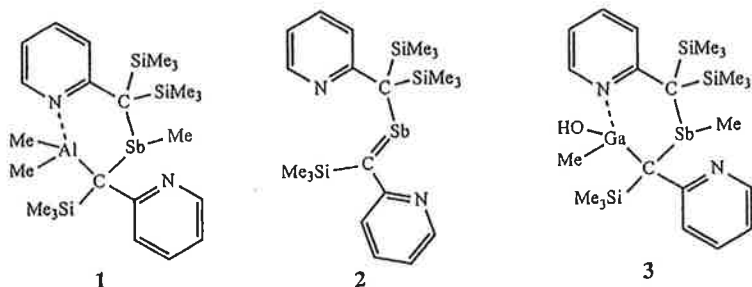
Philip C. Andrews* and Peter. J. Nichols

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Geminal organodimetallic compounds are attracting increasing recognition and importance in organic synthesis¹ due to the attraction of having two reactive metal centres on a single nucleophilic carbon. For many fine synthetic applications this is a qualitative advance on monometallated reagents. Selectivity depends essentially on the having two differing metals on the carbon centre. Thus two p-block elements can result in a 'soft' nucleophile while increased selectivity and reactivity can be obtained by having a s-block and a p-block metal present. The solid state structures of such complexes are of great interest in their own right, though very few have been investigated crystallographically, and can give some insight into their reactivity and selectivity.

In seeking a new synthetic approach to such complexes we found that the carbalumination, with Me₃Al, of the implied stiba-alkene, **2**, formed as a result of the low energy β -elimination of Me₃SiX (X=halogen) from R₂SbCl, gave rise to the *geminal* C-centred Al(III)/Sb(III) six membered heterocycle **1**.²

Developing this carbometallation route as a general method in the formation of such *geminal* dimetallic complexes studies have now focused on alternative ligands and other Group 13 elements. Results to-date are presented.



References:

- [1] I. Marek, J. -F. Normant, *Chem. Rev.*, 1996, 96, 3241-3267
 [2] P.C. Andrews, C. L. Raston, B. S. Skelton, A. H. White, *Chem Comm.*, 1998, 1087

M13

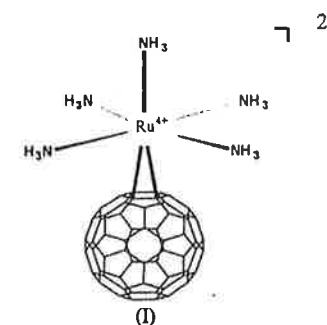
POSTERS

The Characterisation of a Pentaammine Metal Fullerene Complex

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The syntheses of water-soluble fullerene complexes, [Ru^{II}(NH₃)₅(η^2 -C₆₀)](CF₃SO₃)₂ and [Ru^{II}(NH₃)₅(η^2 -C₆₀)]Cl₂ will be discussed. Coordination of the C₆₀ ligand to Ru(II) is believed to occur at the fusion of two six membered rings in an η^2 - fashion (I).



The ¹H NMR spectrum of Ru-C₆₀ is characterised by two NH₃ resonances at δ = 3.21 and 3.45 ppm, with relative intensities of 1:4, due to the *trans* and *cis* ammine ligands, respectively. In the electronic spectrum, the pentaammine(fullerene)ruthenium(II) complex has a shoulder on the main C₆₀ band at 422 nm, which is assigned to a Ru-to-C₆₀ charge-transfer transition [1].

The cyclic voltammetric study shows C₆₀-like redox peaks for the Ru-C₆₀ compound except for an irreversible oxidation peak at +0.25 V (vs. Fc⁺/Fc), representing the formation of [Ru^{III}(NH₃)₅(η^2 -C₆₀)]³⁺. The negative shifts of the redox peaks of the complex compared to those of free C₆₀ reduction peaks are thought to be due to the formation of metal-to-C₆₀ π backbonding, which is expected to raise the energy of the LUMO and therefore decrease the electron affinity of bound C₆₀ [2].

- [1] R. S. Koefod, C. Xu, W. Lu, J. R. Shapley, *J. Phys. Chem.* 1992, 96, 2928.
 [2] S. A. Lörke, B. A. Parkinson, D. H. Evans, P. J. Fagan *J. Am. Chem. Soc.*, 1992, 114, 7807.

M14

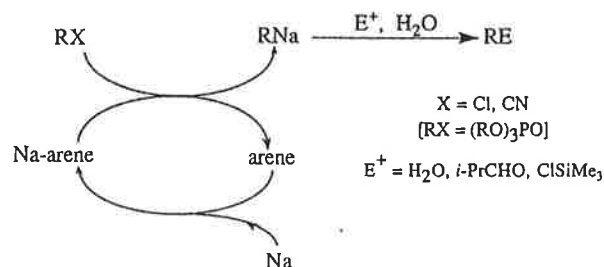
ARENE CATALYSED SODIUM REACTIONS

Tania R. van den Ancker and Margaret Hodgson

School of Science Griffith University, Nathan QLD, Australia

Extensive studies on the use of arene radical alkali metal complexes as metallating agents have been carried out, and are reviewed in the literature.¹ These complexes although successful in the formation of lithium, sodium and potassium complexes, leave reaction product mixtures loaded with the arene by-product. Yus *et al* have developed arene catalysed lithiation, and this process has proven successful in the formation of lithium complexes.² Alternatively macromolecular supported sodium and lithium complexes have been successfully used to generate lithium and sodium complexes.³ These processes (arene catalysed lithiation and supported lithium and sodium complexes) have been used in the preparation of lithium reagents from a range of organic compounds including trialkylphosphates, nitriles, sulfates, sulphides and chlorides, and the sodium complexes of aryl and alkyl chlorides. (The sodium reagents are however difficult to generate due to the highly air-sensitive nature of the supported sodium complexes).

The work reported here extends the chemistry of these processes, investigating the preparation of sodium reagents using arene catalysed reactions.



1. e.g. J. L. Wardell, 'Preparation and Use in Organic Synthesis of Organolithium and Group 1A Organometallics', in *The Chemistry of Metal-Carbon Bond*, F. R. Hartley (Ed.), John Wiley and son, 1987.
2. e.g. M. Yus, *Chem Soc. Rev.*, 1996, 155
3. T. R. van den Ancker, C. L. Raston, *J. Organomet. Chem.*, 1998, 550, 283.

M15

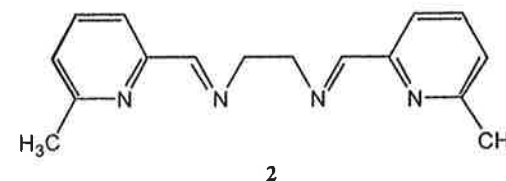
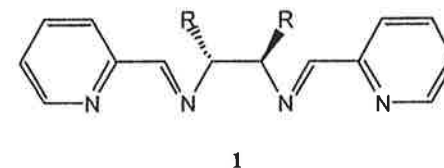
POSTERS

SYNTHESES OF DOUBLE-STRANDED DINUCLEAR SCHIFF-BASE HELICATES

Nicolle C. Habermehl and S. Bruce Wild

Research School of Chemistry, Australian National University,
Canberra, A.C.T. 0200, Australia

In recent work,¹ the enantiomerically pure Schiff-base ligand **1** ($\text{R} = -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), prepared from 2-pyridinecarboxaldehyde and (1*R*,2*R*)-cyclohexane-1,2-diamine, was found to form an infinite coordination polymer when reacted with silver(I) nitrate, rather than the double-stranded dinuclear helicate formed by the parent ligand **1** ($\text{R} = \text{H}$). Further investigations of helicates containing the Schiff-base ligands **1** ($\text{R} = \text{Me}$ or Ph) are in progress. Ligand exchange reactions between helicates containing ligands **1** and **2** are also being investigated.



¹ P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis, S. B. Wild *Chem. Commun.* 1998, 1153.

M16

[Cu₂Br₅]²⁻ A CRYSTAL-ENGINEERED (Cu^{+1.5})₂ CONFACIAL BITETRAHEDRAL COMPLEX WITH A SHORT BUT WEAK Cu–Cu INTERACTION

Caitlin Horn,^a Ian Dance,^a Don Craig,^a Marcia Scudder,^a Graham Bowmaker^b and Cliff Rickards

^a School of Chemistry, University of New South Wales, Sydney 2052.

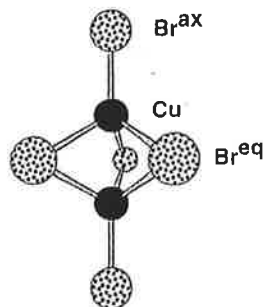
^b Department of Chemistry, University of Auckland, New Zealand.

MePh₃P⁺ cations form a crystal supramolecular motif which we have identified and named as the hexagonal array of sixfold phenyl embraces (HA6PE lattice).¹ This is a host lattice of cations, accommodating small dianions in cavities with D₃ symmetry.

We have discovered that CuBr₂ in i-propanol / HBr in the presence of MePh₃P⁺ Br⁻, crystallises the compound (MePh₃P)₂ [Cu₂Br₅].² The unusual [Cu₂Br₅]²⁻ ion could not be detected in solution, and could not be crystallised with other cations — we believe we have crystal engineered its preparation using the HA6PE lattice.

[Cu₂Br₅]²⁻ is unique.

- it is the only example of a confacial bitetrahedron with bridging Br
- it has a delocalised intermediate oxidation state of +1.5
- it has a short Cu---Cu distance of 2.36 Å
- the singly occupied MO is delocalised σ*
- there is very little bond energy associated with the Cu---Cu interaction



The poster will present: (1) synthetic methods; (2) crystal structures; (3) EPR and electronic spectra; (4) density functional calculations.

1. M. Scudder and I. Dance, *J. Chem. Soc., Dalton Trans.*, 1998, 329-344.
2. C. Horn, I. G. Dance, D. Craig, M. L. Scudder and G. A. Bowmaker, *J. Am. Chem. Soc.*, 1998, 120, in press.

M17

POSTERS

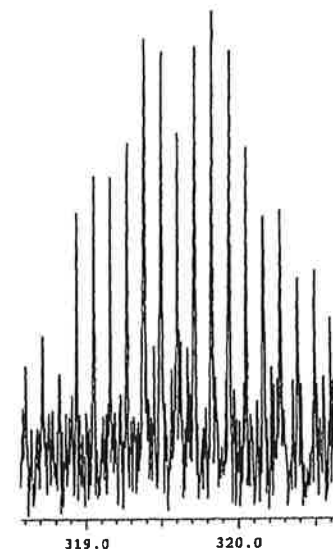
FTICR MASS SPECTROMETRY Keith Fisher, Ian Dance and Gary Willett School of Chemistry, The University of New South Wales, Sydney 2052. Australia

Mass spectrometry has become an important tool for Inorganic Chemists but has mainly been used for identification of molecular species. We use mass spectrometry to carry out ion identification, stability and reactivity studies, in the pristine gas phase environment.

Obtaining suitable ions for study is not difficult. Electrospray ionization is growing in importance for the production of ions in the gas phase from ions in solution. Laser desorption or Matrix assisted laser ionization (MALDI) can produce ions worth studying, either molecular ions or protonated molecular ions or fragments of the molecular ions. Cluster sources using laser ablation techniques are also available for ion studies.

The choice of the mass spectrometer may depend upon size, cost, mass range or ease of use. We use a 7T Fourier transform ion cyclotron resonance mass spectrometer, an ideal instrument for identifying and trapping ions. The instrument has fantastic mass resolution, mass accuracy below 2ppm, ion manipulation exemplary - but at a price.

As an example of the quality of our mass resolution, the spectrum below shows an ion with **nine negative charges** obtained from electrospray studies of phosphotungstic acid.



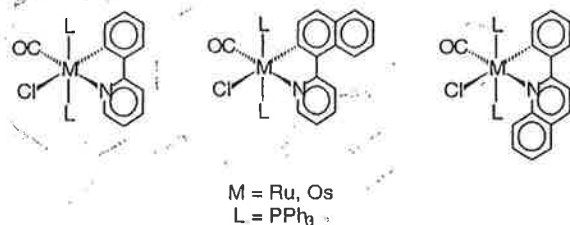
This contribution will outline some of our recent studies of Inorganic systems such as heteropolyacids and transition metal complexes.

M18

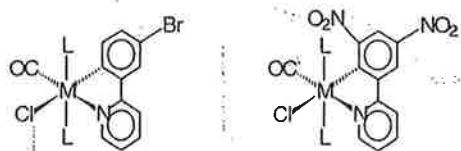
CHELATED ORGANOMETALLICS: EXCEPTIONALLY ROBUST 5-MEMBERED RINGS

Alex M. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright
Chemistry Department, University of Auckland, New Zealand

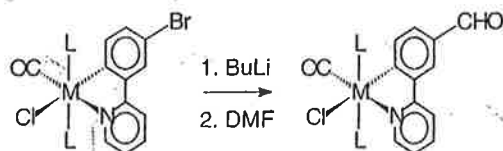
A series of compounds including and related to orthomercurated 2-phenylpyridine have been used to prepare ruthenium and osmium complexes:



The ligands attached to these complexes are not only activated in the positions *ortho* and *para* to the metal, but are also stable enough to undergo bromination or nitration under conditions that would typically cleave the metal-carbon bond.



The brominated complexes can be further functionalised by reaction with BuLi, followed by a suitable electrophile. No side products from the lithiation reactions are observed.



CARBONYL-2-PYRIDYLKETONES RUTHENIUM(II) COMPLEXES

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²Instituto de Química de São Carlos, Universidade de São Paulo,
Av. Dr. Carlos Botelho, 1465, 13560-970, São Carlos - SP - Brasil

Our research group has an ongoing interest in synthesizing Ru(II) complexes which contain a single bis(phosphine) ligand per metal center and examining their activity for catalytic hydrogenation of unsaturated organics¹. Following this line of research and having in mind that in coordination chemistry an important topic is the design and study of ligands and their influences on the structure and reactivity of the resulting metal complex, we are also concerned about the use of hybrid ligands containing atoms with different donor capacities. In this work we describe the synthesis and characterization of ruthenium(II) phosphine complexes, with general formulae [RuCl(dppb)(N-O)(CO)]PF₆ and [RuCl(PPh₃)₂(N-O)(CO)]PF₆, obtained from the reactions of [RuCl₂(dppb)(N-O)] and [RuCl₂(PPh₃)₂(N-O)], respectively, with carbon monoxide (dppb = 1,4-bis(diphenylphosphino)butane; N-O = 2-benzoylpyridine and 2-acetylpyridine). The complexes were characterized by elemental analysis, conductometry, cyclic voltammetry, NMR, UV/Vis, and IR spectroscopies.

The ³¹P NMR spectra of the monophosphine complexes are very similar and showed, in addition to the septet due to PF₆⁻, only a singlet (δ 31 (ref H₃PO₄)), indicating that these compounds have mutually *trans* PPh₃ ligands. Unlike the monophosphine analogues, the presence of inequivalent P atoms is inferred from the ³¹P NMR spectra of the biphosphine complexes, which exhibited two doublets centred at δ 39 and δ 16 with J(P-P) = 33 Hz. The presence of the CO group in these complexes is supported by the elemental analysis and the presence of a strong band between 2025 and 1964 cm⁻¹ assignable to ν(CO) in the IR spectra. All the species are ionic as evidenced by the conductivity data in acetone (1:1 electrolytes typically being 100-140 ohm⁻¹ cm² mol⁻¹).

(1) Queiroz, S.L.; Batista, A.A.; Oliva, G.; Gambardella, M.T.do P.; Santos, R.H.A.; MacFarlane, K.S.; Rettig, S.J. and James, B.R. *Inorg. Chim. Acta* 1998, 267, 209.

CAPES, CNPq, FAPESP, FINEP

PENDANT ARM MACROCYCLIC LIGANDS AND THEIR METAL COMPLEXES AS MOLECULAR RECEPTORS

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[‡]Department of Chemistry, The Flinders University of South Australia, GPO Box 2100.

A range of ligands (including those in Fig. 1.) and their metal complexes have been synthesised and studied to determine the factors controlling their structural, equilibrium and kinetic characteristics. These studies have been undertaken via variable temperature NMR, potentiometric titrations, gas phase *ab initio* calculations and X-ray crystal structures.¹

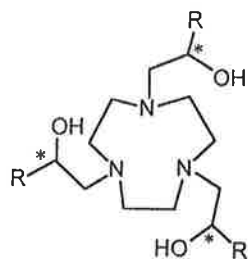


Fig. 1. ΔS -thpc9 (R=CH₃), ΔS -thpec9 (R=Ph), ΔS -thppc9 (R=CH₂Ph) and their alkali metal ion complexes assume single diastereomeric conformation in solution.

The pendant arms were found to adopt the *syn* configuration, and for the cases where R=Ph or R=CH₂Ph, the phenyl rings form a basket-like hydrophobic cavity which can act as a host for smaller molecules. The shape and size of the molecular basket can be diversified by variation of the R group, the macrocycle and the coordinated metal ion.

Host guest complexation should be optimal when the symmetry of the guest is similar to that of the receptor. Additional electrostatic attraction of the bound metal ion towards anionic guests is also favourable and host guest complexation of this type has been explored.

Reference

1. Whitbread, S. L., Weeks, J. M., Valente, P., Buntine, M. A., Lincoln, S. F. and Wainwright, K. P., *Aust. J. Chem.*, 1997, 50, 853-856.

(*n* = 1 or 2, R = Me, Ph)

Susan M. Waterman,^a Mark G. Humphrey^a and Graham E. Ball^b

^a Department of Chemistry, Australian National University, Canberra, A.C.T. 0200, Australia

^b School of Chemistry, University of New South Wales, Sydney, N.S.W. 2052, Australia

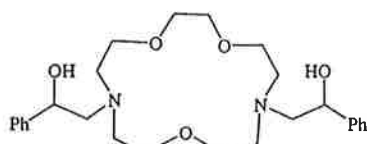
The carbonyl fluxionality at monodentate phosphine derivatives of the tetrahedral cluster Ir₄(CO)₁₂ has been extensively investigated, and has been recently extended to the isostructural CpWIr₃(CO)₁₁.¹ The group 6 - group 9 mixed metal cluster Cp₂W₂Ir₂(CO)₁₀ (1) is conceptually derived from Ir₄(CO)₁₂ by replacement of two Ir(CO)₃ vertices with two CpW(CO)₂ units. We now report the synthesis and characterization of some phosphine-ligated derivatives of 1, namely Cp₂W₂Ir₂(μ-CO)₃(CO)_{7-n}(L)_n [L = PPh₃, *n* = 1 (2), 2 (3); L = PMe₃, *n* = 1 (4), 2 (5), 3], with all clusters existing as mixtures of interconverting isomers in solution. Variable temperature ³¹P and ¹³C NMR, ¹³C exchange spectroscopy (EXSY) spectra and ¹H-³¹P-¹³C triple resonance experiments for 2 - 7 have enabled structural assignment of the isomers, and postulation of the mechanisms of fluxionality for isomers of 4 and 5. The results will be contrasted with those from the isolobally related CpWIr₃(CO)₁₁ and Ir₄(CO)₁₂.

METAL ION COMPLEXATION OF SOME BIBRACCHIAL LARIAT ETHERS: AN EQUILIBRIUM AND MOLECULAR ORBITAL STUDY.

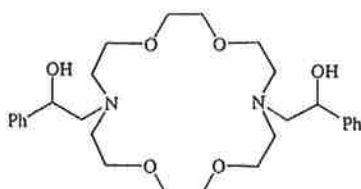
Lee C. West and Stephen F. Lincoln

Department of Chemistry, The University of Adelaide, Adelaide, SA 5005.

Bibracchial lariat ethers are either crown ethers or diazacrown ethers with a sidearm attached to each of two ring carbons or ring nitrogens respectively. When coordinating pendant arms are attached to the ring the side arms and macro ring act cooperatively resulting in complexes of enhanced thermodynamic stability compared to simple monocyclic crown ethers.^{1,2} We have recently synthesized two new bibracchial lariat ethers 7,13-bis((*R*)-2-hydroxy-2-phenylethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane (*R*-BPHE-C21) and 7,16-bis((*R*)-2-hydroxy-2-phenylethyl)-1,4,10,13-tetraoxacyclooctadecane (*R*-BPHE-C22).



BPHE-C21



BPHE-C22

The metal ion complexation of both ligands has been investigated via potentiometric titration. The factors affecting the variation in stability of the complexes of some alkaline earth and alkali metal ions are discussed. The experimental results are compared with those obtained from *ab initio* molecular orbital calculations.

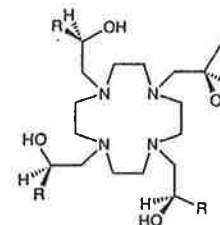
1. Gokel G. W. *Chem. Soc. Rev.*, **1992**, 39-46.
2. Lincoln S. F., Lucas J. and Rodopoulos T. *Inorg. Chim. Acta*, **1995**, 237, 147-150.

METAL ION ACTIVATED SUPRAMOLECULAR RECEPTORS

Christopher B. Smith*, Kia S. Wallwork*, Stephen F. Lincoln†, Max R. Taylor* and Kevin P. Wainwright*

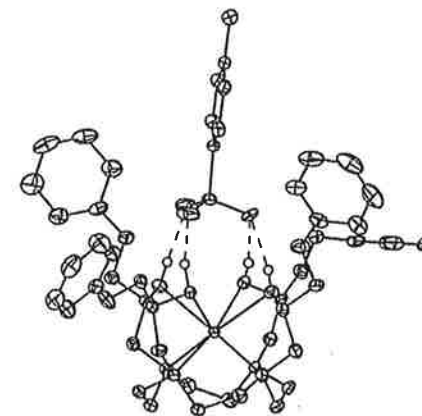
*Department of Chemistry, The Flinders University of South Australia, GPO Box 2100, Adelaide, South Australia 5001 and †Department of Chemistry, University of Adelaide, Adelaide 5005

Pendant donor macrocycles derived from cyclen (1,4,7,10-tetraazacyclododecane) invariably coordinate to a metal ion in such a way that all four pendant arms project in the same direction.¹ If, in addition to carrying a pendant donor group, these arms also have a phenyl or naphthyl group attached to them the possibility arises of using the coordination of the ligand to a metal ion as a way of assembling a molecular receptor with a substantial hydrophobic cavity that arises from the juxtaposition of the four phenyl or naphthyl groups. Upon removal of the metal ion the ligand can lose this conformation and consequently release any guest molecule that has been captured by the complex (the host). We have now prepared a range of these ligands, 1 - 7, and have begun to study their coordination and host-guest chemistry.



- 1 R = Ph-
- 2 R = PhCH₂-
- 3 R = PhOCH₂-
- 4 R = 1-naphthylOCH₂-
- 5 R = 2-naphthylOCH₂-
- 6 R = 4-phenylphenylOCH₂-
- 7 R = 4-PhCH₂OPhOCH₂-

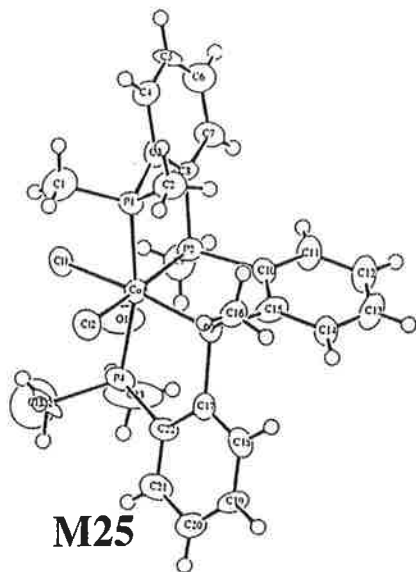
As an illustration of this, complexation of 3 with cadmium(II) or lead(II) leads to eight coordinate complexes, which, as their perchlorate salts, have the desired cavity devoid of any guest molecule. This has been verified by X-ray crystallography and is known to persist in solution from NMR and conductivity data. Upon reaction with sodium *p*-toluenesulfonate or sodium *p*-nitrophenolate, sodium perchlorate is eliminated and inclusion complexes containing *p*-toluenesulfonate or *p*-nitrophenolate can be formed. The inclusion complex derived from the Cd(II) complex of 3 and *p*-toluenesulfonate is shown in the adjacent ORTEP diagram, and is known, from conductivity studies, to exist also in solution. In the solid state the *p*-toluenesulfonate is retained by hydrogen bonding and there is no apparent interaction between any of the aromatic rings. Notwithstanding this, these inclusion forming reactions do not occur in the absence of aromatic moieties appended to the molecule. Thus it appears that the components of the hydrophobic cavity employ quite weak forces to induce the aromatic anion into a position from which it is then captured by hydrogen bond formation.



1. Wainwright, K.P., *Coordination Chem. Rev.*, **1997**, 166, 35-90.
2. Smith, C.B., Wallwork, K.S., Weeks, J.M., Buntine, M.A., Lincoln, S.F., Taylor M.R. & Wainwright, K.P., *J. Am. Chem. Soc.*, submitted.

Swarup Chatterjee^a, Roy Doyle^a, Mark George^a, Geoff Salem^a, and Anthony C. Willis^b^aChemistry Department, The Faculties, Australian National University, Canberra, ACT, 0200, Australia^bResearch School of Chemistry, Australian National University, Canberra, ACT, 0200, Australia

The secondary phosphine (2-methylphosphinophenyl)dimethylphosphine (1), has been prepared by stepwise methylation of (1,2-phenylene)bisphosphine. Subsequent reaction of (1) with sodium, followed by 1,2-dichlorobenzene, gave the di(tertiary phosphine) (\pm)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine (2). Further reaction of (2) with sodium(2-dimethylphosphinophenyl)methylphosphide gave the quadridentate ligand (R^*,R^*)-1,2-[bis(2-dimethylphosphinophenyl)methylphosphino]benzene (3) in a completely stereoselective manner. The quadridentate ligand has been isolated by complexation to cobalt(III) to give a single diastereomeric complex, as confirmed by X-ray crystallography. The resolution of (2) has been undertaken, by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing an orthometallated optically active naphthylamine, and the racemic ligand. Separation of the diastereomers has been achieved by fractional crystallisation from dichloromethane/isopropanol. Coupling of the optically active antipodes of (2) with sodium(2-dimethylphosphinophenyl)methylphosphide should provide a route to optically active (3).

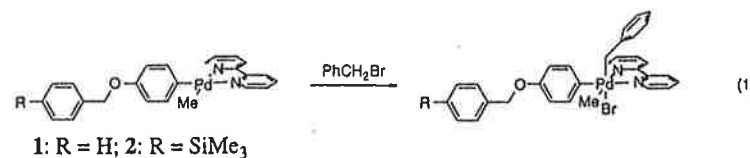
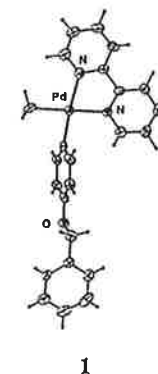
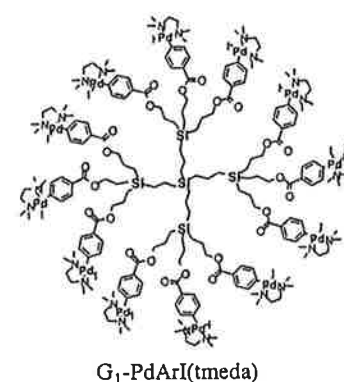


POSTERS

Jason L. Hoare,^a Klaus Lorenz,^b Wilberth J. J. Smeets,^c Neldes J. Hovestad,^c Allan J. Canty,^a Holger Frey,^b Anthony L. Spek^c and Gerard van Koten^c^aUniversity of Tasmania, ^bFreiburger Materialforschungszentrum and ^cUtrecht University

Dendrimers are currently generating considerable interest due to the range of applications and materials properties arising from their nanoscale and precise molecular architecture.¹ We report here the first example of a periphery palladated dendrimer involving Pd-C σ -bond linkages,² and subsequent studies aimed at developing dendrimers containing Pd(IV) centres.

Functionalisation by palladium is achieved via oxidative addition reactions of iodoarene dendrimers with Pd(0) reagents to give, for example, G₁-PdArI(tmeda). However, ArPdI(tmeda) species in which the aryl group is an electron withdrawing acetyl group cannot be converted to Pd(IV) complexes via methylation (by LiMe), replacement of tmeda by bipy, and subsequent oxidative addition of alkyl halides. We have commenced studies aimed at overcoming this difficulty, and report here studies of eq 1 as model reactions for potential synthesis of new dendrimers containing aryl ether arms.

1. Zeng, F.; Zimmerman, S.C. *Chem Rev*, 1997, 97, 1681.2. Hoare, J.L.; Lorenz, K.; Hovestad, N.J.; Smeets, W.J.J.; Spek, A.L.; Canty, A.J.; Frey, H.; van Koten, G. *Organometallics*, 1997, 16, 4167.

M26

THE STRUCTURES OF COPPER SULFIDE CLUSTERS Cu_xS_y

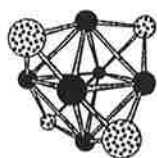
Ian Dance and Keith Fisher

School of Chemistry, University of New South Wales, Sydney 2052.

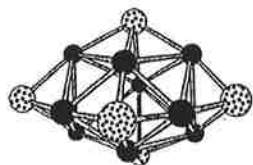
We have been able to generate a set of copper sulfide clusters in the gas phase [*Inorg. Chem.*, 1991, 30, 2957-2958; *J. Chem. Soc., Dalton Trans.*, 1996, 709-718]. The major pattern of composition includes $[\text{Cu}_{2n-1}\text{S}_n]^-$ and $[\text{Cu}_{2n-2}\text{S}_n]^-$, $n \leq 23$.

What are the structures of these species, and what are the structural and electronic principles which account for this band of compositions?

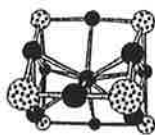
We have responded to these questions with density functional optimisations of postulated geometrical structures, and calculations of electron affinities and electronic structures. A few of the most stable isomers are represented below.



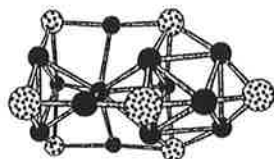
Cu_6S_4



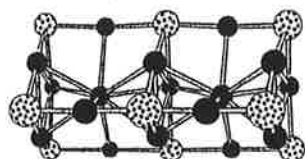
Cu_9S_5



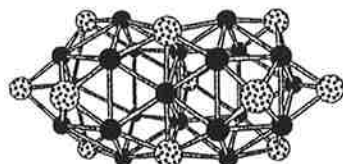
Cu_{10}S_6



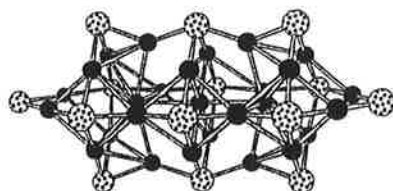
Cu_{13}S_7



Cu_{17}S_9



$\text{Cu}_{21}\text{S}_{11}$



$\text{Cu}_{27}\text{S}_{14}$

Can you identify structural principles in these structures? The poster will present the full array of calculated structures and properties, for further testing of postulates about structural principles.

COPPER(II) AND NICKEL(II) COMPLEXES OF POLYDENTATE LIGANDS AS ARTIFICIAL NUCLEASES

Geoffrey N. De Iuliis,^a Geoffrey A. Lawrance,^a Sabine Fieuw-Makaroff^b and Peter Dunkley^b

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Reports of metal complexes of polydentate ligands as successful reagents for cleaving DNA have appeared in the literature recently. These artificial nucleases apparently act via the metal-catalysed hydrolysis of phosphodiester links in DNA, and presumably involve a coordinated hydroxide nucleophile. The polydentate ligand is usually not itself involved in the chemistry, but plays some role as a 'spectator'. To date there has been little systematic study of the influence of spectator ligands in the complexes employed, but this probably reflects the paucity of investigations of any type reported. The perceived suitability of the spectator ligand has been related simply to the general efficacy of the complex as a DNA artificial nuclease. In a preliminary study reported here, we have begun to examine the characteristics of the ligand which promote catalysis.

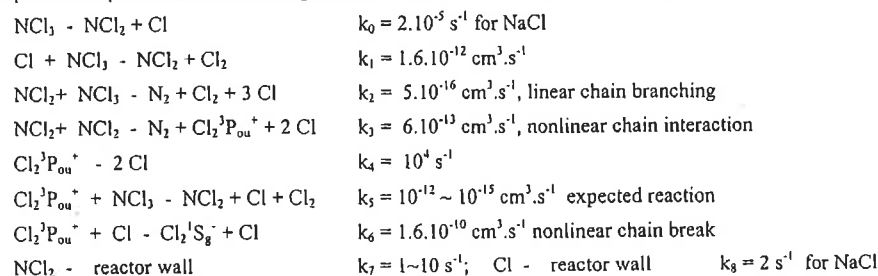
Copper(II) complexes of a number of potentially tridentate ligands carrying a range of different donor groups and having different geometries have been prepared and examined. The molecules prepared included various combinations of carboxylate, alcohol, pyridine, and primary and secondary amine donor groups. Activity was measured against the known highly active complex of cyclohexane-1,3,5-triamine (tach). Complexes (1:1 Cu:ligand) were incubated with pBluescript KS (+/-) supercoiled plasmid DNA in HEPES buffer for several hours. The level of degradation of the double-stranded supercoiled DNA into nicked and linear forms achieved was visualised by gel electrophoresis. The activity of N-(2'-hydroxycyclohexyl)-2-aminomethylpyridine proved to be at least equivalent to that of the known artificial nuclease tach. The presence of carboxylate groups appeared to be detrimental to activity with these tridentate ligands.

Complexes containing two metal ions in adjacent sites were also examined, since it is known that some natural nucleases involve two metal ions at the active site. A chloride-bridged dinickel(II) complex of a cyclic triamine and a dicopper(II) complex of a polyaminopolythioether showed very strong nuclease activity, possibly related to the availability of adjacent sites providing for both coordination and nucleophilic attack.

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Thermal decomposition of NCl₃ being used in laser applications is an example of the branching chain low temperature decomposition of individual substance in gaseous phase, in which the nonlinear chain branching plays an important role, leading to nonthermal flame propagation. It has been also shown, that electronically excited Cl₂³P_{ou}⁺ generated by this reaction takes part in chain branching. The decomposition of NCl₃ may be considered as model process, because the rate constants of the main steps are known. This work is aimed to experimental and theoretical investigation of chemical oscillations in enclosed volume at pressures < 10 Torr and 293 K in NCl₃ decomposition (in He). We have observed the oscillations of chemiluminescence and NCl₃ concentration in the enclosed reactor treated by NaCl; the warming-up did not exceed 5°. The chemical oscillations observed were damped out, amplified or self-sustained with the position of reaction mixture in the self-ignition area. We tried to clarify whether the set of following elementary steps combined with the processes of adsorption/desorption of NCl₃ are enough for modelling the observed oscillation regimes.



ODEs for dimensionless NCl₃, NCl₂, Cl, Cl₂³P_{ou}⁺ were calculated by the 4th order Runge-Kutta method with initial conditions (NCl₃)/(NCl₃)₀ = 1, the others equal to zero. The calculated concentrations of reactants during the ignition and the lower self-ignition limits were in quantitative agreement with experimental values.

We have shown that the following conditions are sufficient for the oscillating solutions: a) the inclusion of adsorption/desorption of NCl₃, b) $k_4, k_6 > 0$, c) $k_5 > 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$. The desorption rate was written as $Z \cdot (\text{NCl}_3)^{1/m}$, $m = 2 \sim 6$, ($Z = \text{const}$); in this case after self-ignition the stationary reaction occurs, or close to the lower self-ignition limit the phase portrait is a stable circle. If we take into account the decrease of the amount of NCl₃ adsorbed on the reactor walls ($Z = Z_0(1 - h \cdot t)$, $h = 10^{-7}$, t - time) the stable circle becomes the unstable limit cycle or stable focus, depending on k_7 value in accordance with amplified or damped oscillations observed experimentally. An agreement between the calculations and the experimental data arises if we take into account the change in the state of surface due to NCl₃ desorption: $k_7 = k_7' \cdot (1 + m \cdot t)$, $m = 10^{-7}$, t - time.

Therefore it has been shown that the modelling of oscillatory regimes in NCl₃ decomposition as an example of the nonlinear chain branching reaction requires not only the external source to exist, but a consideration of the nonlinear chain branching and break as well as the change in the state of reactor surface.

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The coordination chemistry of crown ethers is rich and versatile and led to useful approaches towards ligand design for selective complexation of a wide variety of metal ions, including alkali-, alkaline-earth-metal, lead(II), thallium(I) and ammonium cations. The considerable attention has been paid to understanding the principles of a Mⁿ⁺ - crown ether bonding through the crystal structure studies of the complexes with 18-crown-6 (L), a readily available crown ether. Evidently, that any types of a strong moiety-moiety interaction in the anionic part of the structure may be considered to be important in crystal packing. Such interactions (*cf.* hydrogen bonding or coordination) lead to a most close disposition of anions in the lattice and, respectively, may promote compression of the macrocyclic cationic array. The numerous species of a coordination polymeric structure may be suggested as the suitable counter anions for the stabilization of the 'compressed' macrocyclic array and different types of polymeric cyano- and thiocyanatocuprates(I) are of special interest in this context. In order to clarify the geometry of [Cu(NCS)₂]_n⁻ moiety under the presence of macrocyclic cations, we have attempted to prepare compounds of composition [Kat(18-crown-6){Cu(NCS)₂}] (where Kat = NH₄, Tl) and here we describe the synthesis and crystal structure of a [NH₄(18-crown-6){Cu(SCN)₂}] and [Tl(18-crown-6){Cu(SCN)₂}] complexes. This new macrocyclic complexes has been prepared using a direct method of interaction and characterized by X-ray crystallography. The lattice comprises complex cations [Kat(18-crown-6)]⁺ and infinite polymeric anions [Cu(NCS)₂]⁻ of an one-dimensional zig-zag structure. The copper atoms adopt three-fold coordination [CuN₂S] (Cu-N 1.89(1), 1.90(1) Å; Cu-S 2.278(4) Å).

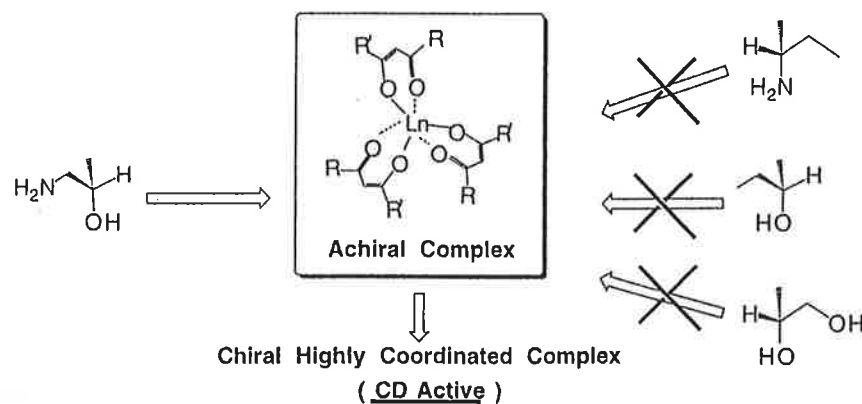
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LANTHANIDE COMPLEXES AS EFFECTIVE CD PROBES OF CHIRAL AMINO ALCOHOLS

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Although induced circular dichroism spectroscopy in molecular recognition chemistry has proved useful for enantiomeric differentiation, the number of effective probes for chirality sensing of the specific guests remains limited.¹⁾ We report specific binding and chirality sensing of neutral amino alcohols by lanthanide tris(β -diketonates). They are electrically neutral complexes, but have potentials to form highly coordinated complexes with neutral guests. Interestingly, the employed lanthanide tris(β -diketonates) preferred amino alcohols to amine, alcohol and diol guests and offered induced CD signals of which signs were dependent on the stereochemistry of the amino alcohol guests. Since there are many combinations of central lanthanide cations and coordinating ligands, such specific functions of the lanthanide complexes have many extensions in the coordination chemistry, molecular recognition chemistry, sensing / separation chemistry and related fields.²⁾



1) H. Tsukube, *Tetrahedron Lett.*, **38**, 4239 (1997).

2) H. Tsukube, *et al. Inorg.Chem.*, **37**, 1585 (1998).

CHEMICAL AND BIOLOGICAL STUDIES OF DICHLORO(2-PHENYLPYRIDINE) GOLD(III) COMPLEX

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The discovery of the antitumor activity of cisplatin (Fig 1) in 1969 generated considerable interest in the pharmacology of metal complexes^[1]. As Au(III) and Pt(II) are isoelectronic (4f¹⁴5d⁸), Au(III) complexes also show a square-planar configuration and might have biological activity similar to cisplatin and its homologues.

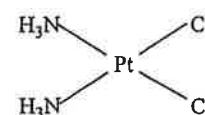


Fig1 Cisplatin

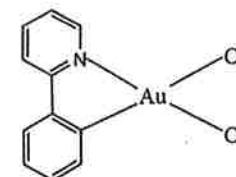


Fig2 Au(ppy)Cl₂

To investigate the chemical and biological properties of gold(III) complexes, we prepared dichloro(2-phenylpyridine) gold(III) complex [Au(ppy)Cl₂] (Fig 2) in which an orthometalated C,N-chelate ring is formed. Using [Au(ppy)Cl₂] as the precursor, several complexes of the types [Au(ppy)X₂] and [Au(ppy)(X-X)] (X, X-X=mono- and bidentate monoanionic ligands) have been obtained. The ¹H NMR spectra indicate that there is a significant upfield chemical shift of ppy ligand resonances after the two chloride donors were replaced by X ligands.

The derivative [Au(ppy)(ace)₂] (ace=acetate anion) has the expected structure, in which the two Au-O bond length are appreciably different, with that trans to C being the longer as expected due to its higher trans-influence. In the structure of [Au(ppy)(tsc)] (tsc=thiosalicylic anion), unusually, the thiol group is trans to C while the carboxylate group also coordinates to gold, giving a five-membered chelate ring.

We also investigated the hydrolysis reaction of [Au(ppy)(ace)₂] by ¹H and ¹³C NMR in D₂O and H₂O-DMF. The NMR spectra show that one acetate ligand is undergoing exchange with a water molecule rapidly on the NMR time-scale. On the basis of the trans effect, this would be expected to be that trans to the Au-C bond, since a carbanion has a stronger trans-labilising effect than N.

The cytotoxicity of five complexes on MOLT-4 human leukemia cells showed them to be significantly more cytotoxic than cisplatin.

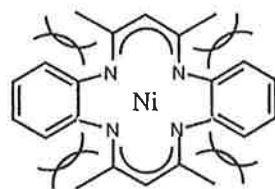
[1] B. Rosenberg, L. Van Camp and T. Krigas, *Nature(London)*, **9165**, 205, 698.

SYNTHESIS OF NEW CONTAINER MOLECULES FOR THE
SUPRAMOLECULAR COMPLEXATION OF GLOBULAR GUESTS.

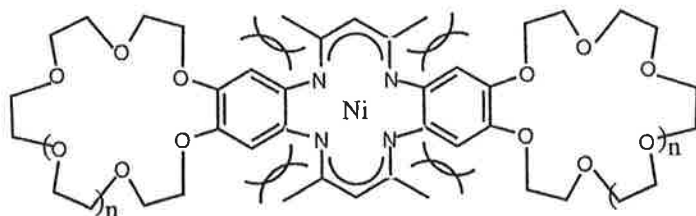
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We have previously reported the supramolecular complexation of globular molecules (C_{60} , 1,2-dicarbododecaborane(12) and P_4S_3) by the saddle shaped Nickel macrocycle 5,7,12,14-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinenickel(II), $(Ni(TMTAA))^1$ (I). The suitability of $Ni(TMTAA)$ for supramolecular complexation led us to pursue the synthesis of analogous macrocycles with larger concave surfaces better able to complex globular guests in a deeper cavity. By a Nickel template condensation of (diaminobenzo) crown ethers with 2,4-pentanedione, the crown ether appended macrocycles (II) may be synthesised. Some recent results in the synthesis of these crown ether appended macrocycles will be reported.



(I)



(II)

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POSTERS

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Macropolycyclic hexamine cages form complexes with extraordinary stability [1, 2], and depending on the substituents at their apices, have potential applications in areas such as selective biological activity, electron transfer agents, and imaging and therapeutic agents [3,4]. The ability of the primary amine groups of these cages to condense with aldehydes leads to several alkylated cages. The resulting imine complexes can then give saturated amines which can be easily separated by chromatographic methods. We report here the synthesis and characterisation of hexamine cage complexes with several aromatic substituents (Figure 1). Their electrochemistry is also represented.

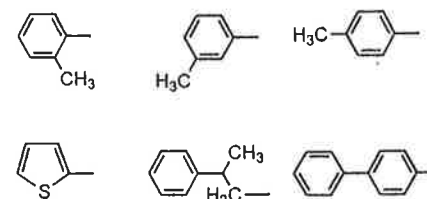


Figure 1

References

- [1] A.M. Sargeson, *Chem. Br.*, **15** (1979) 23
- [2] G.A. Bottomley, I.J. Clark, I.I. Creaser, L.M. Engelhardt, R.J. Geue, K.S. Hagen, J.M. Harrowfield, G.A. Lawrance, P.A. Lay, A.M. Sargeson, A.J. See, B.W. Skelton, A.H. White and F.R. Wilner, *Aus. J. Chem.*, **47** (1994) 143
- [3] A.M. Sargeson, *Coord. Chem. Rev.*, **151** (1996) 89
- [4] M. Gajhede, A. Hammershoi and L.K. Skob, *Acta Chim. Scand.*, **45** (1991) 474

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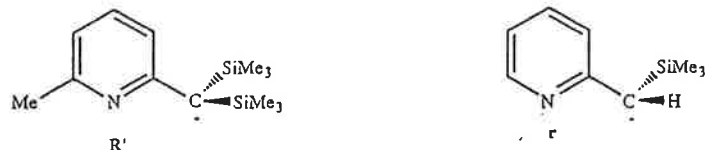
SYNTHETIC AND THEORETICAL STUDIES ON GROUP 15 ALKYLDIHALIDES STABILISED WITH SiMe₃

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We have been investigating structural conformations and stability aspects of complexes of the type R'MCl₂ and rMCl₂.

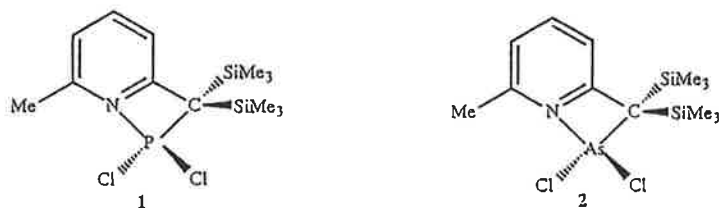


In main group chemistry ligand R' has been important in that ¹:

- steric demand reduces the tendency for oligomerisation.
- there is the possibility of internal stability offered by the pyridyl nitrogen.
- In contrast, r with its reduced steric bulk has been investigated to a lesser extent.

Although difficult to isolate because of β -elimination of ClSiMe₃, we have managed to obtain crystal structures of the alkyldihalides R'PCL₂ (1) and R'AsCl₂ (2) which have extremely short N...M dative bonds of 2.238(3)Å and 2.285(2)Å respectively.

These short dative bonds are most likely a result of the close proximity and steric bulk of the two SiMe₃ groups. Synthetic experiments and high level *ab initio* MO calculations have been undertaken on R'PCL₂, R'AsCl₂, rPCL₂ and rAsCl₂.



1. Review; T.R. Van den Ancker and C.L. Raston, *J. Organomet. Chem* 1995 (500) 289.

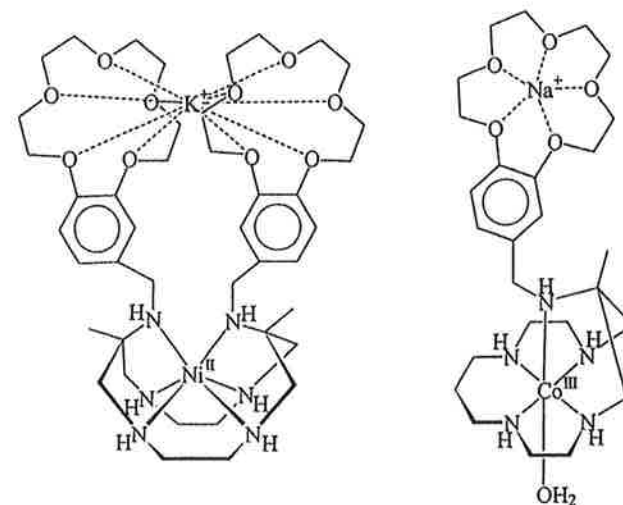
MACROCYCLIC COMPLEXES AS REDOX-ACTIVE RECEPTORS

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Receptors are molecules that bind specific substrates through weak or reversible intermolecular forces. Redox-active receptors traditionally consist of a redox-active centre attached to a host binding site. Efficient communication between these two subunits is crucial if the binding of guest ions is to be detected electrochemically.

Crown ethers are well known to bind alkali and alkaline earth cations selectively. Metal complexes of cyclam-type macrocycles have desirable electrochemical properties (reversible one electron oxidation/reduction in aqueous solution). A combination of these two subunits should lead to a new class of redox-active receptors, such as those shown below.



THE SYNTHESIS AND METAL BINDING PROPERTIES OF *N*-BENZYLATED MIXED DONOR MACROCYCLES

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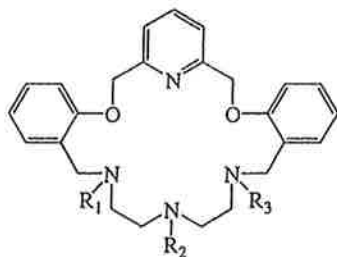
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Previous studies of the effect *N*-alkylation of aza-crown macrocycles on their metal binding properties for transition and post transition metal ions have demonstrated that there is sometimes preferential selectivity towards individual metal ions.¹ Current understanding of this metal ion selectivity is not well understood.² An investigation of the properties of the series of the progressively benzylated macrocycles, (1) – (6), has been undertaken in an attempt to further explain the above behavior.



- (1) $R_1 = R_2 = R_3 = H$
- (2) $R_1 = \text{Benzyl}, R_2 = R_3 = H$
- (3) $R_1 = R_3 = H, R_2 = \text{Benzyl}$
- (4) $R_1 = R_2 = \text{Benzyl}, R_3 = H$
- (5) $R_1 = R_3 = \text{Benzyl}, R_2 = H$
- (6) $R_1 = R_2 = R_3 = \text{Benzyl}$

An outline of the synthesis of the macrocycles will be presented along with metal complexation studies. A discussion of possible mechanisms for metal ion recognition by these species will also be presented.

¹ A. J. Leong, and L. F. Lindoy, unpublished work.

² G. Golub, H. Cohen, P. Paloletti, A. Bencini, L. Messori, I. Bertini, and D. Meyerstein, *J. Am. Chem. Soc.*, 1995, 117, 8353.

ANTI-INFLAMMATORY DINUCLEAR COPPER(II) COMPLEXES WITH INDOMETHACIN. MAGNETISM AND EPR SPECTROSCOPY; CRYSTAL STRUCTURE OF THE *N,N*-DIMETHYLFORMAMIDE ADDUCT.

Jane E. Weder,[†] Trevor W. Hambley,[†] Brendan J. Kennedy,[†] Peter A. Lay,[†] Dugald MacLachlan,[†] Richard Bramley,[‡] Christopher D. Delfs,[‡] Keith S. Murray,[§] Boujemaa Moubaraki,[§] Barry Warwick,[#] John R. Biffin[#] and Hubertus L. Regtop.[#]

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Veterinary anti-inflammatory Cu(II) complexes of indomethacin (1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indole-3-acetic acid = IndoH), of the general formula $[Cu_2(\text{Indo})_4L_2]$ ($L = N,N$ -dimethylformamide (DMF), N,N -dimethylacetamide (DMA), N -methylpyrrolidone (NMP), and water), were studied by zero-field and X-band EPR spectroscopy, electronic spectroscopy, magnetic measurements and X-ray powder diffraction. The complexes are similar to Cu(II) acetate monohydrate, with a strong antiferromagnetic exchange interaction, J , ranging from -141 to -152 cm^{-1} . Variable temperature magnetic susceptibility data for all the complexes are similar, with the exception of a $[Cu_2(\text{Indo})_4(\text{H}_2\text{O})_2]$ complex, which displays an unusual increase in magnetic moment with decreasing temperature from 50 K to 10 K. The X-ray powder diffraction patterns of the DMF and DMA dimers show that they are isostructural. All of the complexes crystallize in the triclinic space group $P\bar{1}$. Single crystal X-ray diffraction analysis of the DMF complex, $[Cu_2(\text{Indo})_4(\text{DMF})_2] \cdot 1.6(\text{DMF})$, shows that it is similar to the previously reported $[Cu_2(\text{Indo})_4(\text{DMSO})_2]$ complex; with a Cu---Cu vector length of $2.630(1) \text{ \AA}$, Cu---O_{RCOO} $1.960(4) \text{ \AA}$ to $1.967(4) \text{ \AA}$, and Cu---O_{DMF} of $2.143(5) \text{ \AA}$ and crystal parameters a $10.848(3) \text{ \AA}$, b $13.336(6) \text{ \AA}$, c $16.457(4) \text{ \AA}$, α $104.67(3)^\circ$, β $100.94(2)^\circ$, γ $107.16(3)^\circ$. The hydrophobic nature of the exterior of the $[Cu_2(\text{Indo})_4(\text{DMF})_2]$ complex may be important in facilitating its dissolution in micelles and transport through biological membranes.

IN VITRO PLASMID DNA CLEAVAGE BY CHROMIUM(V/IV) 2-HYDROXYCARBOXYLATO COMPLEXES

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The abilities of relatively stable Cr(V) and Cr(IV) complexes with 2-hydroxycarboxylato ligands (2-ethyl-2-hydroxybutanoate(2-) = ehba; (1*R*,3*R*,4*R*,5*R*)-1,3,4,5-tetrahydroxycyclohexanecarboxylate(2-) = quinate = qa) to induce single strand breaks in plasmid DNA have been studied under a wide range of reaction conditions. The Cr(V) complex, Na[Cr^VO(ehba)₂], causes substantial DNA cleavage over the pH range 4.0 - 8.0 ([Cr(V)]₀ = 0.010 - 0.75 mM, phosphate buffer, 37 °C). The DNA cleavage is inhibited by the presence of excess ligand, by exclusion of O₂, or by the additions of organic compounds, such as alcohols, carboxylic acids or DMSO, but it is not affected by traces of catalytic metals (Fe(III) or Cu(II)), or by the addition of catalase. The Cr(IV)-qa complexes, unlike the Cr(V) complexes, are able to cleave DNA in the presence of the ligand in large excess ([Cr(IV)]₀ = 0.50 mM; [qa] = 20 - 100 mM, pH = 3.5 - 6.0, 37 °C). This is the first direct evidence for DNA cleavage induced by well-characterised Cr(IV) complexes. The proposed mechanism for DNA cleavage includes the following: (i) partial aquation of the bis-chelated Cr(V/IV) complexes with the formation of reactive monochelated forms; (ii) binding of the Cr(V/IV) monochelates to the phosphate backbone of DNA; (iii) one- or two-electron oxidations at the deoxyribose moieties of DNA by Cr(V/IV); and (iv) cleavage of the resultant DNA radicals or cations with or without participation of O₂. The patterns of DNA damage by Cr(V/IV) can include strand breaks, abasic sites and the formation of Cr(III)-DNA complexes. These results support the hypothesis [1,2] about the significant role of Cr(V/IV) intermediates in Cr(VI)-induced genotoxicities *in vivo*.

References:

- [1] Connett, P.; Wetterhahn, K. E. *Struct. Bonding (Berlin)* 1983, 54, 93-124.
- [2] (a) Farrell, R. P.; Judd, R. J.; Lay, P. A.; Dixon, N. E.; Baker, R. S. U.; Bonin, A. M. *Chem. Res. Toxicol.* 1989, 2, 227-229. (b) Barr-David, G.; Hambley, T. W.; Irwin, J. A.; Judd, R. J.; Lay, P. A.; Martin, B. M.; Bramley, R.; Dixon, N. E.; Hendry, P.; Ji, J.-Y.; Baker, R. S. U.; Bonin, A. M. *Inorg. Chem.* 1992, 31, 4906-4908.

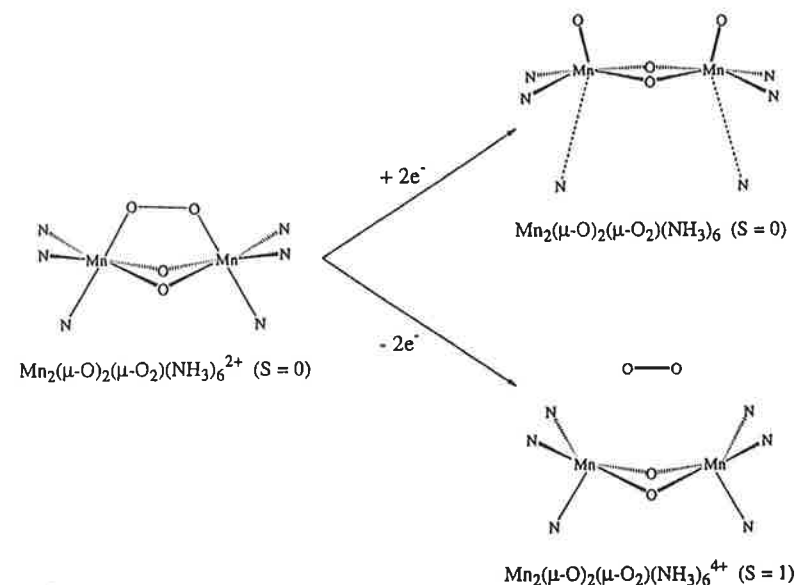
COMPUTATIONAL INVESTIGATION INTO REDOX-INDUCED O-O BOND FORMATION & CLEAVAGE ON A DIMANGANESE CLUSTER

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Two-electron reduction and oxidation of a model peroxo-bridged dimanganese(IV/IV) complex are investigated using approximate density functional theory. In each case, the redox process is initially localised on a metal-based orbital, giving Mn₂^{III/III} or Mn₂^{V/V} respectively. When the geometry of the redox-altered products is allowed to relax, electrons are spontaneously transferred to or from the {O₂} unit, regenerating the stable Mn₂^{IV/IV} core. Two-electron reduction therefore leads to the cleavage of the O-O bond, while oxidation results in the formation of an O=O double bond and release of a molecule of O₂. The nature of the coupling (antiferromagnetic or ferromagnetic) between the manganese ions plays a major role in determining the stability of the initial metal-based redox products, and hence the kinetic barrier to bond formation or cleavage. Reductive O-O cleavage is favoured by antiferromagnetic coupling between the metal ions, while oxidative release of O₂ is favoured by ferromagnetic coupling. The significance of these conclusions to the mechanism of photosynthetic O₂ evolution will also be discussed.

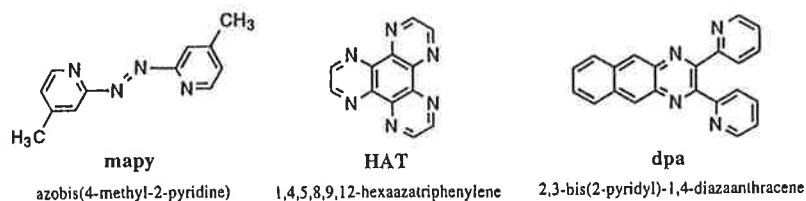


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Recently, the chromatographic separation of the stereoisomers of a number of mono-, di- and tri-metallic species has been achieved and it has been demonstrated that these isomers exhibit differences in their photophysical, electrochemical and spectral properties.^{1,2} Examples of such systems include dinuclear and trinuclear ruthenium complexes involving the bridging ligand HAT and diruthenium complexes containing the bridging ligands mapy and dpa. Mechanistic investigations of the chromatographic separation have identified the involvement of specific interactions between eluent anions and the substrate complex.^{1,2}



Recently developed high-pressure voltammetry techniques enable the measurement of molar volume changes ($\Delta V^\circ_{\text{cell}}$) of electron-transfer reactions.³⁻⁵ A major contributor to $\Delta V^\circ_{\text{cell}}$ is the volume change resulting from the interaction of polar solvent molecules and electrolyte anions with the ionic charge of the complex. This study of redox molar volume changes in diastereoisomers of polymetallic species provides information about the nature of anion-complex interactions and allows further examination of factors influencing molar volume changes accompanying electron transfer.

1. F.R. Keene, *Coord. Chem. Rev.*, 1997, 166, 121 and references therein.
2. F.R. Keene, *Chem. Soc. Rev.*, 1998, 27, 185 and references therein.
3. J. Sachinidis, R.D. Shalders and P.A. Tregloan, *J. Electroanal. Chem.*, 1992, 327, 219.
4. J. Sachinidis, R.D. Shalders and P.A. Tregloan, *Inorg. Chem.*, 1994, 33, 6180.
5. J. Sachinidis, R.D. Shalders and P.A. Tregloan, *Inorg. Chem.*, 1996, 35, 2497.

Lyndal M. R. Hill,* Matthew T. Cox, Lawrence R. Gahan

Department of Chemistry, The University of Queensland, Brisbane, QLD, Australia 4072.

The piezoelectric detector, specifically a quartz crystal microbalance (QCM), consists of a thin circular quartz crystal with circular gold electrodes placed centrosymmetrically on opposite faces. Application of an alternating electric field across the crystal, using an electronic oscillator, results in vibration of the crystal at its resonant frequency. The frequency of the oscillating crystal is decreased by deposition of mass on its surface. It has been shown that by placing a receptor on the gold electrode of the piezoelectric crystal, it is possible to "sense" the chelation of the metal ion by the receptor by observing the change in resonance frequency of the crystal. The most successful technique we have found to derivatise the surface of the crystal is to use 5 micron spherical silica beads functionalised with appropriate ligands, in the present case a triacid analogue of ethylenediaminetetraacetic acid.

We have developed a device which responds reversibly to metal ions in solution. We will describe the results of experiments in which the kinetics of interaction of lead(II) with the bound ligand have been investigated. Kinetic parameters for the interaction have been extracted from the frequency response of the crystal with time. Additionally, the data have been fitted to a Langmuir-type isotherm to obtain an apparent binding constant for the interaction. The interaction of the device with other metal ions (cadmium(II), silver(I)) is not as simply understood as in the case of lead(II), although evidence for metal ion discrimination has been obtained.

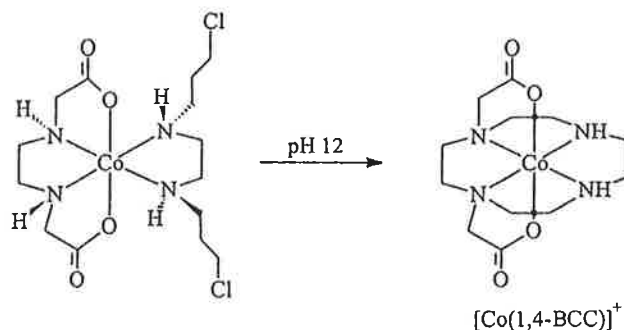
The technique and device under development have similarities with BIAcore™ sensor technology employed for the study of highly specific protein-protein or receptor-ligand and antibody-antigen associations.

FORMATION OF A MACROCYCLIC LIGAND BY INTRAMOLECULAR ALKYLATION REACTIONS ON A COBALT(III) COMPLEX

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Condensation reactions of coordinated amines constitute a class of reaction which has generated a wealth of new ligands and interesting chemistry. In contrast, template alkylation reactions are less well known. We have recently developed cobalt(III) mixed ligand systems which are predisposed for intramolecular alkylation. The complexes contain alkyl ligands bearing N-chloroalkyl substituents which act as intramolecular agents to form new cobalt(III) complexes of acyclic and macrocyclic hexadentate ligands. One example is the cyclam derivative 1,4-BCC illustrated below.¹ The cobalt(III) centre in $[\text{Co}(\text{1,4-BCC})]^+$ can be reduced to form an isolable cobalt(II) complex containing the same ligand. Photochemical decarboxylation of the $[\text{Co}(\text{1,4-BCC})]^+$ generates a complex which incorporates a three-membered chelate ring containing a Co-C σ -bond.



1. Ware, D.C.; Tonei, D.M.; Baker, L.J.; Brothers, P.J.; Clark, G.R. *Chem. Commun.* 1996, 1303.

$\text{Ca}_7\text{Zr}_7\text{Ta}_6\text{O}_{36}$ - SYNTHESIS AND STRUCTURE REFINEMENT OF A NEW ANION-DEFICIENT, FLUORITE-RELATED SUPERSTRUCTURE PHASE

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2601, Australia

An attempt to systematically investigate the CaZrO_3 - LiTaO_3 system has led to the discovery of a new long period anion-deficient, fluorite-related superstructure phase with experimentally determined composition of $0.304(4)\text{TaO}_{2.5} \cdot 0.347(4)\text{ZrO}_2 \cdot 0.349(4)\text{CaO}$ [1]. Electron diffraction suggested a space group symmetry for this phase of $Fddd$. It is interesting to note that the strongest satellite reflections fall close to the $G_F \pm 1/2 \langle 111 \rangle_F^*$ positions of reciprocal space (F for fluorite substructure) and suggests a relationship to the so-called cubic stabilised zirconias (CSZs) and other fluorite-related superstructure phases such as CaZr_4O_9 which also show additional scattering in similar regions of reciprocal space.

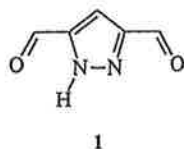
It proved possible to grow very small single crystals of the superstructure phase ($a = 36.394(1)$, $b = 7.3674(5)$, $c = 31.006(2)\text{\AA}$) and a full sphere of intensity data was collected at the vertical wiggler beamline BL-14A of the Photon Factory, Tsukuba, Japan at $\lambda = 1.2682\text{\AA}$. The structure was solved from Direct Methods and refinement using 1299 unique reflections with $I > 2\sigma(I)$ led to final values $R = 0.031$ and $R_w = 0.034$. The refined metal ordering is far from fully ordered and reminiscent of the A/B ordering characteristic of the pyrochlore structure type. The apparent structural flexibility may well manifest itself in interesting, technologically useful properties.

- [1] S. Schmid, C. Lobo, R. L. Withers and J. G. Thompson (1996), *Journal of Solid State Chemistry* 127, 82 - 86.

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When coordinated in an *exo*-bidentate fashion, the pyrazolate anion is able to bridge two metal centres to give complexes with metal-metal separations of a similar magnitude to those found in bimetallic biosites.¹ As a result, the coordination chemistry of this moiety, and of ligands into which it is incorporated, has received much attention.² Given the interest in both acyclic and macrocyclic Schiff base ligands and their complexes, it is perhaps surprising that few examples of these which incorporate the pyrazolate anion are known. The preparation, in four steps from 3,5-dimethyl-1*H*-pyrazole, of 3,5-dicarbaldehyde-1*H*-pyrazole (**1**)³ provides a convenient precursor to such systems. The preparation, characterisation and properties of selected examples are presented.



References

- [1] M. Itoh, K. Motoda, K. Shindo, T. Kamiyuki, H. Sakiyama, N. Matsumoto, H. Okawa, *J. Chem. Soc., Dalton Trans.*, **1989**, 3635 and references therein.
- [2] G. La Monica, G. A. Ardizzoia, *Prog. Inorg. Chem.*, **1997**, *46*, 151.
- [3] T.G. Schenk, J.M. Downes, C.R.C. Milne, P.B. MacKenzie, H. Boucher, J. Whelan, B. Bosnich, *Inorg. Chem.* **1985**, *24*, 1079; M. Kumar, V.J. Aran, P. Navarro, *Tetrahedron Lett.*, **1993**, *34*, 3159.

M45

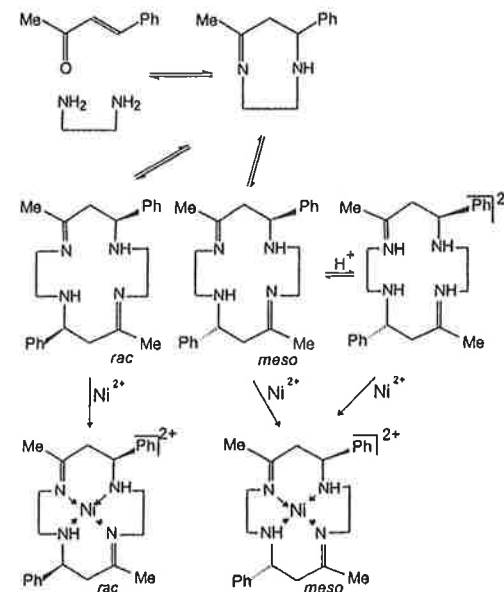
POSTERS

COMPOUNDS OF NICKEL(II) WITH *RAC*- AND *MESO*-5,12-DIMETHYL-7,14-DIPHENYL-1,4,8,11-TETRAAZA-CYCLOTETRADECA-4,11-DIENE

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The macrocycle 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-diene, formed by reaction of ethane-1,2-diamine with benzylidene acetone, reacts with nickel(II) to form a mixture of the *meso*- and the previously unreported *rac*-isomers of the complex nickel(II) cation. The yields and ratio of isomers depend upon reaction conditions, and are explicable if there is an equilibrium in solution of the seven-membered cyclic imine, 5-methyl-7-phenyl-2,3,6,7-tetrahydro-1*H*-1,4-diazapine and its *meso* and *rac* dimers. Methods of separation of the isomeric perchlorate salts and preparations of a selection of nickel(II) compounds of the *rac*-isomer are described. A molecular modelling analysis of the relative strain energies of the possible isomeric nickel(II) cations is presented.



M46

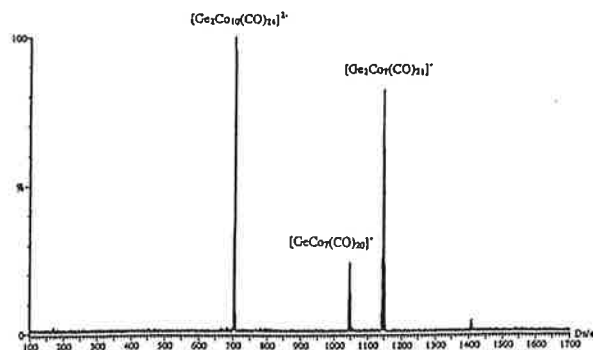
ANALYSIS OF HIGH-NUCLEARITY AIR-SENSITIVE METAL CARBONYL CLUSTERS BY ELECTROSPRAY MASS SPECTROMETRY.

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Handling methods are being developed to allow Electrospray Mass Spectrometry (ESMS) to be used for the characterisation of air-sensitive transition metal carbonyl clusters. Initial research involves the re-investigation of a series of partially characterised cluster reactions in order to identify a greater variety of reaction products.

The reaction of $\text{GeCo}_4(\text{CO})_{14}$ with $[\text{Co}(\text{CO})_4]^+$ has previously been reported¹. Re-investigation of this reaction using ESMS identified the previously characterised ions $[\text{GeCo}_7(\text{CO})_{20}]^+$ and $[\text{Ge}_2\text{Co}_7(\text{CO})_{21}]^+$, together with a third, previously unreported cluster, $[\text{Ge}_2\text{Co}_{10}(\text{CO})_{24}]^+$ ². The anion $[\text{GeCo}_5(\text{CO})_{16}]^-$, previously assumed to be the major product, has yet to be detected by ESMS. This presentation will describe the results of a series of germanium and silicon cluster anion reactions.



ESMS spectrum of the reaction of $\text{GeCo}_4(\text{CO})_{14}$ with $\text{PPN}[\text{Co}(\text{CO})_4]$ in CH_2Cl_2 . Mobile phase = 1,2-dichloroethane, Applied cone voltage = 5 V.

¹ - D. N. Duffy, K. M. Mackay, B. K. Nicholson and W. T. Robinson, *J. Chem. Soc., Dalton Trans.*, 1981, 381; R. A. Croft, D. N. Duffy and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1982, 1023; D. N. Duffy, K. M. Mackay, B. K. Nicholson and R. A. Thomson, *J. Chem. Soc., Dalton Trans.*, 1982, 1029.

ISOMERIC STUDIES OF Ti(IV) AND Zr(IV) COMPLEXES OF SOME N_2O_2 -DONOR IMINE-ETHER MACROCYCLES.

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This project has focussed on mixed donor tetradentate macrocycles that have potential as good metal complexing ligands. We report here developments of our previously presented work on titanium(IV) macrocyclic complexes and studies on some isomers of these complexes.

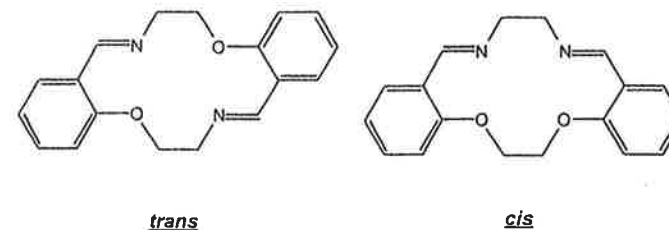


Figure 1: Isomers of "O-en-N-en"

The cis and trans isomers of (O-en-N-en), as shown in Figure 1, have been prepared and isolated as free-macrocycles. In addition, NMR results indicate that in solution and at various temperatures the cis isomer exists in two discrete conformations.

Geometrical isomers of nickel(II) complexes of trans (O-en-N-en) also exist. Kluiber and Sasso have reported a trans Ni(II) complex while a cis variation has been reported by Lalancette and coworkers. Evidence from these papers suggests that subtle changes in the ligand's design can dramatically influence the coordination geometry of the resultant metal complex.

The capability of macrocycles (such as O-en-N-en) to coordinate metals in various ways has provided the impetus to conduct further studies involving titanium(IV) and zirconium(IV).

Refs:

- R.W. Kluiber and G. Sasso, *Inorg Chim Acta*, 4, 226, (1970)
R.A. Lalancette, D.J. Macchia and W.F. Furey, *Inorg Chem*, 15, 548, (1976)

PHOSPHINE-FUNCTIONALISED INDENYL LIGAND SYSTEMS

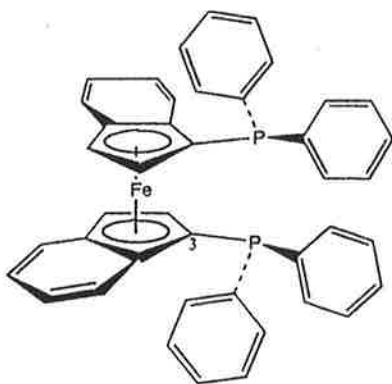
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Functionalised aromatic ligands have played an extensive role in the development of organometallic chemistry. Phosphines are one of the most utilised functional groups and cyclopentadienyl is the most common aromatic ligand. Although phosphine-cyclopentadienyl systems are well studied, their indenyl analogues are almost unknown.

Indenyl-diphenylphosphine can coordinate to form chiral complexes and bis-(indenylphosphine) systems are able to form C_2 -symmetric systems such as the one shown below. We will present details on this and related complexes as well as investigations into its coordination chemistry.



M49

POSTERS

MODIFIED CYCLOPENTADIENYL LIGANDS FOR

EARLY TRANSITION METAL CATALYSIS

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Modification of cyclopentadienyl ligands allows the adjustment of metal complex properties essential for homogeneous catalysis. For example, asymmetry can be introduced using chiral building blocks, solubility properties for e.g. super-critical CO₂ applications can be enhanced using properly modified ligand structures. During recent years we have developed in our laboratory a number of novel cyclopentadienyl ligands and novel transition metal complexes.¹ This paper will report on recent developments and results of our work.

¹ see for example:

N-2-(1-indenyl)ethyl-*p*-toluenesulfonamide.

Gainsford, J.G.; Lensink, C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **1996**, *52*, 2.

Synthesis of chiral N-alkyl-cyclopentadienyl sulfonamides.

Lensink, C. *Tetrahedron: Asymmetry*, **1995**, *6*, 2033.

Synthesis and Structure of sulfonamido cyclopentadiene titanium complexes: X-ray Ti(η^5 - $C_5H_4CH_2CH_2NSO_2C_6H_4CH_3$)Cl₂.

Lensink, C. *J. Organomet. Chem.*, **1998**, *553*, 387-392

Organometallic Molecular Catalysts, Small Molecule Machines.

Lensink, C. *Chemistry in New Zealand*, **1997**, *61*, 20-25.

Synthesis and structure of two isomers of di(indenyl)phenylphosphine sulfide.

Lensink, C.; Gainsford, G.J. *Aust. J. Chem.*, **1998**, *51*, 667-672.

M50

ANTIPROLIFERATIVE PROPERTIES OF GOLD(I), SILVER(I) AND COPPER(I) COMPLEXES CONTAINING CHIRAL TERTIARY PHOSPHINES

Mark J. McKeage,^a Peter Papathanasiou,^b Geoff Salem,^b Alan Sjaarda,^c G. F. Swiegers,^d Paul Waring^c and Bruce Wild^d

^a Department of Pharmacology and Clinical Pharmacology, Faculty of Medicine and Health Services, The University of Auckland, Private Bag 92019, Auckland, New Zealand

^b Chemistry Department, The Faculties, Australian National University, Canberra, A. C. T. 0200, Australia.

^c John Curtin School of Medical Research, Australian National University, Canberra, A. C. T. 0200, Australia.

^d Research School of Chemistry, Australian National University, Canberra, A. C. T. 0200, Australia.

The *in vitro* cytotoxicities of a number of gold(I), silver(I) and copper(I) complexes containing chiral tertiary phosphine ligands have been examined against the mouse tumour cell lines P815 mastocytoma, B16 melanoma and P388 leukaemia with many of the complexes having IC₅₀ values comparable to that of the reference compounds *cis*-diamminedichloroplatinum(II), cisplatin, and bis[1,2-bis(diphenylphosphino)ethane]-gold(I) iodide.^{1,2} The ligands used in the study include (R)- and (±)-(2-aminophenyl)-methylphenylphosphine; (R,R)-, (S,S)- and (R*,R*)-1,2-phenylenebis(methylphenylphosphine) [and their arsenic analogues]; (R,R)-, (S,S)- and (R*,R*)-bis((2-diphenylphosphinoethyl)phenylphosphino)ethane; (R*,R*)-1,3-bis((2-aminophenyl)-methylphosphino)propane and the achiral tertiary phosphine (2-aminophenyl)diphenylphosphine. The *in vitro* cytotoxicities of gold(I) and silver(I) complexes containing the optically active forms of the tetra(tertiary phosphine) have also been examined against the human ovarian carcinoma cell lines 41M and CH1, and the cisplatin resistant 41McisR, CH1cisR and SKOV-3 tumour models. IC₅₀ values in the range 0.01 - 0.04 μM were determined for the most active compounds. All of the gold(I) complexes have been shown to rapidly accumulate in mitochondria by virtue of their lipophilic, cationic nature and in most cases to inhibit the activity of ATP synthase leading to rapid cell death. Importantly, the gold(I) complexes of the tetra(tertiary phosphine) appear to selectively target mitochondria with relatively high membrane potentials, a key consideration in the development of an antimitochondrial antitumour agent.

¹ P. Papathanasiou, G. Salem, P. Waring and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1997, 3435. ² M. J. McKeage, P. Papathanasiou, G. Salem, A. Sjaarda, G. F. Swiegers, P. Waring and S. Bruce Wild, *Metal-Based Drugs*, 1998, 5, 217.

M51

POSTERS

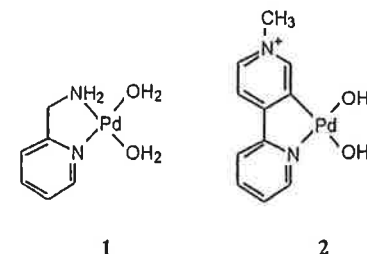
ACIDITY AND DIMERISATION CONSTANTS OF SOME PALLADIUM(II) *cis*-DIAQUA COMPLEXES

Franz L. Wimmer^a, Smita Wimmer^a, Paule Castan^b and Paul L. Fabre^b

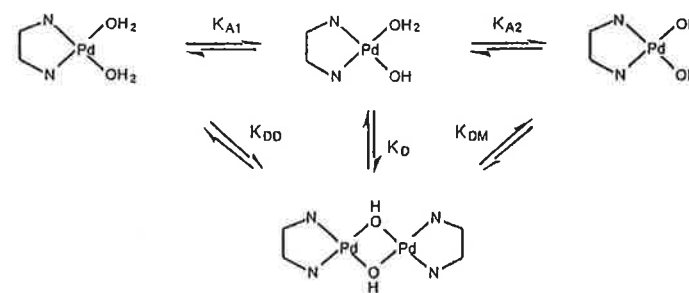
a. Department of Chemistry, Universiti Brunei Darussalam, Bandar Seri Begawan BE1411, Brunei.

b. Laboratoire de Chimie Inorganique, Université Paul Sabatier, 180 route de Narbonne, 31062 Toulouse Cedex, France.

The acidity and dimerisation constants were determined for [Pd(L)(H₂O)₂]²⁺ (L = 2-(amino-methyl)pyridine (AMP) (1) and N'-methyl-2,4'-bipyridin-3-ylum (2,4'-bpyMe-H) (2)) by pH and spectrophotometric titration.



These complexes react with NaOH according to the scheme:



For L = AMP, pK_{A1} = 6.8; pK_{A2} = 7.6; K_D of [Pd(AMP)(H₂O)(OH)]⁺ is 10^{7.0}, while K_{DD} for [Pd(AMP)(H₂O)₂]²⁺ is 10^{-6.6}.

For L = (2,4'-bpyMe-H) only one endpoint is observed; pK_A = 7.1, K_D = 10^{13.9} and K_{DD} = 10^{-8.7}. The dimer does not react with hydroxide. This is interpreted as a kinetic phenomenon.

M52

THE FORMATION OF NOVEL RARE EARTH ASSEMBLIES USING CALIXARENE AND CROWN ETHER BUILDING BLOCKS

A.Drljaca, M.J.Hardie, J.Johnson*, C.L.Raston, H.R.Webb

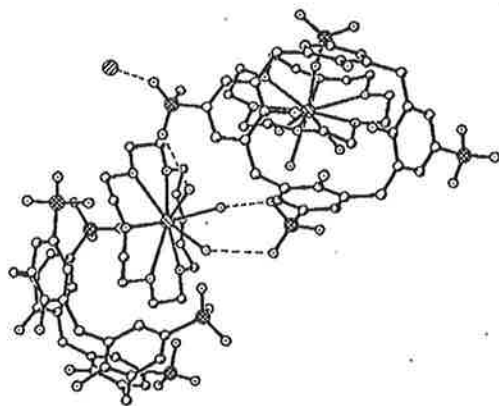
Department of Chemistry, Monash University, Clayton, Melbourne, Victoria, 3168, Australia

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email: c.raston@sci.monash.edu.au

The interactions between rare earth metals and a variety of macrocyclic molecules, particularly crown ethers and novel calixarenes, are currently being explored. Such components serve as ideal building blocks to engineer frameworks of seemingly limitless variety. For instance, not only can each component be modified to achieve the desired functionality or conformation, but the combination of components may be varied.

Whilst a variety of rare earth: calixarene and rare earth: crown ether complexes have been reported, the association which occurs from the combination of these components remains an unexplored area. The x-ray crystal structure of an assembly consisting of a chloride-bridged series of lanthanum trications, each enclosed by a crown ether which is in turn cupped by a sulphonated calixarene, has been obtained under mild conditions.



M53

POSTERS

DIAMMINEPLATINUM(II) METABOLITES STUDIED USING HPLC COUPLED WITH NMR

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^a Chemistry Department, ^b School of Pharmacy, The University of Queensland, Brisbane, Qld. 4072

Cisplatin, which is the most used chemotherapeutic anticancer drug¹, has been the subject of many chemical and pharmaceutical studies. There are effective procedures available for the monitoring of cisplatin itself *in vitro* and *in vivo*, but reliable studies of the pharmacokinetics of cisplatin metabolites are rare. Among the reasons for this are:

- (i) Authors have not always appreciated the high reactivity of diammine(aqua)platinum(II) species (*e.g.*, $cis-[Pt(NH_3)_2Cl(H_2O)]^+$) toward nucleophiles, including some that have been used as mobile phases used in their HPLC studies.²
- (ii) There have been few attempts to identify and monitor the more complex complexes formed, including those with sulfur-donor amino acids (*e.g.*, cysteine, methionine), including the possibility of further chemical transformations in the bloodstream.
- (iii) For results to be biologically relevant, the concentration of the platinum species needs to be comparable to that *in vivo* when cisplatin is used therapeutically.

In this work, we prepare and characterise compounds anticipated as possible metabolites, using ¹⁵N NMR techniques, and determination of HPLC retention times with a variety of mobile phases. ICP-MS is used to indicate HPLC peaks corresponding to platinum-containing species, and the information gained from the study of known compounds used to identify them where possible. Sensitive NMR techniques may also be used to assist in the identification of species that have not been previously prepared.

Our recent results show that cysteine reacts rapidly with $cis-[Pt(NH_3)_2Cl(H_2O)]^+$ when it is added in low concentrations to ultrafiltered plasma.

- 1) T. W. Hambley, *Coord. Chem. Rev.* 166 (1997) 181.
- 2) M. A. El-Khateeb, T. G. Appleton, B. G. Charles, and L. R. Gahan, *J. Pharm. Sci.*, in press

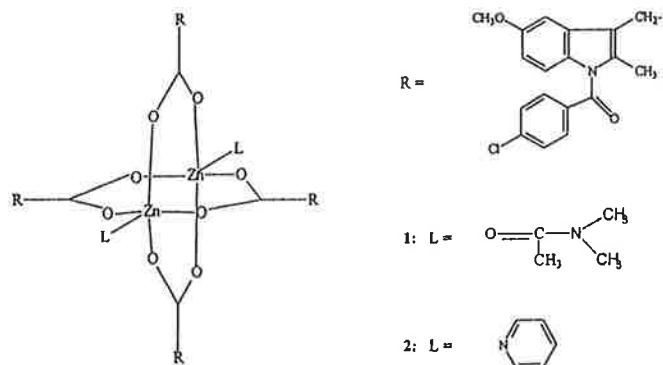
M54

SYNTHESES, SPECTRAL AND STRUCTURAL CHARACTERISATION OF TWO NEW
DINUCLEATING ZINC COMPLEXES $[\text{Zn}_2(\text{INDOMETHACIN})_4(N,N\text{-}$
DIMETHYLACETAMIDE) $]\text{2}$ AND $[\text{Zn}_2(\text{INDOMETHACIN})_4(\text{PYRIDINE})\text{2}]$

Qingdi Zhou, Brendan J. Kennedy, Peter A. Lay, Trevor W. Hambley and Peter Turner

School of Chemistry, the University of Sydney, NSW 2006, Australia

The syntheses, spectral and structural characterization of the two new dinucleating zinc-indomethacin $\{[1-(4\text{-chlorobenzoyl})-5\text{-methoxy-2-methindol-3-yl}] \text{ acetic acid}\}$ complexes with *N,N*-dimethylacetamide (DMA) or pyridine (Py) as solvent ligands, $[\text{Zn}_2(\text{indomethacin})_4(N,N\text{-dimethylacetamide})\text{2}]$ (1) and $[\text{Zn}_2(\text{indomethacin})_4(\text{pyridine})\text{2}]$ (2), respectively, are presented.



Both complexes crystallise in the triclinic space group $P\bar{1}$ (#2), $a = 13.628(2)$, $b = 17.462(2)$, $c = 11.078(1)$ Å, $\alpha = 99.49(1)$, $\beta = 108.13(1)$, $\gamma = 110.10(1)^\circ$, $V = 2241.0(7)$ Å³, $Z = 1$ for complex 1 and $a = 13.347(3)$, $b = 16.499(5)$, $c = 10.857(1)$ Å, $\alpha = 99.48(2)$, $\beta = 108.25(2)$, $\gamma = 106.24(2)^\circ$, $V = 2094(1)$ Å³, $Z = 1$ for complex 2. Both complexes exhibited the typical dinuclear paddle-wheel cage structures, with bond lengths of Zn-Zn 2.9686(6), Zn-ORCOO 2.035(2) to 2.060(2) and Zn-ODMA 1.989(2) Å in 1, and Zn-Zn 2.969(1), Zn-ORCOO 2.020(3) to 2.049(3) and Zn-N_{Py} 2.036(3) Å in 2. The zinc ions are in a square-pyramidal geometry bridged by four carboxylate anions in the xy plane, with the solvent ligands containing either a O or N-donor atom at the apex.

ACYCLIC N_xS_2 THIOETHER PYRIDINE LIGANDS WITH Ag^+ and Cu^+

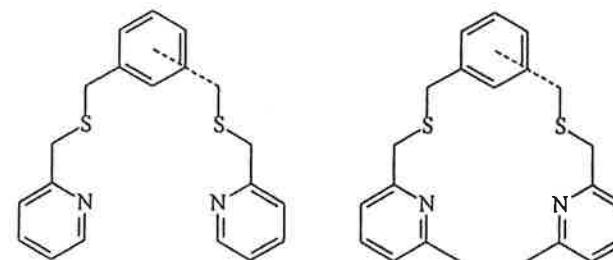
Lyall Hanton and Kitty Lee

Chemistry Department, University of Otago, PO Box 56, Dunedin, New Zealand.

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The design of ligands incorporating both sulfur and nitrogen donors is of considerable interest in coordination synthesis. A series of acyclic N_xS_2 ligands will be presented. These are based on an arene spacer from which two thioether pyridine arms hang. The spacer is used to vary the angle between the two arms (ortho, meta and para positions) and to provide additional nitrogen donors. The chemistry of these ligands with d^{10} transition metals (Ag^+ and Cu^+) will be presented.

These ligands have a high affinity for Ag^+ . Electro-Spray Mass Spectrometry and aqueous extraction studies show that Ag^+ affinity varies depending on the spacer group involved. Cu^+ complexes have been characterized by ¹H NMR spectroscopy. The solution chemistry of these complexes exhibit interesting processes varying with which spacer is used. Steric bulk may be introduced on the ligand arms affecting their coordination properties with Ag^+ and Cu^+

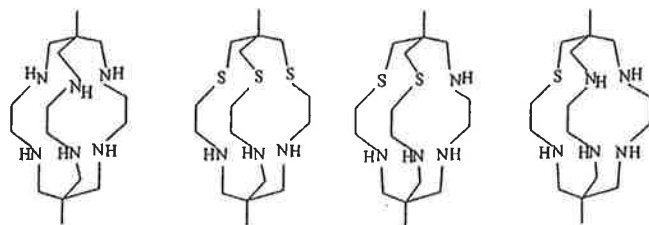


Spacer Group:
Ortho, meta, para, pyridine

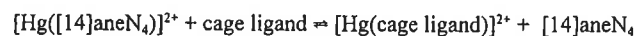
Clint A Sharrad,* Lisbeth Grøndahl and Lawrence R Gahan

The Chemistry Department, The University of Queensland, Brisbane, QLD, Australia 4072.

The cage ligands, first described in 1977, represent a group of macrobicyclic ligands which has been studied extensively.¹ The cages have a fully saturated organic framework typified by the ligand 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (sar). The free ligands, and metal complexes, have been prepared with various mixed donor sets (sarN_{6-x}S_x; x = 0, 1, 2, 3).² The properties of the cage complexes which have attracted much attention include their unusually rapid outer-sphere electron transfer reactions and their high kinetic and thermodynamic stability.



We have commenced a study aimed at the determination of the stability constants of ligands with the mixed nitrogen-thioether donor set (sarN_{6-x}S_x; x = 3) with mercury(II). We have employed potentiometric methods utilizing competition titration techniques with the macrocyclic ligand [14]aneN₄, the reaction described by the equilibrium



The stability constants for [Hg(sar)]²⁺ (log₁₀K = 28.1 ± 0.1) and [Hg(diAMsar)]²⁺ (log₁₀K = 26.4 ± 0.5) have been reported previously.³

1. Creaser, I. I., Harrowfield, J. MacB., Herlt, A. J., Sargeson, A. M., Springborg, J., Geue, R. J., Snow, M. R., *J. Am. Chem. Soc.*, 1977, 99, 3181.
2. (a) Donlevy, T. M., Gahan, L. R., Hambley, T. W. *Inorg. Chem.*, 33, 2668, 1994. (b) Bruce, J. I., Gahan, L. R., Hambley, T. W., Stranger, R. *Inorg. Chem.*, 32, 5997, 1993.
3. Grøndahl, L., PhD Thesis, University of Copenhagen, 1994.

Eric W. Ainscough, Andrew M. Brodie, Anthony K. Burrell and Craig V. Depree

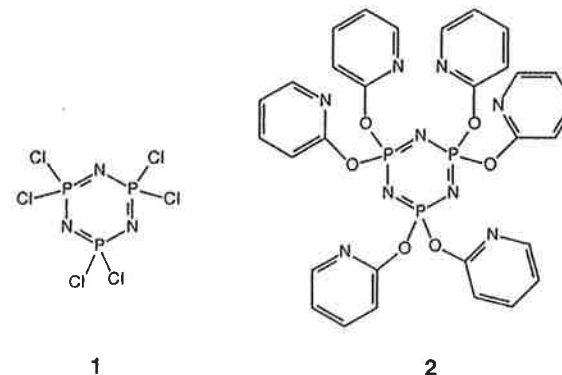
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The nucleophilic substitution chemistry of cyclophosphazenes (e.g. hexachlorotricyclophosphazene, 1) has been extensively studied, although a number of researchers are now focussing their attention towards the use of cyclophosphazenes as transition-metal ligands. The large range of nucleophilic substitution reactions of 1 make cyclophosphazenes, potentially, very versatile ligands.

Much of the attention to date has focussed on tricyclopophosphazenes containing dimethylpyrazole groups, and these have displayed a variety of coordinating modes.^{1,2}

We have prepared hexakis(2-hydroxypyridine)tricyclopophosphazene (2), and investigated the coordination properties with a number of transition-metal halides. The reaction of 2 with CoX₂ (X = Cl, Br), forms novel zwitterion binuclear-phosphazene complexes containing octahedral κ⁵N CoX, and tetrahedral κ¹N CoX₃ coordinated moieties. These structures, as well as those with other N-donor containing phosphazene ligands, will be discussed in detail.

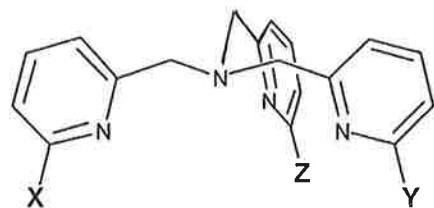
1 Byun, Y.; Min, D.; Do, J.; Yun, H. and Do, Y. *Inorg. Chem.* 1996, 35, 3981.2 Koo, B. H.; Byun, Y.; Hong, E.; Kim, Y. and Do, Y. *J. Chem. Soc.; Chem. Commun.*, 1998, 1227.

Synthesis and Copper(II) Coordination Chemistry of Novel Derivatives of Tris(2-pyridylmethyl)amine

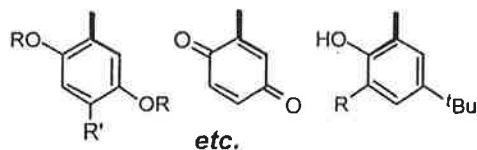
Zhicong He, D. Lonnon and Stephen B. Colbran

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Coordination complexes of the tetradentate, tripodal ligand tris(2-pyridylmethyl)amine (tmpa) and its simple ring-alkylated derivatives have recently played an important and prominent role as models for metalloenzyme active sites.^{1,2} The general focus of the research to be reported in this poster is on modification of tmpa to give new ligands with redox active substituents or to afford multinucleating ligands for construction of metallo-oligomers. The poster will describe our most recent progress.



X, Y, Z = H, CH₂OH, CHO, CH₂NHBU^t

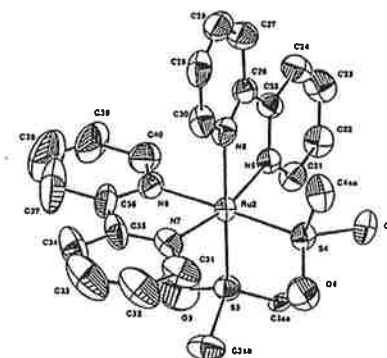


PHOTOINDUCED LINKAGE-ISOMERISM IN RUTHENIUM COMPLEXES

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School of Biomedical and Molecular Sciences,
James Cook University, Townsville, Qld. 4811, Australia

Photo-promoted structural changes in molecular assemblies have attracted significant recent research interest. These studies include linkage isomerism induced by the absorption of light. The current study investigates a reversible photo-induced reaction of the species [Ru(bpy)₂(DMSO)₂]²⁺, (bpy = 2,2'-bipyridine; DMSO = dimethylsulfoxide) which in the solid state contains S-bound DMSO ligands.¹



Upon exposure to sunlight a DMSO solution of this species turns rapidly from yellow to red, which subsequently reverts back to yellow in the dark. A proposed mechanism is that in the excited state formed on light absorption, linkage isomerism occurs and the S-bound DMSO ligands (yellow complex) switch to become O-bound (red). Relaxation back to the thermodynamically stable yellow form occurs in the dark. The process has been studied by UV/VIS spectrophotometry, NMR and IR spectroscopy, which indicate the reaction occurs via a dissociative mechanism, involving ligand exchange with solvent DMSO molecules.

1. C.G. Young, J.A. Gibson and J.A. Broomhead, unpublished work.

¹ L. Que, Jr. and Y. Dong, *Acc. Chem. Res.* 1996, 29, 190.

² K. Karlin *et al.* *Acc. Chem. Res.* 1997, 30, 139

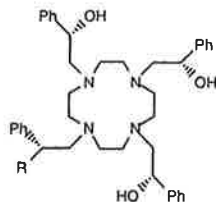
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[†]Department of Chemistry, The Flinders University of South Australia, GPO Box 2100.

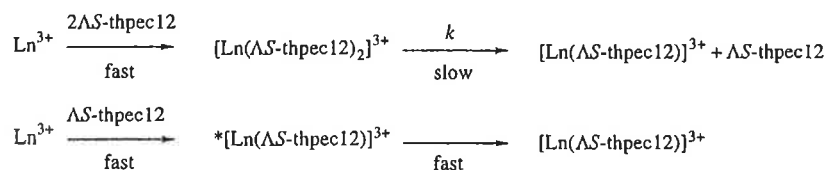
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The use of gadolinium(III) magnetic resonance imaging reagents in nuclear medicine and the luminescent europium(III) and terbium(III) complexes used as biochemical probes have resulted in considerable attention on the coordination chemistry of lanthanide(III) macrocyclic complexes.¹ Nevertheless, the mechanism by which the lanthanide ion becomes complexed by the macrocyclic ligand is poorly understood. As a consequence, we have extended our studies² of pendant arm macrocyclic ligand complexation to include the lanthanide(III) ions (Ln³⁺). We have demonstrated that the ligand Λ -1,4,7,10-tetrakis((S)-2-hydroxy-2-phenylethyl)-1,4,7,10-tetraazacyclododecane, Λ S-thpec12 (Figure 1) forms a stable intermediate complex, in which Ln³⁺ is trapped by the pendant arms, prior to being fully encapsulated by the ligand.

Fig. 1. Λ S-thpec12 assumes a single diastomeric conformation in solution, which it retains in its complex ions.



Our ¹H and ¹³C nmr studies show that Λ S-thpec12 complexes Ln³⁺ by two major pathways:



In $[\text{Ln}(\Lambda\text{S-thpec12})_2]^{3+}$, Ln³⁺ is thought to be bound by the four hydroxy groups of each Λ S-thpec12 ligand and in $[\text{Ln}(\Lambda\text{S-thpec12})]^{3+}$, Ln³⁺ is bound by all eight ligand donor atoms. In $*[\text{Ln}(\Lambda\text{S-thpec12})]^{3+}$, the major interaction is thought to be between Ln³⁺ and the tetraaza ring, such that the final encapsulation of Ln³⁺ occurs much more readily than from $[\text{Ln}(\Lambda\text{S-thpec12})_2]^{3+}$. The second pathway is important only for the lighter lanthanides and *k* decreases in the sequence: La³⁺ > Ce³⁺ > Pr³⁺ > Nd³⁺ > Sm³⁺ > Eu³⁺ > Tb³⁺ > Lu³⁺.

1. Parker, D.; Williams, J. A. *J. Chem. Soc., Dalton Trans.* **1996**, 3613 and references therein.
2. Dhillon, R. S.; Madbak, S. E.; Ciccone, F. G.; Buntine, M. A.; Lincoln, S. F.; Wainwright, K. P. *J. Am. Chem. Soc.* **1997**, 119, 6126.

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POSTERS

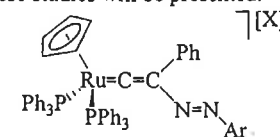
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There has been considerable interest recently in the nonlinear optical (NLO) merit of organometallic complexes.¹ The two most intensively investigated systems have been ferrocenyl derivatives and alkynylmetal complexes. These materials are comparatively environmentally robust and have significant molecular optical nonlinearities. It has been suggested that, to maximize the NLO responses, it is desirable to couple the ligated metal to the organic π -system via a M-C multiple bond linkage. Our attention has therefore turned to vinylidene complexes. Some time ago we reported the bulk susceptibilities of a range of systematically-varied aryldiazovinylenes complexes,² a structural study of one example confirming the presence of an M=C interaction. These are amongst the most stable of vinylidene complexes, having survived seven years under ambient conditions. We have now investigated the molecular NLO merit of these complexes; the results of these studies will be presented.



Ar = Ph, C₆H₃(NO₂)_{2-3,5}, C₆H₄NO₂-4, C₆H₄OMe-2, C₆H₄OMe-4
X = Br, I, Cl, CH₃C₆H₄SO₃-4, NO₃.

1. (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.*, **1998**, 42, 291.
(b) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.*, **1998**, 43, 349.
2. I.R. Whittall, M.P. Cifuentes, M.J. Costigan, M.G. Humphrey, S.C. Goh, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, **1994**, 471, 193.

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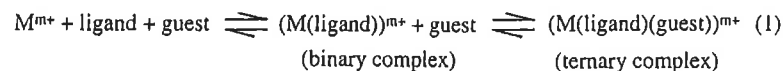
PENDANT ARM MACROCYCLIC LIGANDS AS METAL ION ACTIVATED RECEPTORS

Stephen F. Lincoln^a, Kevin P. Wainwright^b and Oska Wyness^a

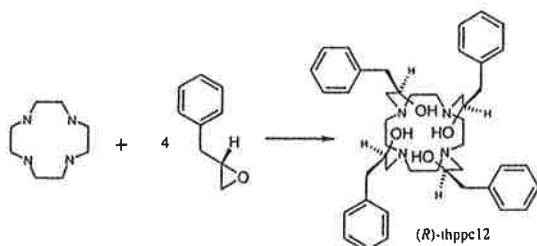
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A metal ion activated molecular receptor is based on the principle of metal ion complexation by an appropriate ligand (the receptor) with this binary complex assuming a conformation suitable for the selective complexation of a guest molecule forming a ternary complex as described by Equation 1.



The choice of pendant arm modified macrocyclic ligands as potential receptors stems from extensive synthetic, structural and mechanistic studies of hydroxyalkylated macrocycles.^{1,2} One such macrocycle is 1,4,7,10-tetraazacyclododecane also known as cyclen. Pendant arm modification is achieved by the reaction of an enantiomerically pure terminal epoxide with cyclen as exemplified below.



The use of an enantiomerically pure epoxide avoids the formation of more than one diastereomer. Studies of these systems show that all four pendant arms occupy the same side of the tetraaza plane adopting a square anti-prismatic geometry. Solution ¹³C nmr studies of (R)-thppc12 show one set of arm signals indicating all four arms are in equivalent environments. The (R)-thppc12 ligand and its alkali metal complex ion undergo a double inversion at the nitrogen centre that results in the arms oscillating between equivalent positions either side of the tetraaza plane. In assessing the suitability of (R)-thppc12 as a receptor the rate of oscillation has been studied from ¹³C nmr data. Stability constants for some alkali metals are also reported.

1. Lincoln, S.F., *Coordination Chem. Rev.*, 1997, 166, 255-289

2. Wainwright, K.P., *Coordination Chem. Rev.*, 1997, 166, 35-90

Deactivation of Coordinated Chlorosulfonate Ion

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Characterised salts of ClSO₃⁻ are unknown. The species is unstable, spontaneously hydrolysing on the millisecond time scale ($k = 270 \text{ s}^{-1}$, 25°C) following its very rapid generation ($k = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, 25°C) from HOCl and SO₃²⁻.¹ We have synthesised the complex [Co(NH₃)₅O₃SCI](ClO₄)₂ which, remarkably, survives rapid recrystallisation from water. It has been completely characterised by microanalysis, though Cl⁻, HSO₄⁻ and H⁺ release on hydrolysis, and the co-formation of [(NH₃)₅CoCl]²⁺, [(NH₃)₅CoOSO₃]⁺ and [(NH₃)₅Co(sol)]³⁺ in a variety of solvents. The co-formation of [(NH₃)₅CoO₃S¹⁷O]⁺, [(NH₃)₅Co¹⁷OH₂]³⁺ and SO₃¹⁷O²⁻ on reaction in H₂¹⁷O has been demonstrated using ¹⁷O NMR spectroscopy. It behaves as a typically reactive 2+ cation [(NH₃)₅CoX]²⁺ in aqueous acid ($t_{1/2}$ ca 10 s, 25°C) and base (10% N₃⁻ competition; 1 M NaN₃). Reasons for the deactivation (ca 10³-fold) towards S-Cl cleavage on coordination to Co(III) are discussed, and comparisons are drawn with the analogous FSO₃⁻ system.²

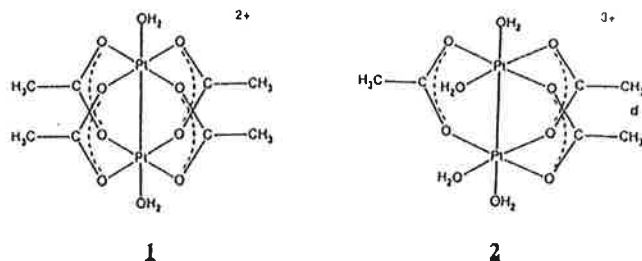
¹ B.S. Yiin and D.W. Margerum, *Inorg. Chem.*, 1988, 27, 1670-2.

² W.G. Jackson and C.M. Begbie, *Inorg. Chem.*, 1981, 20, 1654-9.

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The quadruply bridged dinuclear Pt(III) acetate, $[\text{Pt}(\mu - \text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]\text{X}_2$ ($\text{X} = \text{ClO}_4^-$, NO_3^- , CF_3SO_3^-) **1** was recently synthesized and characterized by Appleton and his co-workers¹. Unlike the other reported "lantern shaped" Pt(III) dinuclear complexes with sulfate² or phosphate³ bridges, in aqueous media, one of the acetate bridging ligands from **1** was dissociated⁴ to form $[\text{Pt}(\mu - \text{O}_2\text{CCH}_3)_3(\text{H}_2\text{O})_4]^{3+}$ **2**.



This tetra aqua dinuclear Pt(III) complex with three bridging acetate ligands is stable in solution for about 140-150 minutes. We report the reactivity of **2** with different anionic ligands in aqueous media. Multinuclear NMR is used to monitor the reactions and characterize the products formed in solution.

References

1. Appleton T.G., Byriel K.A., Hall J.R., Kennard C.H.L., Mathieson M.T., *J. Am. Chem. Soc.*, **114**, 7305, 1992; Appleton T.G., Barnham K.J., Byriel K.A., Hall J.R., Kennard C.H.L., Mathieson M.T., Pennam K.G., *Inorg. Chem.*, **43**, 6040, 1995.
2. Muraveiskaya G.S., Kukina G.A., Orlava V.S., Poraikoshits M.A., *Dokl. Akad. SSSR.*, **226**, 596, 1976; Bancroft D.P., Cotton F.A., Falvello L. R., *Inorg. Chim. Acta.*, **87**, 147, 1984.
3. Muraveiskaya G.S., Abashkin V.E., Evstaf'eva N., Goloneva I.F., Shcelokov R.N., *Koord. Khim.*, **6**, 463, 1980; Cotton F.A., Falvello L.R., *Inorg. Chem.*, **21**, 1709, 1982.
4. Appleton T.G., Byriel K.A., Garrett J.M., Hall J.R., Kennard C.H.L., Mathieson M.T., *Inorg. Chem.*, **34**, 5646, 1995.

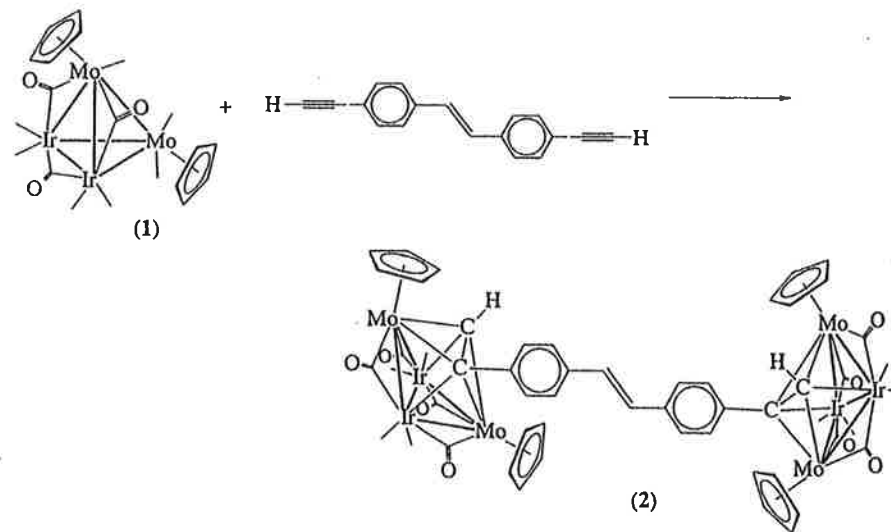
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The tetrahedral heterometallic cluster $\text{Cp}_2\text{Mo}_2\text{Ir}_2(\text{CO})_{10}$ (**1**) undergoes addition of one equivalent of an alkyne under mild conditions¹. The $\mu_4-\eta^2$ -bridged alkyne adduct, possessing a butterfly metal core geometry, results from insertion of the alkyne into the Mo-Mo bond. Reacting **1** with di- and tri-ynes provides a method for linking together clusters in a systematic fashion. In particular, where the alkyne groups are linked through a conjugated bridge (e.g. **2**), electronic communication between clusters may be possible giving rise to some interesting properties (optical limiting is one such property for which the potential of clusters has already been demonstrated²). An alternate strategy to prepare conjugated linked clusters is to C-C couple two fragments, following coordination of appropriately functionalized alkynes to cluster **1**. Both approaches have been assayed; the results from these investigations will be reported.



1. N.T. Lucas, M.G. Humphrey, P.C. Healy and M.L. Williams, *J. Organomet. Chem.*, 1997, **545-546**, 519.
2. R. Dagani, *Chem. Eng. News*, January 1, 1996, 24.

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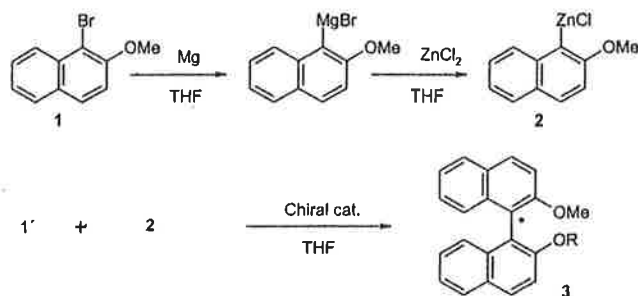
NOVEL APPROACH TO THE SYNTHESIS OF BINAP ANALOGS.

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Wellington, New Zealand (e-mail <oleg.zubkov@vuw.ac.nz>)

BINAP and analogs of it are very important among chiral diphosphine ligands. They demonstrate excellent yields and enantiomeric excesses in a variety of organic reactions. However, syntheses of BINAP ligands often involves expensive chiral complexes as precursors¹ or multistep chiral resolution by building molecular complexes with reagents such as “+” or “-” camphor sulphonic or dibenzoyltartaric acids². Alternatively BINAPs could be made by treatment of enantiomerically pure dihydroxy binaphthalene triflate with secondary phosphines in presence of a nickel/diphosphine catalyst³. 2,2'-Dihydroxy-binaphthalene, precursor for this reaction, is made from b-naphthol and copper salts in good yields, but the disadvantage is that a huge excess of chiral amphetamine is needed⁴.

1-Bromo-2-methoxynaphthalene (1) looks like a good candidate to overcome the above problems. Palladium catalysts are known to give good yields for variety of coupling reactions by using organozinc reagents. The attempt has been made to couple (1) with organozinc reagent (2) to in order to obtain the chiral product.



Palladium(0) chelated with BINAP was chosen as catalyst, and is usually prepared from Pd(dba)₂ and ligand *in situ* just prior to reaction. Organozinc complex (2) coupled with the modified bromide (1) under appropriate conditions affording an intermediate (3) with different protection groups, allowing the synthesis of heterodentate BINAP analogues.

¹ A. Miyashita, H. Takaya, T. Souchi, R. Noyori, *Tetrahedron*, 40, 1245 (1984)

² H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa, R. Noyori, *J. Org. Chem.*, 51, 629 (1986)

³ D. Cai, J. F. Payack, D. R. Bender, D. L. Hughes, T. R. Verhoeven, P. J. Reider, *J. Org. Chem.*, 59, 7180 (1994)

⁴ J. Brussee, J. L. G. Groenendijk, J. M. te Koppele, A. C. A. Jansen, *Tetrahedron*, 41, 3313 (1985)

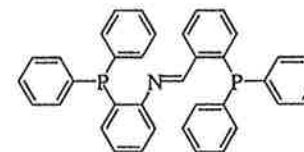
STRUCTURE AND REACTIVITY OF d⁸ METAL COMPLEXES CONTAINING THE MIXED DONOR MULTIDENTATE LIGAND PNCHP.

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Examples in coordination chemistry of bidentate mixed donor ligands containing a PN donor set are relatively few when compared to the chemistry of ligands with homologous donor sets such as P₂ and N₂. Rarer still is the coordination chemistry of tridentate P₂N systems such as demonstrated by our ligand PNCHP.

The synthesis and structure of the compounds M(PNCHP)X_n, where M is Pt²⁺, Pd²⁺ (n = 2) or Rh⁺ (n = 1) and X is Cl or BF₄, will be presented. Substitution of Cl with a series of pyridines and phosphanes, CO addition and oxidative addition reactions of the M(PNCHP)X_n compounds will also be discussed.



PNCHP

Synthesis, Characterisation and Magnetic Properties of Heteropolynuclear Complexes Formed by Encapsulation of Hexacyanometallates with Transition Metal Complexes

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One of the challenges in the field of molecular magnetism is to design polynuclear discrete entities with high spin ground states.^{1,2} Such materials allow the study of the transition from molecular to bulk-like magnetic behaviour by 'breaking-up' the infinite frameworks of bulk ferromagnets. One approach to the synthesis of such molecules currently being exploited in the group is focussed on the use of hexacyanometallates as templates for heteropolynuclear complexes. For example, we recently reported the encapsulation of hexacyanoferrate(II) by the Cu(II) complex of tris(2-pyridylmethyl)amine (tpa) to yield a heptanuclear complex, $[\text{Fe}(\text{CN})\text{Cu}(\text{tpa})_6][\text{ClO}_4]_6 \cdot 3\text{H}_2\text{O}$.³ Following on from this work, a series of heptanuclear and trinuclear complexes with respective general formula $[\{\text{LM}'\text{CN}\}_6\text{M}]^{n+}$ and $[\{\text{LM}'\}_2\text{M}(\text{CN})_6]^{n+}$ (where $\text{M} = \text{Cr}^{\text{III}}$, Fe^{II} or Fe^{III} and $\text{M}' = \text{Cu}^{\text{II}}$, Ni^{II} or Mn^{II}) have been isolated and characterised. An example is shown in the figure. An important recent development has been the assembly of a H-bonded complex with composition $[\{\text{Mn}(\text{dmptacn})\text{CN}\}_6\text{Cr}][\text{Cr}(\text{CN})_6][\text{ClO}_4]_6 \cdot 6\text{H}_2\text{O}$ which exhibits long range magnetic ordering at low temperature.

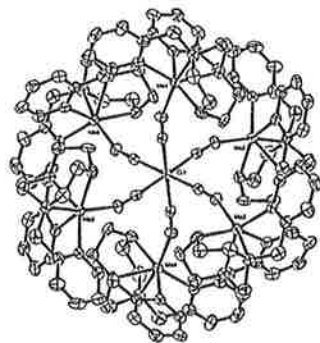


Figure. ORTEP diagram of the heptanuclear cation $[\{\text{Mn}(\text{dmptacn})\text{CN}\}_6\text{Cr}]^{9+}$

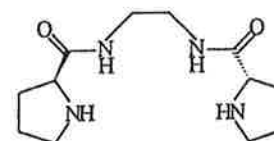
References

- 1) Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* 1991, 113, 5873.
- 2) Gatteschi, D.; Muller, A.; Peters, F.; Pope, M. *Chem. Rev.* 1998, 98, 239.
- 3) Parker, R. J.; Hockless, D. C. R.; Moubaraki, B.; Murray, K.; Spiccia, L. *Chem. Commun.* 1996, 2789.

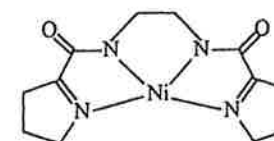
Colin L. Weeks, Peter Turner, Ronald R. Fenton, Peter A. Lay

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S,S -bprolenH₂



$[\text{Ni}^{\text{II}}(\text{bprolen}(-4\text{H}))]$

The amide group can coordinate to metal ions through either the nitrogen or the carbonyl oxygen atoms. The strongest metal-amide bonds are formed with the deprotonated nitrogen atoms. The weak acidity of the hydrogen on the amide nitrogen means that high pH or the chelate effect is normally necessary to achieve metal coordination in this fashion.¹

The compound S,S -bprolenH₂ has been reported as an intermediate in the synthesis of a tetraamine ligand,² but it was not purified or characterised. There are no reports of its use as a ligand. We have synthesised S,S -bprolenH₂ and characterised it by ¹H NMR spectroscopy. In the synthesis of the Ni(II) complex with S,S -bprolenH₂ the addition of sodium hydroxide resulted in an oxidative dehydrogenation reaction. The crystal structure of the complex showed that it was $[\text{Ni}^{\text{II}}(\text{bprolen}(-4\text{H}))]$ instead of the expected $[\text{Ni}^{\text{II}}(\text{bprolen})]$.

References

1. Sigel, H.; Martin, R. B., *Chem. Rev.*, (1982) 82, 385-426.
2. Jun, M.-J.; Liu, C. F., *Inorg. Chem.*, (1975) 14, 2310-2314.

SELF-ASSOCIATION OF SOME TERNARY RUTHENIUM COMPLEXES THROUGH NON-COVALENT π INTERACTIONS

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Ternary octahedral ruthenium(II) complex ions of the general form $[\text{Ru}(\text{N}_4\text{-tetradentate})(\text{N}_2\text{-bidentate})]^{2+}$ have been prepared using combinations of the following ligands: tetradentates 1,6-di(2'-pyridyl)-2,5-dimethyl-2,5-diazahexane (picenMe₂) and 1,6-di(2'-pyridyl)-2,5-dibenzyl-2,5-diazahexane (picenBz₂) and bidentates 2,2'-bipyridine (bipy), 1,10 phenanthroline (phen) and dipyrro[3,2-f:2'3'-h]quinoxaline (dpq). Appropriate $[\text{Ru}(\text{N}_4\text{-tetradentate})(\text{dmso})\text{Cl}]\text{PF}_6$ precursors were prepared via reaction of the tetradentate with *cis*- $[\text{Ru}(\text{dmso})_4\text{Cl}_2]$. PicenMe₂ was observed to form only the *cis*- α species while picenBz₂ forms both the *cis*- α and *cis*- β ions. These latter stereoisomers were separated by fractional crystallisation. After reaction with the chosen bidentate, each ternary complex was obtained as its water soluble chloride salt using cation exchange chromatography.

We are investigating whether there is a correlation between the propensity of these compounds to form π -stacking dimers or aggregates in aqueous solutions, and their ability to intercalate into DNA. The ¹H-NMR spectral features of most of these complexes are concentration dependent. This dependence is thought to be caused by intermolecular association between cations at higher concentrations via π -stacking interactions involving the aromatic bidentates. The ability of complexes such as these to intercalate into calf-thymus DNA has been studied using visible absorption hypochromism methods. A number of these studies have been performed, and the correlations observed will be reported and interpreted.

PHOTO-INDUCED ENHANCEMENT OF SUPERCONDUCTIVITY IN K_3C_{60}

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The discovery of relatively high superconducting critical temperatures (T_c) for alkali metal-fullerides has generated great theoretical and experimental interest. The main objective of such studies is to improve the superconducting properties, e.g., increasing T_c and enhancing the diamagnetic shielding fraction (χ_{sf}). Recently, light illumination has been used to generate new physical and chemical properties in a variety of materials.

In this study, we report that the photo-induced modification of the near surface region of K_3C_{60} powders generates very large enhancement of the χ_{sf} value. Before illumination, only ~10 vol.% of the K_3C_{60} powder sample exhibited diamagnetism. However, after illumination, values close to 100 vol.% of χ_{sf} were obtained, whereas T_c was unchanged. This is a remarkable achievement since most superconductors of this family have very low superconducting shielding fraction (< 50% vol.). Moreover, χ_{sf} was found to return to its original value upon heating, demonstrating that the transformation is reversible. The Raman measurements indicate that this reversible behaviour is due to photopolymerisation and thermal depolymerisation of C_{60} molecules. Similar results were also observed for Rb_3C_{60} powders. We therefore predict that this type of behaviour is general for the alkali-metal C_{60} family and leads to the formation of high quality superconductors.

CATALYZED vs. UNCATALYZED DIBORATION OF ALDIMINES: DIRECT ROUTES TO ALPHA-AMINOBORONIC ACIDS AND C₂-SYMMETRIC DIAMINES

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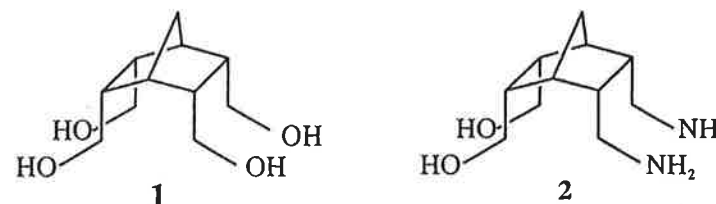
Addition of B₂cat'₂ to aldimines RN=CHR' gives the *rac*-diborylamines in a stereospecific C-C coupling reaction (cat' = 4-*t*-butylcatecholato). Effects of R,R' and the diol-derived boron substituent on the reaction rate are discussed. Pt-catalyzed addition of B₂cat'₂ to aldimines gives a mixture of 1,2-diboration and C-boration accompanied by formation of HBcat'. Catalyzed hydrogenation of the reaction mixture, followed by hydrolysis, affords a direct route to alpha-aminoboronic acid enzyme inhibitors. Investigations into the scope of the aldimine substrate and effects of the boron substituent will be described.

NEW FOUR STRAND MOTIFS FOR METAL ION ENTRAPMENT

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Traditionally, metal-binding molecules possessing four strands have encompassed mainly the N-based pendant tetraaza macrocycles. These molecules usually include sterically congested tertiary nitrogens as donor atoms and often lack stereochemical control or pre-organisation.



These effects may be overcome by the use of a small rigid and stereochemically defined molecular cap as a 'bridgehead' for the four strands. These molecules represent a new class of metal binding encapsulating ligands.

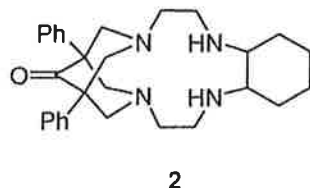
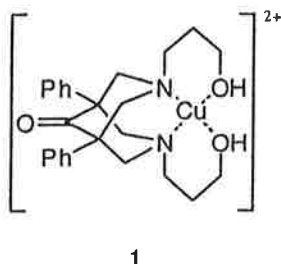
Two such four strand motifs (1 and 2) have been developed based on a bicyclo[2.2.1]heptane 'skeleton' with the stereochemistry exclusively as shown in the figure. The preparation and characterisation of these molecules and metal ion interactions with these templates will be described. Further, routes towards the elaboration of these motifs to yield longer chains will be described.

SYNTHESIS AND METAL COMPLEXATION OF NOVEL BISPIDINONE MACROCYCLES

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A variety of 3,7-diazabicyclo[3.3.1]nonan-9-one (bispidinone) ligands were prepared via the Mannich condensation of formaldehyde, primary amines and 1,3-disubstituted ketones. As very few coordinated bispidinones have been reported in the literature, complexes, such as (1), were prepared using divalent first row transition metals. These complexes and ligands have been characterised by infrared, UV-visible, mass, and NMR spectroscopy.



Use of monotosylated diamines in the Mannich condensation leads to reaction at the primary site, yielding tetraaza ligands which are ideal candidates for subsequent cyclisations. Bispidinone macrocycles, such as (2), have been prepared by the Richman Atkins cyclisation method.

THE APPLICATION OF MODIFIED SUZUKI BORONIC ACID COUPLING PROCEDURES TO THE SYNTHESIS OF TAMOXIFEN DERIVATIVES AND TETRAARYLETHENES.

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Department of Chemistry,
Monash University,
November, 1997.

Supervisors;

Prof. W. R. Jackson, B.Sc. (Manc.), Ph.D., D.Sc. (Lond.), F.R.A.C.I., F.T.S.,
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3169.

Abstract.

Tamoxifen has historically been used to inhibit the growth of hormone dependent mammary cell carcinoma. Studies that indicate a possible prophylactic action of Tamoxifen against mammary carcinoma and the isolation of highly active hydroxylated metabolites have renewed interest in this class of therapeutic agents.

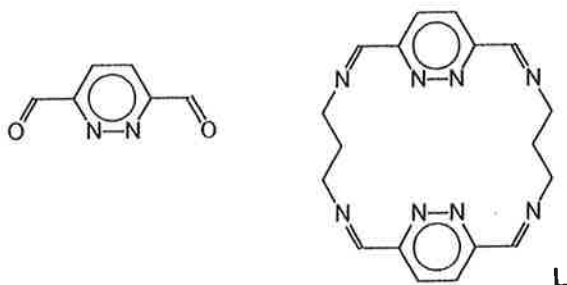
A stereoselective synthesis of Tamoxifen derivatives based on the Pd(0) catalysed (Suzuki) coupling of vinyl bromides with a variety of organoboron nucleophiles has been achieved. Trifluoroacetic anhydride promoted acylation of aromatic ethers by 2-phenylbutanoic acid delivers 1,2-diphenylbutanones. These ketones are subsequently converted to their enol triflates which take part in a stereoselective bromide ion trapping reaction to yield 1-bromo-1-(4-alkoxyphenyl)-2-phenylbutenes. Suzuki coupling of these vinyl halides (which need not be purified) with phenyl and tolyl boronic acids gives the title compounds.

The Suzuki coupling behavior of 1-bromo-1,2,2-tetraarylethene with arylboronic esters generated *in situ* and arylboronic acids, has also been investigated. The *in situ* techniques developed allow functionalised aryl halides to be coupled with vinylhalides in a high yield, 'one pot' reaction. The high yields and excellent functional group tolerance displayed by these reactions make them amenable to use in combinatorial synthesis.

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The preparation of molecular materials which could have nano-technological applications is an area of intense interest. In order to produce molecules which can act as switches, detectors or memory devices the property of bistability is required. Classic examples of bistability are provided by spin crossover compounds in which the transition from low- to high-spin is accompanied by a measurable change in magnetism and often also in colour.

We are studying complexes of chelating ligands based on 3,6-diformylpyridazine (Fig).^[1,2] To date, very few pyridazine- or phthalazine-bridged dicobalt(II) complexes have been studied, and all of these have contained high-spin cobalt(II) ions throughout the temperature ranges studied. Here we present the first examples of macrocyclic pyridazine-bridged dicobalt(II) complexes along with their unique electrochemical and magnetic properties.^[2] Of particular note is an air stable dicobalt(II) complex of the Schiff-base macrocyclic ligand L (Fig) which exhibits unique magnetic properties for a cobalt complex and represents a first step towards the development of a "usable" spin-transition polymer.^[2]



References

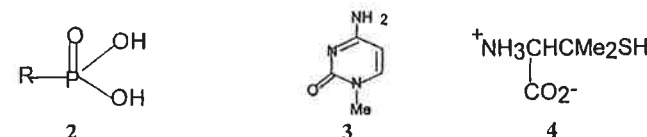
- [1] S. Brooker, R.J. Kelly, G.M. Sheldrick, *J. Chem. Soc. Chem. Commun.* 1994, 487; S. Brooker, R.J. Kelly, *J. Chem. Soc. Dalton Trans.* 1996, 2117; S. Brooker, R.J. Kelly, B. Moubaraki, K.S. Murray, *Chem. Commun.* 1996, 2579.
- [2] S. Brooker, R.J. Kelly, P.G. Plieger, *Chem. Commun.* 1998, 1079; S. Brooker, R.J. Kelly, P.G. Plieger, B. Moubaraki, K.S. Murray, E. Bill, E. Bothe, unpublished results.

DINUCLEAR PLATINUM (III) COMPLEXES WITH NEW O-, N- AND S-DONOR LIGANDS

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To date, the only preparative route to dinuclear Pt (III) complexes with O-donor bridges (e.g. $(\mu\text{-O}_2\text{CR})$, $\mu\text{-SO}_4^{2-}$ and $\mu\text{-HPO}_4^{2-}$) is the reaction of a nitro-platinum (II) complex, $[\text{Pt}(\text{NO}_2)_4]^{2-}$, *cis*- $[\text{Pt}(\text{NO}_2)_2(\text{H}_2\text{O})_2]$ or *cis*- $[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2]$ with aqueous acids^{1,2}. Thus the platinum (III) carboxylates, **1**, $[(\text{H}_2\text{O})\text{Pt}(\mu\text{-O}_2\text{CR})_2]_2(\text{A})_2$ (where $\text{A} = \text{ClO}_4^-$, NO_3^- or CF_3SO_3^- ; $\text{R} = \text{Me}$, Et , *i*-Pr, *n*-Bu and CF_3), were prepared in this laboratory by the reaction of $\text{K}_2[\text{Pt}(\text{NO}_2)_4]$ with a solution of $\text{RCOOH}/\text{H}_2\text{O}/\text{HA}$ in the presence of dioxygen¹. However, attempts to prepare other Pt (III) complexes containing new O-, N- and S-donor ligands (e.g. **2**, **3** and **4**) by a similar procedure were unsuccessful.



In contrast to the robustness in aqueous solution of the analogues with sulfate or hydrogenphosphate bridges, **5** and **6** respectively², one of the carboxylate bridges in **1** ($\text{R} = \text{CH}_3$) was cleaved in water, to give Pt (III) complexes in which three bridging carboxylate ligands remained. If this reactivity is due to structural strain in the acetate complex, which is not present in **5** and **6**, then, **1** ($\text{R} = \text{CH}_3$) is potentially the best starting material for the preparation of new platinum (III) complexes by replacing the acetate bridges with other ligands. We present, in this contribution, the reactions of **1** with 1-methylcytosine and some polyimines, phosphonates, sulfonates and thiolates.

References

1. Appleton, T.G., Byriel, K.A., Garrett, M., Hall, J.R. Kennard, C. H. L., Matthieson, M.T., Stranger, R., *Inorg. Chem.* 1995, 34, 5646; T. G. Appleton, G. A. Ayoko, D. Bedgood, Jr., S. Begum and E. Hubner, unpublished results.
2. Muraveiskaya, G.S., Kukina, G.A., Orlova, V.S., Evastaf'eva, O.N., Porai-Koshits, M.A. *Dokl. Akad. Nauk. SSSR* 1976, 226, 596; Bancroft, D.P., Cotton, F.A., Falvello, L.R., Han, S., Schwotzer, W., *Inorg. Chim. Acta* 1984, 87, 147

THE FORMATION OF *cis* - BIS BUTADIYNYL PLATINUM COMPLEXES AND MOLECULAR SQUARES.

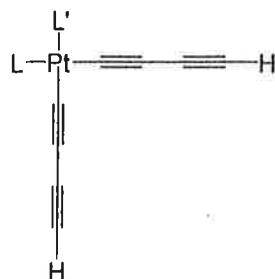
Benjamin C. Hall^a, Michael I. Bruce^a, Brian W. Skelton^b, Allan H. White^b.

a) Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005.

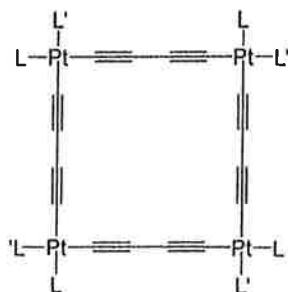
b) Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907.

Transition metals containing π -conjugated organic fragments are a subject of continuing interest due to their potential as new materials with novel and interesting properties. Complexes containing two all-carbon ligands in close proximity exhibit interesting behaviour, and may exhibit "tweezer" effects with small reactive compounds¹. Several such complexes were prepared by coupling 1,3-butadiyne or $\text{CpW}(\text{CO})_3\text{C}_4\text{H}$ with *cis*-(L-L')PtCl₂ (L-L' = dppe, dppp, PEt₃, PPh₃ and cod) (1) utilising standard Hay catalyst conditions.

The construction of discrete supramolecular species is also an area of interest, with recent developments in the self-assembly of organometallic and inorganic frameworks. Previous examples of "molecular squares" have been charged, typically +2, +4 or +8². Neutral tetra-nuclear complexes (2) were prepared via self-assembly from *cis*-(L-L')Pt(C₄H)₂ and *cis*-(L-L')Pt(OTf)₂.



(1)



(2)

1. H. Lang, K. Köhler, S. Blau, *Coord. Chem. Rev.*, 1995, **143**, 113-168.
2. P. Stang, *Chem. Eur. J.*, 1998, **4**, 1, 19-27; B. Olenyuk, A. Fechtenkötter, P. Stang., *J. Chem. Soc., Dalton Trans.*, 1998, 1707-1728.

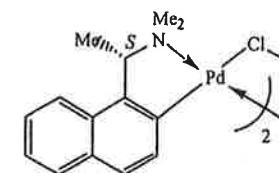
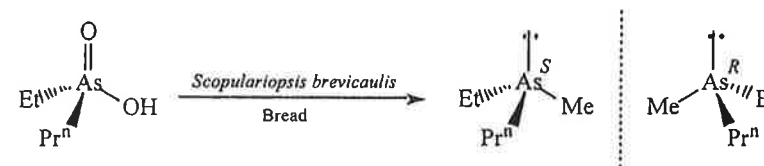
STERESELECTIVE BIOMETHYLATION OF ARSENIC

Martha E. Bernardo and S. Bruce Wild

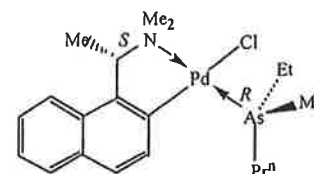
Research School of Chemistry, Australian National University

Canberra, A.C.T. 0200, Australia

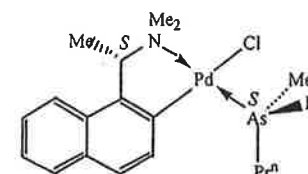
A variety of micro-organisms are capable of converting tri- or penta-valent arsenic oxides into trimethylarsine.¹ Among others, the mould *Scopulariopsis brevicaulis* has been shown to convert a number of arsonic and arsinic acids into the corresponding methyl-substituted tertiary arsines.² It has since been demonstrated that the reductive methylation of the unsymmetrically substituted ethyl-*n*-propyl arsinic acid by *S. brevicaulis* is stereoselective in favour of the *R*-enantiomer of the tertiary arsine (60% e.e.).³ The arsine produced by the fungus is trapped using a solution of (*S*)-1 in 1,2-dichlorobenzene, and the ratio of the diastereomeric products (*S,S*)-2 and (*S,R*)-2 determined by ¹H NMR spectroscopy. Current work is concerned with exploring the effect of substituents on the stereochemistry of the bromoethylation with use of appropriate unsymmetrically substituted arsinic acids.



(*S*)-1



(*S,R*)-2



(*S,S*)-2

¹ W. R. Cullen and K. J. Reimer, *Chem. Rev.*, 1989, **89**, 713.

² F. Challenger, C. Higginbottom, and L. Ellis, *J. Chem. Soc.*, 1933, 95; F. Challenger and A. A. Rawlings, *J. Chem. Soc.*, 1936, 264.

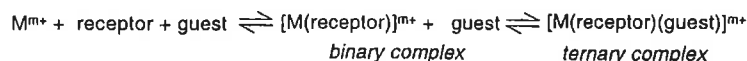
³ P. Gugger, A. C. Willis and S. B. Wild, *J. Chem. Soc., Chem. Commun.*, 1990, 1169.

Cassandra J Martin[†], Stephen F Lincoln[‡] and Kevin P Wainwright[†]

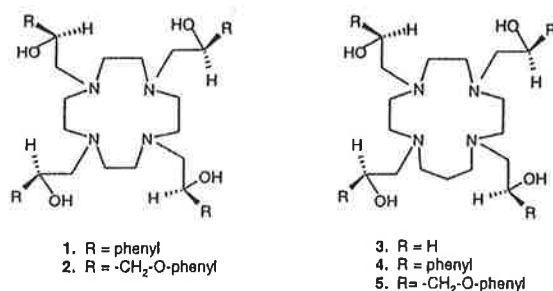
[†] Department of Chemistry, Flinders University of South Australia, Adelaide, SA, 5001

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Selective molecular recognition of a substrate by a guest has been an area of great interest in recent years. An advanced form of chemical molecular recognition involves complexes of a ternary nature as demonstrated during the formation of metalloenzymes in biological molecular recognition. The basic principle behind this form of molecular recognition is dependent upon the complexation of a metal ion to an appropriate ligand (the receptor) resulting in a binary receptor-metal complex. This complex assumes a basket-like configuration suitable for selective complexation of a guest molecule in a ternary complex.



It was anticipated that binding of a secondary substrate molecule might be achieved in a pendant arm macrocyclic system. Recent studies have revolved around tetraaza pendant arm macrocycles and in particular THPEC-12 (1). A preliminary crystal structure of the cadmium complex [Cd(S-THPEC-12)]²⁺ displays a rigid eight coordinate system with all four of the pendant arms lying on the same side of the macrocyclic plane forming a basket-like structure. It is thought that this basket may be too shallow to act as a guest receptor and hence the depth of the basket has been modified by increasing the number of atoms in each of the pendant arms. (2) These ligands possess four fold symmetry with each of the arms being identical.



The symmetry of the receptor may be varied by utilizing the 13 membered tetraaza system. The symmetry is reduced and we encounter two sets of distinct pendant arms. The successful synthesis of N,N',N''N'''-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclotridecane (3) has been achieved and determination of stability constants via potentiometric titrations with various metal ions has begun. It is envisaged that substituted pendant arms containing phenyl groups (4) and (5), upon coordination of an appropriate metal ion, will produce a structure suitable for inclusion of a guest molecule.

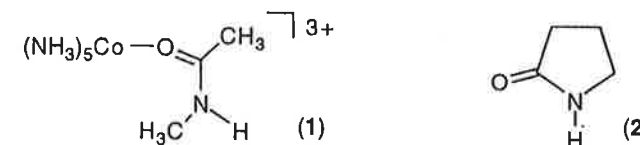
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Patricia M. Angus

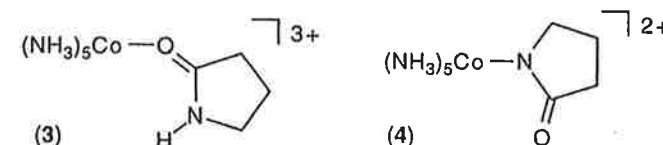
Department of Chemistry, Faculty of Science,
Australian National University, Canberra ACT 0200 Australia

Unidentate cobalt(III) complexes of secondary amides bonded through the amide nitrogen have not been reported previously, although this type of ligand is important since it is a model of the peptide bond.¹ To date, only some oxygen-bonded unidentate complexes have been prepared, for example that of *N*-methylacetamide (1):²



It is commonly held that secondary amides are weaker ligands than their primary analogues because the substituent on the nitrogen causes steric hindrance in both the N- and O-bonded forms. This effect is diminished in the case of a small cyclic amide which is necessarily in the *cis* configuration. 2-Pyrrolidinone (2) is a secondary amide with the structure of a five-membered ring. It is found as a terminal structural unit in some peptides and in related compounds of biological importance.

The preparation of complexes of 2-pyrrolidinone bonded through the amide oxygen (3) and nitrogen (4) and the properties and reactions of the complexes will be described and compared with those of complexes of primary and acyclic secondary amides.



References

- (1) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385.
- (2) Angus, P. M.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1993**, *32*, 450.

M82

CHIRAL QUADRIDENTATE LIGANDS CONTAINING STEREOGENIC ARSENIC AND / OR PHOSPHORUS DONOR ATOMS

Roy J. Doyle, Mark George and Geoff Salem

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Appropriately designed chiral quadridentate ligands bearing two or more stereogenic phosphorus or arsenic donor atoms and that selectively form *cis-α* complexes with transition metal ions offer an enormous potential as chiral auxiliaries in asymmetric synthesis, particularly in controlling the stereoselectivity of reactions involving substrates that bind in a bidentate fashion. The chiral quadridentate ligand (R_{As}^{*},Sp^{*})-(±)-1-[(2-dimethylarsinophenyl)methylarsino]-2-[(2-aminophenyl)methylphosphino]benzene, (R_{As}^{*},Sp^{*})-1, is one such example. It can be prepared in a completely stereoselective manner by the reaction of (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine with an equimolar quantity of sodium (2-dimethylarsinophenyl)methylarsenide in tetrahydrofuran at 50±5 °C albeit in low yield. Furthermore, the *cis-α* complex is formed exclusively upon coordination of the ligand to cobalt(III), as confirmed by an X-ray analysis of the parent complex *cis*-[CoCl₂{(R^{*},S^{*})-1}]Cl.¹ When the coupling reaction was performed at lower temperatures a 1:1 diastereomeric mixture of the chiral pentadentate ligands (R_{As}^{*},R_{As}^{*},Sp^{*})-(±)- and (R_{As}^{*},S_{As}^{*},Sp^{*})-(±)-5-amino-1,4,11,14-tetraarsino-2,3,6,7,9,10,12,13-tetrahydrotetrabenzo-1,1,4,8,11,14,14-heptamethyl-8-phosphinotetradecine was isolated in high yield.

Current work is focusing on the synthesis of the related chiral quadridentate ligand (R_{As}^{*},Rp^{*})-(±)-1-[(2-dimethylphosphinophenyl)methylphosphino]-2-[(2-aminophenyl)methylarsino]benzene, (R_{As}^{*},Rp^{*})-2, via the coupling of (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine with sodium (2-aminophenyl)methylarsenide. The presence of the 2-aminophenyl moiety in the arsenide reagent should preclude formation of the analogous pentadentate ligand. The optically active antipodes of the ligands (R_{As}^{*},Sp^{*})-1 and (R_{As}^{*},Rp^{*})-2 have been specifically designed to be used as a chiral auxiliaries in the stereoselective derivatisation of the glycinate ion.

¹ R. J. Doyle, G. Salem and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1997, 2713.

SYNTHESIS AND REACTIONS OF PHOSPHINO-PHOSPHONIUM SALTS

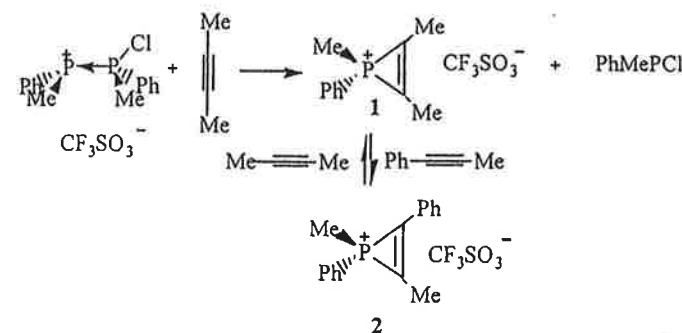
Keith A. Porter and S. Bruce Wild

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Canberra, ACT 0200, Australia

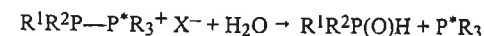
Many tertiary phosphines react with halogenoarsines, halogenostibines¹ or chloroamine² to form arsino-phosphonium, stibino-phosphonium or amino-phosphonium salts, respectively; for example



The synthesis of similar phosphino-phosphonium salts from halogenophosphines and tertiary phosphines is being investigated and their chemistry is being explored. Phosphino-phosphonium salts can also be considered as phosphine-stabilised phosphonium salts, viz. [R₂P⁺-PR₃]⁺X⁻. Accordingly, PhMeP-PClMePh⁺ OTf⁻ reacts with but-2-yne to give a quantitative yield of the phosphirenium salt 1.³ Moreover, addition of 1-phenylprop-2-yne to 1 leads to the establishment of an equilibrium between 1 and 2. The mechanism of the pi-ligand exchange between 1 and 2 has been modelled by high level *ab initio* calculations.⁴



Although amino-phosphonium salts are hydrolysed to phosphine oxides, phosphino-phosphonium salts give phosphinous acids and phosphine.⁵ Thus, the asymmetric synthesis of phosphinous acids should be feasible by the hydrolysis of appropriate phosphino-phosphonium salts containing resolved tertiary phosphines.



¹ Braddock J. M. F., Coates G. E. *J. Chem. Soc.*, 1961, 3208.

² Sisler H., Sarkins A., Ahuja H. S., Drago R., Smith N. L. *J. Am. Chem. Soc.*, 1959, 81, 2982.

³ Hockless D. C. R., McDonald M. A., Pabel M., Wild S. B., *J. Organomet. Chem.* 529, 1997, 189

⁴ Sölling T., McDonald M. A., Wild S. B., Radom L., *J. Am. Chem. Soc.* 1998, 120, 7063.

⁵ Issleib K., Seidel W., *Chem. Ber.*, 1959, 2681.

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Mono(bidentate)platinum(II) complexes of the type $[PtClMeL]$ (where $L = 2-H_2NC_6H_4PPhR$ and $R = Me$ or Ph) have been prepared by reacting the appropriate ligand with $[PtClMe(1,5-cyclooctadiene)]$ in dichloromethane.¹ Further reaction with HCl gives the dichloroplatinum(II) complexes $[PtCl_2L]$. The analogous dichloropalladium(II) complexes also been prepared via a standard route which involves a bridge splitting reaction between the dimer $di-\mu-chlorobis[2-(dimethylaminomethyl)phenyl-C^1,N]dipalladium(II)$ and the appropriate ligand in methanol followed by treatment with concentrated hydrochloric acid in acetone. Substitution of the chloro groups in $[MCl_2L]$ can be achieved by reaction with silver nitrate in acetonitrile followed by the addition of sodium oxalate to give the complexes $[M(C_2O_4)L]$. These mono(bidentate) complexes are seen as potential anticancer agents as they possess two important features: the presence of a chirotopic phosphorus stereocentre in close proximity to the metal centre and an amino group, in keeping with empirical structure-activity relationships of related mononuclear platinum(II) complexes. Preliminary biological studies have shown them to be active against the mouse tumour model P815 *in vitro* with cytotoxicities of certain of these complexes being comparable to that of cisplatin.

Current work is focusing on the synthesis of related dinuclear compounds of the type $[(MX_2)_2(\mu-L)]$ where L is a linear quadridentate ligand containing two stereogenic phosphorus donor atoms and two terminal primary amine groups e.g. $(R^*,R^*)-1,3-bis\{(2-aminophenyl)phenylphosphino\}propane$. The two diastereomeric forms of the ligand have been separated by complexation to palladium(II) and the (R^*,R^*) form of the ligand is to be resolved by the method of metal complexation. The *in vitro* cytotoxic properties of the complexes $[(MX_2)_2(\mu-L)]$ are to be assessed against several murine tumour cell lines.

¹ S. Chatterjee, D. C. R. Hockless, G. Salem and P. Waring, *J. Chem. Soc., Dalton Trans.*, 1997, 3889.

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PAHs are ubiquitous in the environment and are found in high concentrations on many industrial sites, particularly those associated with petroleum gas-production and wood preserving industries¹. Many PAHs and their metabolites are known carcinogens. The US Environmental Protection Agency (EPA) has identified a list of 16 priority pollutants for PAHs¹.

Biological treatment has been proved to be feasible remediation technology, with success for single PAHs such as naphthalene and phenanthrene, however the complex mixtures that are encountered at industrial sites have proved more difficult to degrade².

Over recent years chemical oxidation of organic pollutants, either on its own or in conjunction with bioremediation has generated a lot of interest. Over the same period a great deal of work has been done on the use of manganese complexes as oxidation catalyst.³

Results from the oxidation of Acenaphthene, Anthracene, Fluroanthene, Chrysene, and Pyrene by a variety of manganese complexes are reported.

¹ Wilson, S.C, Jones, K.C.(1993).*Environmental Pollution*, 81, 229-249

² Van Kemenade, I., Anderson, W.A., Scharer, J.M., Moo-Young, M. (1996) *Trans IChemE*, 74,125-131

³ Hage, R.(1996) *Recl.Trav.Chim.Pays-Bas*, 115, 385-396

RECENT DEVELOPMENTS IN MICRO-, MESO- AND MACRO-STRUCTURED INORGANIC COMPOSITIONS AT INDUSTRIAL RESEARCH LIMITED

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Exciting new initiatives in the synthesis and application of a wide range of porous solids suitable as catalysts and catalyst supports are being developed by the Advanced Materials Group at Industrial Research.

Routes for the synthesis of zeolites such as ZSM-5, TS-1 and MOR from naturally occurring and synthetically precipitated geothermal silica starting materials, both with and without templates, have been developed. This work is part of an expanding collaboration with University of Calabria, Italy and Victoria University of Wellington.

A new macroporous silicate has been prepared using a kinetically stable, continuous non-ionic foam. This material is a robust solid which replicates the macro void structure of the foam, with silicate walls containing voids in the mesoporous diameter range. It can be prepared either as small particles or as large monoliths (2 x 10cm). We are currently exploring the application of these materials as supports for the growth of biophases and for immobilizing enzyme molecules for use in bio-catalytic reactions.

Mesoporous silicates have been prepared using the more conventional dilute solutions of inexpensive and environmentally benign, non-ionic, alkyl polyethylene oxides surfactants as templates. We are examining the potential applications of metal substituted (Al, Fe, Ti, Zr and V) forms of these materials for isomerization and oxidation reactions of natural terpenes.

The aim of our programme is to provide New Zealand's chemical and biotechnological industries with new materials for catalysts, catalyst supports, absorbents and substrates for biocatalysis, photocatalysis and tethered homogeneous catalysts.

PREPARATION OF HYPOXIA SELECTIVE ANTI-TUMOR AGENTS.

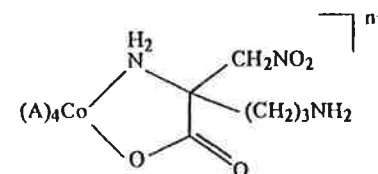
Andrea J Clarkson,^a Charles R Clark,^a Allan G Blackman,^a Alan M Sargeson.^b

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b. Chemistry Department, Australian National University, Canberra, Australia.

Hypoxic or oxygen deficient cells found in solid tumors are resistant to ionizing radiation and conventional chemotherapy.¹ Our approach is to develop drugs which are selectively cytotoxic in the hypoxic environment and not in normal cells. It has been shown that the polyamines putrescine ($\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$), spermidine ($\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}_2$) and spermine ($\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_3\text{NH}_2$), derived via ornithine ($\text{H}_2\text{NCH}((\text{CH}_2)_3\text{NH}_2)\text{COOH}$), are required to maintain cell growth and function.²

This is why the polyamine-biosynthetic pathway has been chosen as a target for agents capable of inhibiting carcinogenesis and tumor growth. Inhibition comes from blocking the ornithine decarboxylase-catalysed conversion of ornithine to putrescine. Certain cobalt (III) complexes of α -nitromethylornithine (Figure) are considered to have the potential to block activity following controlled release of the suicide inhibitor α -nitromethylornithine by reduction of the Co(III) centre to Co(II). Strategies for the synthesis of α -nitromethylornithinato complexes will be discussed.



1. Ware, D. C, Palmer, B. D, Wilson, W. R, Denny, W. A., *J. Med. Chem.*, 1993, 36, 1839.

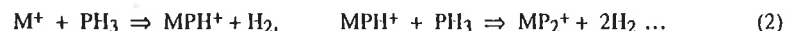
2. Pegg, A. E., *Cancer Research*, 1988, 48, 759.

MODELLING THE GAS-PHASE REACTIONS OF TRANSITION METAL IONS WITH PHOSPHINE, PH₃

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Our experiments generate transition metal ions M⁺_(g) and react them with PH₃_(g) in the cell of an Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer. Two reaction patterns are observed, namely addition (eq 1) and dehydrogenation (eq 2). The type of reaction for each metal is indicated in the periodic table below: Mn⁺ and Fe⁺ do not react, while Au⁺ undergoes both reaction types.



Sequential multiple dehydrogenation forms species as large as OsP₉H⁺.

Forms MPH_3^+ only				No Reaction		Adds one or more PH_3		
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
Zr	Nb	Mo		Ru	Rh	Pd	Ag	
Hf	Ta	W	Re	Os	Ir	Pt	Au	

Forms MP_xH_y , where $y=0$ if x is even and $y=1$ if x is odd

Density functional theoretical methods have been used to investigate the structures of the products and the mechanisms of the reactions. These calculations show the structures of the adducts. For the metals which are experimentally observed to dehydrogenate phosphine, the calculations reveal a barrierless transfer of H atoms from phosphorus to metal in MPH₃⁺. If this transfer occurs twice then a likely dehydrogenation intermediate is formed with two H atoms bound to the metal. The density functional calculations have evaluated transition states for the loss of H₂ from either P or M.

There is good agreement between the observed reactivity types and the calculated transformations.

M89

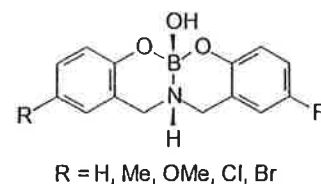
POSTERS

Zeev Goldschmidt and Ilana Ben-Arie

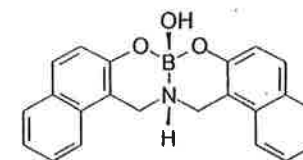
Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

Oxazaborines (1, 2) crystallize from a wide range of polar solvents (dioxane, nitromethane, acetonitrile, acetone, pyridine), forming one of four *inorganic* (H-O-B-N-H) hydrogen bonding motifs:

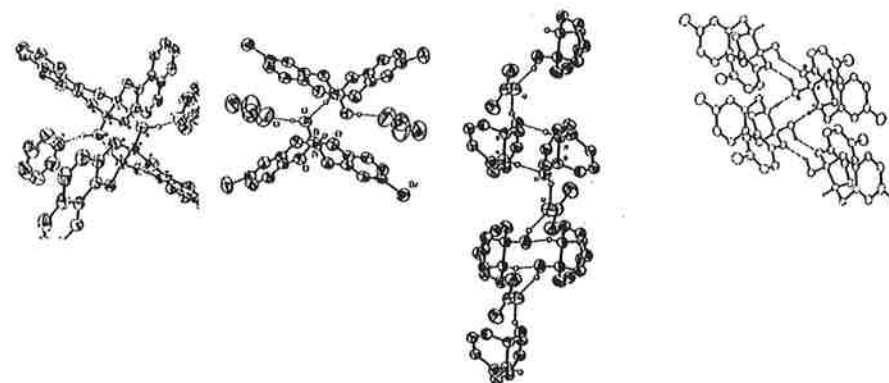
1. Ring inclusion compounds which self-assemble as 8-membered ring aminoborate dimers, H-bonded to solvent molecules.
2. Chain clathrates which constitute a self assembly of infinite head-to-tail inorganic strands of aminoborates, each H-bonded to a solvent molecule.
3. Chain clathrate of infinite self-assembled strips of aminoborate dimers H-bonded to each other by a solvent (acetone) molecule.
4. Ribbons of aminoborates which self-assemble *without* solvent molecules in infinite inorganic "tunnels" of dimers, H-bonded through 8-membered ring patterns.



1

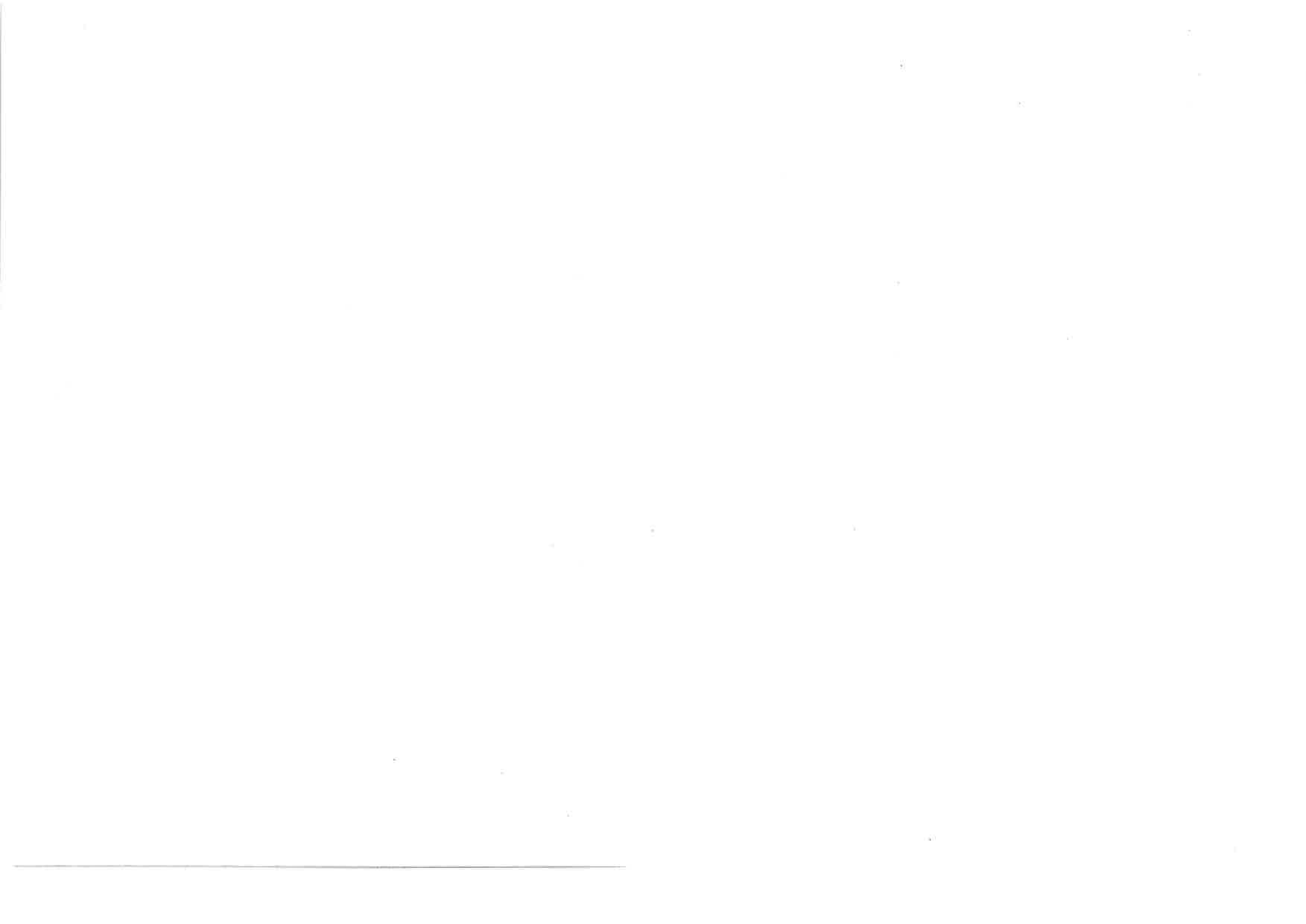


2



M90

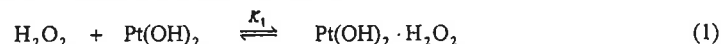




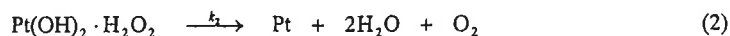
Peroxide At Platinum Electrodes.

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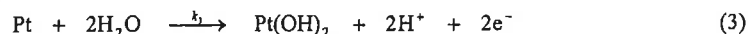
Recently we have shown that the electrochemical oxidation of hydrogen at platinum electrodes follows a complex mechanism [1]. This is assumed to involve a surface Pt(II) site (although Pt(IV) is also a candidate) we have chosen to identify as Pt(OH)₂.



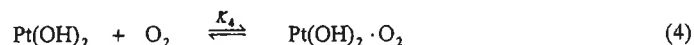
This complex undergoes internal charge transfer with liberation of O₂.



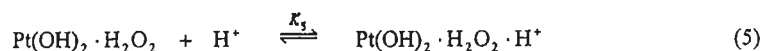
The catalytic cycle is completed with the electrochemical oxidation of Pt to give rise to the amperometric response.



Inhibiting side interactions involving both products were proposed, the first involving O₂ competing with H₂O₂ for formation of the surface complex.



The second involves protonation of the surface complex.



In our previous studies [1,2] we have shown that the rate of the reaction is given by

$$j = \frac{k_2 N K_1 [\text{H}_2\text{O}_2]}{1 + K_4 [\text{O}_2] + K_1 [\text{H}_2\text{O}_2] (1 + K_5 [\text{H}^+] + k_2 / k_3)} \quad (6)$$

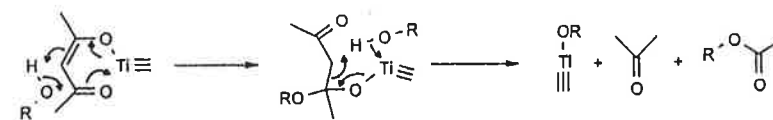
where *N* is the number of surface sites per unit area. We explored the dependence upon the electrode potential [2] and showed that *K*₁, *K*₄ and *K*₅ were potential invariant whilst the rate constants *k*₂ and *k*₃ increase logarithmically with increasing anodic potential.

In this paper we will present our findings on the response of this system to both phosphate electrolyte concentration and pH. The rate of H₂O₂ oxidation is dependent on the buffer concentration with a maximum response found for pH 7. This indicates that the species H₂PO₄⁻ is likely to be involved in the binding site; at pH > 7 the concentration of this phosphate species decreases, whilst the lower response for pH < 7 we associate with the inhibiting reaction (5).

[1] Hall, S.B.; Khudaish, E.A.; Hart, A.L. *Electrochim. Acta.* 1998, 43, 579.[2] Hall, S.B.; Khudaish, E.A.; Hart, A.L. *Electrochim. Acta.* 1998, 43, 2015.

Tim Kemmitt and Marc Daglish, Industrial Research Ltd, PO Box 31-310, Lower Hutt, New Zealand

Sol-gel processing from metal alkoxide precursors is increasingly being used to produce advanced materials with specific properties and activities. However, metal alkoxides are commonly hydrolytically unstable and precipitate hydrated oxides on exposure to moisture. Controlling the hydrolysis and condensation reactions to produce a stable sol has been the aim of a number of strategies to overcome this problem. The addition of a modifier to stabilise the sol, or reduce the hydrolysis rate has been extremely successful, and several distinct methods have been used. Modifiers are typically chelating ligands and have included glycols, glycol ethers, carboxylates, 1,3-diketones, hydroxyacetates etc. Acetylacetone, (acacH) and a wide range of analogues have often been used in this context. For example, acac complexes of titanium and zirconium were used in recent studies¹ of lead titanate (PT) and lead zirconate titanate (PZT) precursor solutions. In addition to improved hydrolytic stability, the method was reported to produce thicker films (up to 1 μm single layers) than other common methods. The processing involved refluxing the acac complexes in a range of diols to give reproducible sols suitable for thin film deposition. The reactions between the diol and the metal complexes, however, are not well characterized. Part of our interest lies in the chemistry occurring prior to sol formation in this and related sol precursor systems, and in particular in determining the fate of the acac ligands. This poster describes the initial reactions occurring between some titanium or zirconium acac complexes with refluxing alcohols or diols. By following the decomposition processes by NMR and GC we have identified the reaction products and arrived at a reasonable mechanism to explain our observations.



References

1. Tu, Y.; Calzada, M. L.; Phillips, N. J.; Milne, S. J. *J. Am. Ceram. Soc.* 1996, 79, 441.

HOMOLEPTIC IMIDO COMPLEXES : THE IMIDO LIGAND AS A LEAVING GROUP

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A number of homoleptic imido complexes have been prepared and their reactivity with a variety of nucleophiles have been investigated. For example, the reaction of the homoleptic rhenium dimer $\text{Re}_2(\text{NAr})_6$ with an excess of methyl Grignard results in the substitution of two terminal imido ligands with four methyl groups ($\text{Ar} = 2,6$ diisopropylphenyl) (Fig. 1 and 2)

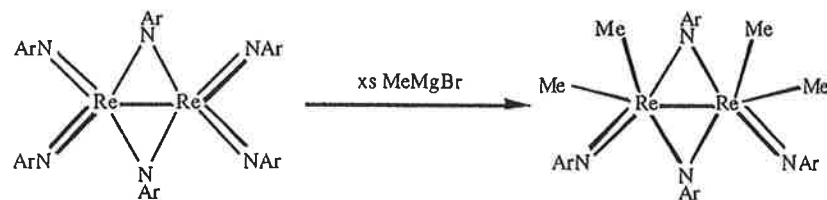


Fig. 1

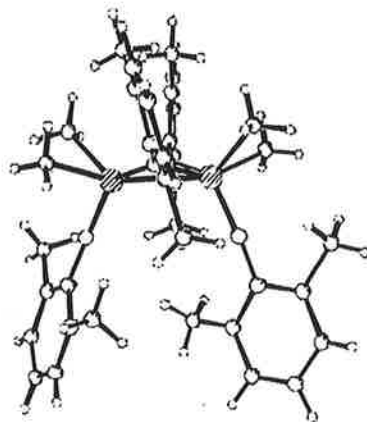


Fig. 2

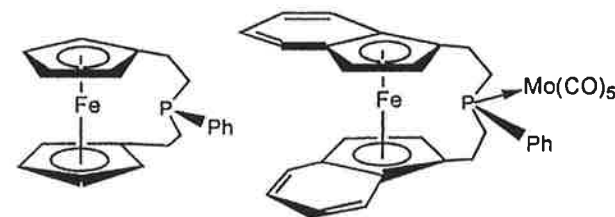
Recent results of this research, the compounds formed by these reactions and their reactivity will be presented.

ETHYLENE-BRIDGED PHOSPHINO-CYCLOPENTADIENYL AND -INDENYL LIGANDS

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Ferrocenes have played an extensive role in the development of inorganic chemistry. The addition of functional groups to the delocalised cyclopentadienyl rings of ferrocene has enabled chemists to combine the best features of the functional group and ferrocene into one molecule. These functional groups allow tuning of the catalytic properties of these complexes. Functionalised dicyclopentadienyl ligands are rare, but including a phosphine in the tethering bridge allows coordination of the ferrocenyl-phosphine to a second metal. We report here examples of dicyclopentadienyl and diindenyl ligands; the latter are able to exhibit chirality.



ALTERING THE BALANCE BETWEEN LIGAND-BASED RADICAL ANION
FORMATION AND DECHELATION IN ELECTROCHEMICALLY REDUCED
BINUCLEAR COPPER(I) COMPLEXES: A RESONANCE RAMAN
SPECTROELECTROCHEMICAL STUDY.

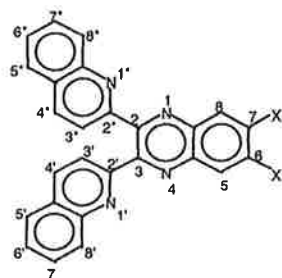
Simon E. Page^a, Keith C. Gordon^a, Anthony K. Burrell^b

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^b Department of Chemistry, Massey University, Private Bag 11122, Palmerston North.

We have synthesized and characterized a series of mono- and binuclear copper(I) complexes with bridging ligands based on the new ligand dqq (1). The solid state structures of two complexes, $[\text{Cu}(\text{dqqCl}_2)(\text{PPh}_3)_2]^+$ and $[(\text{PPh}_3)_2\text{Cu}(\text{dqqCl}_2)\text{Cu}(\text{PPh}_3)_2]^{2+}$ are reported.

The electrochemical and spectral properties of these complexes were investigated. It was found that the mononuclear complexes reduce at the ligand and dechelate. Using resonance Raman spectroscopy it was found that the two binuclear complexes with more electron-withdrawing groups (-H and -Cl), reduce at the ligand, forming ligand-based radical anion species. The third binuclear complex, having more electron donating groups (-CH₃), reduces at the metal and dechelates to form the corresponding mononuclear complex. Our results suggest that the dechelation versus BL reduction processes are balanced by electronic and structural factors.



(1) 2,3-di(2-quinolyl)quinoxaline (dqq).

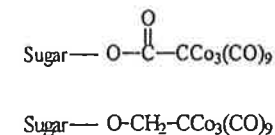
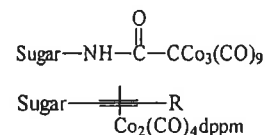
WATER SOLUBLE- μ_3/μ_2 -CARBYNE CLUSTERS AS SENSORS

Joy L Kerr, Brian H Robinson and Jim Simpson

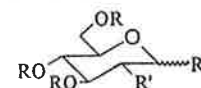
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The past 25 years has seen substantial progress in the *de novo* design of molecular abiotic sensors incorporating a binding (acceptor) site and a sensor sensitive to changes at the binding site, linked by a mechanism for communication. Low valent transition metal clusters have not been used as substrates for sensors probably because of aqueous insolubility and the difficulty of coordinating electronegative donor atoms. Herein we describe a system which could function as a sensor and a bioprobe for specific proteins. Our work takes advantage of the reactivity of μ_3 -carbyne of tricobalt carbon clusters and μ_2 -carbyne dicobalt clusters which allows the formation of a hydrophilic sphere and their 'tunable', chemically reversible, redox couples.

Previous work demonstrated that amino acids did not provide the designed solubility nor specificity for bases. The new strategy uses a sugar backbone to provide the nucleophilic site for electrophilic attack by the cluster and the hydrophilic functional groups. Syntheses, reactivity, electrochemistry and sensor properties will be described for the molecules shown below. In general terms the electrochemical results show that the redox chemistry of the deprotected sugar clusters are unaffected by water and these systems may be sensitive to specific cations and anions.



Where sugar =



R = Ac, Bn or H
R' = OAc, OBn, OH or NH₂
R'' = OAc, OBn, OH, OMe or NH₂

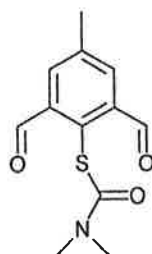
THIOLATE CONTAINING MACROCYCLES

Sally Brooker, * Paul D. Croucher, Tony C. Davidson, Geoffrey S. Dunbar

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The co-ordination chemistry of thiolate-containing ligands with nickel, copper and zinc is of great biological significance in the preparation of model compounds that mimic the properties of a number of metalloproteins, such as Ni-Fe hydrogenase, cytochrome c oxidase and Zinc fingers. In addition to acting as model compounds, the resulting complexes provide an interesting contrast to the more prevalent macrocycles that are derived from phenol and pyridine "head units".

We have incorporated the "head unit" *S*-(2,6-diformyl-4-methylphenyl)dimethylthiocarbamate (Figure), which contains a masked thiolate, into a number of macrocycles.¹ Here a series of di-nickel macrocycles will be presented and the redox chemistry discussed.²



Figure

References

1. S. Brooker and P.D. Croucher, *J. Chem. Soc., Chem. Commun.*, 1993, 1278; *ibid.*, 1995, 1493; *ibid.*, 1995, 2075; *ibid.*, 1997, 459; S. Brooker, P.D. Croucher and F.M. Roxburgh, *J. Chem. Soc., Dalton Trans.*, 1996, 3031; S. Brooker and T.C. Davidson, *Chem. Commun.*, 1997, 2007.
2. S. Brooker, P.D. Croucher, T.C. Davidson, G.S. Dunbar, A.J. McQuillan and G.B. Jameson, *Chem. Commun.*, 1998, *in press*; S. Brooker, P.D. Croucher, T.C. Davidson, G.S. Dunbar unpublished results.

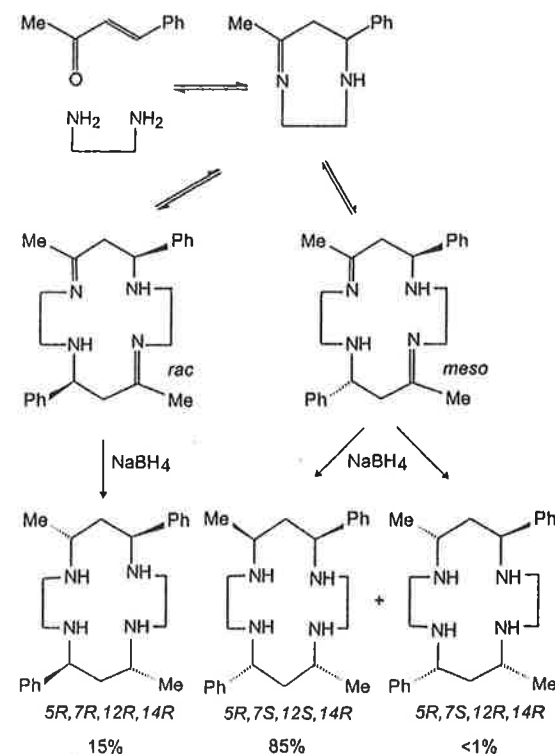
COMPOUNDS OF NICKEL(II) WITH THREE ISOMERS OF 5,12-DIMETHYL-7,14-DIPHENYL- 1,4,8,11-TETRAAZACYCLOTETRADECANE

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The reduction of *7RS,12SR*-5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene by sodium borohydride in ethanol yields three isomeric cyclic amines in 85, 15 and <1% yields. Structural studies of nickel(II) compounds show that these are the *5RS,7RS,12SR,14SR*, *5RS,7RS,12RS,14RS* and *5RS,7SR,12SR,14RS* isomers, respectively. The second (*rac-rac*) isomer is formed by reduction of the *rac*-isomer of the diene, present in solution in equilibrium with the *meso* isomer. All three isomers form nickel(II) compounds with the amine in planar and in folded coordination, the planar arrangement being most stable for the first, and the folded arrangement for the second, while the third isomer is ambivalent about folding. Nickel(II) compounds of the isomers are described, with structural studies and molecular modelling of the isomeric forms.



COBALT SUBSTITUTION IN ALPOS & SAPOS : SOME RECENTLY DETERMINED STRUCTURES

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A David Rae, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

There has been continued interest in the substitution of transition metals in microporous aluminophosphates (ALPO's) and their silicon-for-phosphorus relatives (SAPO's). As part of a concerted program utilising various cobalt sources, such as Co(ethylenediamine)₃Cl₃, we have formed under hydrothermal conditions ALPOs & SAPOs with up to ~70% cobalt content. Several of the ALPO structures have been partially reported by other researchers¹; although the framework atoms are well ordered, residual disordered template molecules frequently limit structural refinements based on X-ray diffraction measurements. By utilising the program RAELS96², we have been able to successfully refine two structures that contained disordered template molecules :

- I A SAPO with the Merlionite(MER) zeolite topology (with 63.5% Co for Al substitution)
Formula : $\text{Co}_{1-x}\text{P}_{1-y}\text{Al}_x\text{Si}_y\text{O}_4 \cdot \frac{1}{2} \text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3 \cdot \frac{3}{16} \text{H}_2\text{O}$, $x = y = 0.365(9)$ a, b 14.758, c 9.675 Å; tetragonal, Space group P 4/nnc]
- II $\text{Al}_{1-x}\text{Co}_x\text{Si}_{1-y}\text{Py O}_4 \cdot \frac{1}{3} \text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3$, $x = 0.13(1)$, $y = 0.46(1)$; a SAPO, with 13% cobalt substitution, cubic, Sodalite (SOD) topology, a 8.986 Å Space Group P $\bar{4} 3n$

The structural parameters & synthesis details will be presented for I & II. Two others have been defined to be of the same MER family but with different substitution patterns; twinning and disorder has precluded their refinement. The T(tetrahedral atom)-O bond lengths in I & II follow a linear relationship with the cobalt site percentage as noted previously^{1,2}.

References :

1. Feng, P.Y., Bu, X.H., Tolbert, S.H. & Stucky, G.D., (1997), J Am. Chem. Soc. 119, 2497-2504.
2. Rae, A.D., RAELS96 (1996) A Comprehensive Constrained Least-Squares Refinement Program, ANU, Canberra, Australia.
3. Gainsford, G.J., Morgan, K.R. & Rae A.D. (1998), Acta Cryst. C54, 000-000.

A RESTRAINED REFINEMENT DETERMINATION OF INTERSTITIAL OXYGENS AND Ce^{III}/Ce^{IV} ORDERING IN THE CeTaO_{4+x} (x = 0.17) SUPERSTRUCTURE.

A. David Rae, John G. Thompson, Nina Bliznyuk and Ray L. Withers, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.

Ce^{III}TaO₄ is stable in air above 1265 °C. Below this temperature it unmixes in air to form Ce^{IV}O₂ and Ce^{III}Ta₃O₉. However rapid quenching allows Ce^{III}TaO₄ to be obtained as a single phase at room temperature ($a = 7.6161(3)$, $b = 5.5254(2)$, $c = 7.7588(3)$ Å, $\beta = 100.87(2)^\circ$, $P2_1/c$, $Z = 4$,) and there is a known structure from neutron diffraction on a powder. A recent electron diffraction study showed that the phase generated when Ce^{III}TaO₄ is annealed in air at 650 °C had probable space group $P2_1$ ($a = 7.616(2)$, $b = 16.459(5)$, $c = 7.704(2)$ Å, $\beta = 102.48(2)^\circ$) and is a superstructure with 3 times the previous b axis. At the end of the stability field it has the approximate composition Ce^{III}₄Ce^{IV}₂Ta₆O₂₅ with $Z = 2$, i.e. cell contents of 12 CeTaO₄ + 2 O. We propose a structure in which a single interstitial O and its 2_l related equivalent are included per three unit cells of the CeTaO₄ structure with a subsequent adjustment to the structure.

We have determined the structure from this starting model using restrained refinement procedures available in the program RAELS. Initial models did not use diffraction data, simply restraining atoms to comply with bond valence requirements and to obey bounds on interatomic distances while staying near their positions from the previous cycle. An essential feature was the selection of which Ce were the Ce^{IV} and determining what criteria defined a satisfactory answer as comparable bond valence sums could be obtained from any initial choice.

The preferred answer involved the least structural adjustment and had the 4 inequivalent Ce surrounding the interstitial O as Ce^{III}. The interstitial O pushes away the adjacent O atoms towards the remaining two Ce sites in the asymmetric unit and these become the Ce^{IV} sites. The Ce^{IV} sites have smaller Ce - O distances and a lower coordination number. Subsequent refinement included reflection intensities obtained from X-ray powder data and enabled an already satisfactory model to become even better.

The program RAELS designed for single crystal least squares refinement was used in conjunction with the standard Rietveld refinement program GSAS. The XRD profile was refined using only 15 non atomic variables. Observed intensities were extracted from this analysis and these were used as input to RAELS to enable the restrained refinement of the atomic parameters. Refinement converged with $R(F) = 0.047$, $R(F^2) = 0.063$ and $wR(I) = 0.040$. Details of the restraints used and the final structure will be presented.

CHIRO-INOSITOL PHOSPHORUS LIGANDS

Cees Lensink

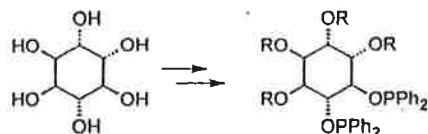
Industrial Research Limited

PO Box 31-310, Lower Hutt

New Zealand

Both D- and L-*chiro*-inositol enantiomers are readily available. We have explored the use of these natural resources (part of which is of New Zealand origin) in homogeneous catalytic applications. In many instances it is not always possible to synthesize, economically, both enantiomers of an asymmetric homogeneous catalyst from natural resources; however, the availability of both *chiro*-inositol enantiomers allows us to explore the development of complementary (i.e. mirrored) catalyst systems and libraries.

A suitable synthetic strategy was developed and this paper will report on recently synthesized novel ligands and catalytic studies.



Precision Potentiometry as a means of Investigating the low pH Solution Chemistry of Metal Complexes

Gerhard F. Swiegers

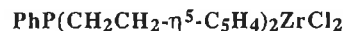
CSIRO Molecular Science, Pvt. Bag 10, Rosebank, Clayton, VIC 3169, Australia

Investigation of the aqueous solution chemistry of metal complexes in the pH range 1.5 - 3.0 can constitute a significant challenge since protons often compete very effectively for coordination of the ligands under these conditions. However, several industrial and extractive techniques involve low pH mixtures, so that the development of a useful research technique in this regard has significant advantages.

The standard means of determining the stability constants of metal complexes in such cases is by a competition method entailing potentiometric titration of metal and ligand at buffered pH's in this range. Because of the competition with protons however, this technique often relies on tiny quantities of metal chelate species present (as a proportions of the total metal or ligand) in the experimental solution. In principle, greater accuracy and detail may be obtained in such studies by combining the results of a series of potentiometric titrations at different ligand: metal ratio's in which the proton concentration is varied over the entire available pH range.¹ Data in which the competition of protons for the ligand is smallest can then be included in the calculations. However, such an approach requires exceptional precision to allow an accurate combination of the data obtained. This poster details a study of this type in which various procedures and precautions have been employed to assess and achieve the precision required.

¹ J. G. H. du Preez, G. F. Swiegers *J. Chem. Soc. DaltonTrans.* 1995, 2697 and references therein.

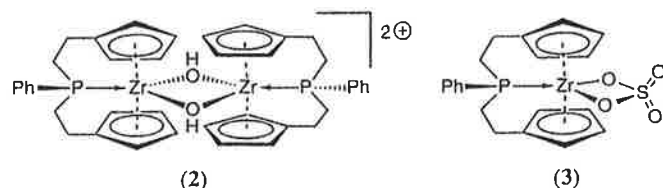
INVESTIGATIONS INTO THE AQUEOUS CHEMISTRY OF THE FIVE-COORDINATE ZIRCONOCENE COMPLEX



James R. Butchard, Owen J. Curnow*

Department of Chemistry, University of Canterbury, Private Bag 4800,
Christchurch, New Zealand

Phosphine ligands and cyclopentadienyl ligands are two of the most important classes of ligands in organometallic chemistry; this is largely because it is reasonably easy to tune their steric and electronic properties. There are relatively few tethered bis-cyclopentadienyl ligands that contain an additional functional group which is able to coordinate to the same metal centre as the two cyclopentadienyl groups. The bis-cyclopentadienyl-phosphine ligand, $[\text{PhP}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2]^{2-}$, $((\text{bcep})^{2-})$, provides an example of a ligand which exhibits such a coordination mode. The aqueous chemistry of the five-coordinate zirconocene dichloride complex $(\text{bcep})\text{ZrCl}_2$ (1) in which the phosphorus atom is also coordinated to the zirconium atom and tethered to both cyclopentadienyl rings will be presented. The complexes $[(\text{bcep})\text{Zr}(\mu\text{-OH})_2][\text{BPh}_4]_2$ (2) and $(\text{bcep})\text{Zr}(\text{SO}_4)$ (3) have been synthesised from (1) and structurally characterised.



CHEMICAL OXIDATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH's) USING FERRIC COMPLEXES

Deborah Traynor and David Weatherburn

School of Chemical and Physical Sciences

Victoria University of Wellington, Wellington, New Zealand

PAH's are ubiquitous in the environment, but are present in relatively high concentrations in the soils of manufactured gasworks sites. Previously PAH's have been found to be relatively difficult to degrade, other methods of remediation have either had limited success or significant disadvantages.

Over recent years chemical oxidation, either on its own or to enhance bioremediation, has generated a lot of interest with respect to remediation of contaminated soils. Fenton's Reagent, ferrous salt in conjunction with hydrogen peroxide, is capable of oxidising many organic compounds under acidic aqueous conditions. Using a Fenton-like system of ferric complexes and hydrogen peroxide, the pH of the system is relatively neutral, similar to that of soils avoiding the need for soil acidification. Ferric complexes are also more efficient catalysts than ferrous salts in Fenton systems.

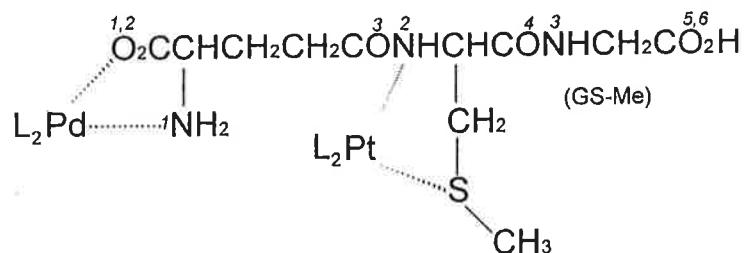
The results from a series of buffered and unbuffered reactions will be presented.

THE REACTION BETWEEN PLATINUM (II) AND PALLADIUM (II) COMPLEXES AND S-METHYLGLUTATHIONE (GS-Me)

Huy Hoang, Trevor G. Appleton, and G. Ade Ayoko
Department of Chemistry, University of Queensland, Brisbane Qld 4072

Tripeptides present metal ions with a choice of potential donor atoms. In a recent review¹, Appleton showed that the thermodynamic and kinetic stabilities of the complexes formed and sizes of the potential chelate rings play crucial roles in determining the donor atom preferences.

We report in the present study, the reaction of the tripeptide model, GS-Me, which presents six coordination sites (S, N₁, N₂, N₃, O_{1,2}, O₃, O₄, O_{5,6}) to platinum (II) and palladium (II) complexes, *cis*-ML₂(H₂O)²⁺ (M= Pd, L= ½(en); M= Pt, L= NH₃, ½(en)).



Multinuclear NMR studies showed that its reaction with L₂Pt (II) complexes gave S, N₂ five membered chelate rings as the main products. In the Pt (II) complexes with L= NH₃, the ammine trans to S was lost in reactions carried out at pH > 7. With (en)Pd (II) complexes, the main products contained N₁, O₁ five membered rings at pH < 7.

1. Appleton, T.G, *Coord. Chem. Rev.*, **166**, (1997) 313.

Fullerene-Porphyrin Cocrystallates

Michael C. Hodgson, Peter D. W. Boyd, Penelope J. Brothers, Allen G. Oliver and

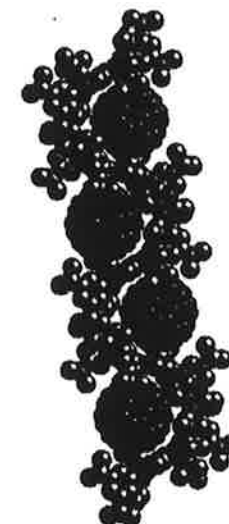
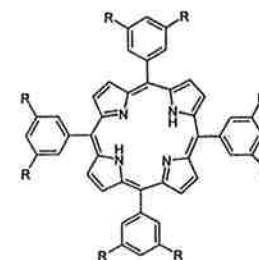
Clifton E. F. Rickard

Chemistry Department,
The University of Auckland
Auckland
New Zealand

Christopher A. Reed

Chemistry Department
University of California
Riverside, California
USA

It has recently been discovered that an intermolecular attraction exists between the purple chromophores C₆₀ and tetraphenylporphyrin¹. This paper reports the x-ray crystal structures of a series of compounds formed by cocrystallisation of the fullerene C₆₀ or C₇₀ with a series of tetraphenylporphyrin derivatives (TXP, R=Me; TBP, R=t-Bu; TPP, R=H; T_{ph4}PP, R₁=H, R₂=-NHCO-tBu).

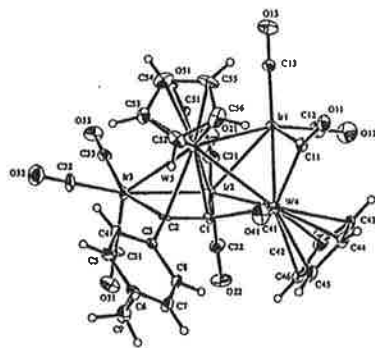


The effects on the stoichiometry, lattice assembly and intermolecular distances with phenyl substituents are described.

1. Sun, Y.; Drovetskaya, T.; Bolskar, R. D.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Org. Chem.* **1997**, *62*, 3642-3649

Susan M. Waterman,^a Mark G. Humphrey,^a and David C. R. Hockless.^b^aDepartment of Chemistry, Australian National University, Canberra, ACT 0200, Australia^bResearch School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Mixed-metal clusters incorporating disparate metals are of significant interest for a variety of reasons, including the possibility of bond selectivity by organic substrates.¹ Shapley and co-workers have previously reported the reaction of the tungsten-iridium mixed-metal clusters $\text{Cp}_x\text{W}_x\text{Ir}_x(\text{CO})_{12-x}$ ($x = 1$ or 2) with internal acetylenes.² Extension of the earlier studies to include terminal acetylenes and "inorganic acetylenes" such as alkynylmetal complexes is logical;³ the latter potentially affords a method of expanding the metal core under controlled conditions. Reactions of $\text{CpWIr}_3(\text{CO})_{11}$ (**1**) with equimolar amounts of tungsten acetylides $\text{CpW}(\text{CO})_3(\text{C}\equiv\text{CR})$ afford the products $\text{Cp}_2\text{W}_2\text{Ir}_3(\mu_4-\eta^2-\text{C}_2\text{R})(\mu-\text{CO})(\text{CO})_9$. The tolylacetylene adduct has been structurally characterized, with the structural study revealing an edge-bridged tetrahedral metal core geometry and an unusual $\mu_4-\eta^2$ ($3\sigma + \pi$)-coordinated alkynyl ligand. The reaction corresponds to formal insertion of the alkynyltungsten reagent into an Ir-Ir linkage of **1**. Reactions of $\text{Cp}_2\text{W}_2\text{Ir}_2(\text{CO})_{10}$ (**2**) with these tungsten acetylides were not successful under the experimental conditions attempted. In contrast, **2** reacts with terminal alkynes by insertion into the W-W bond to afford $\text{Cp}_2\text{W}_2\text{Ir}_2(\mu_4-\eta^2-\text{RC}_2\text{H})(\mu-\text{CO})_4(\text{CO})_4$, but does not react with tungsten acetylides. Reasons for these differences will be presented.

1. Waterman, S. M.; Lucas, N. T.; Humphrey, M. G. *Adv. Organomet. Chem.*, in press.2. Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. *Organometallics* 1984, 3, 1595; Shapley, J. R.; Humphrey, M. G.; McAteer, C. H. In *Selectivity in Catalysis*, ACS Symposium Series, vol. 517, Davis M., Suib, S. Eds; ACS, Washington, DC, 1993, ch 9.3. Waterman, S. M.; Humphrey, M. G.; Tolhurst, V.-A.; Bruce, M. I.; Low, P. J.; Hockless, D. C. R. *Organometallics*, in press.

Lyall Hanton and Paula Caradoc-Davies

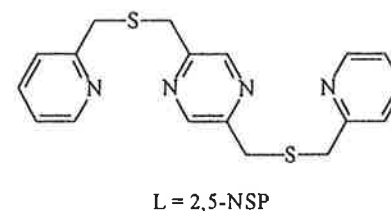
Chemistry Department, University of Otago, PO Box 56, Dunedin New Zealand

Email: lhanton@alkali.otago.ac.nz, paulag@alkali.otago.ac.nz

The construction of porous coordination materials using rigid spacers (eg. pyrazine and 4,4'-bipyridine) is currently of considerable interest. The key role which weak interactions such as H-bonding and π - π interactions play in stabilising molecular arrays is also of particular interest.

Our aim was to design a new type of polymeric building block which retained some of the elements of the traditional metal-linkers, but in addition had a degree of flexibility and slightly different coordination sites. The incorporation of extensive aromaticity within the ligand structure was intended to promote the packing of the coordination polymers through π - π interactions.

We report the synthesis of a Cu(II) proto-polymer held together in two-dimensional sheets via π - π interactions at graphitic distances. This successful probe into the potential polymeric coordination of the ligand lead to the synthesis and characterisation of a second polymer containing iodide bridged Cu(I) moieties.

 $[\text{Cu}_2\text{I}_2\text{L}]_\infty$ 

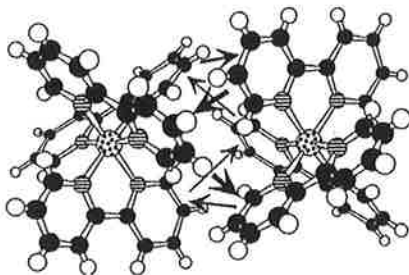
INORGANIC SUPRAMOLECULAR MOTIFS FORMED BY M(BIPY)₃ AND M(TERPY)₂

Marcia Scudder, Harry Goodwin and Ian Dance

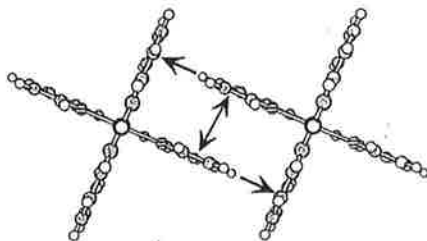
School of Chemistry, University of New South Wales, Sydney 2052.

We have reported motifs which exist in compounds containing highly phenylated species, such as the cation, [Ph₄P]⁺. In particular, there are two common motifs, the sextuple phenyl embrace, the 6PE and the parallel quadruple phenyl embrace, the P4PE. The attractive nature of these motifs arises from a concerted ring of six edge-to-face phenyl...phenyl interactions in the case of the 6PE and a combination of two edge-to-face interactions with an offset face-to-face interaction in the case of the P4PE.

We have found that there are analogous attractive motifs in the crystal structures of metal complexes of the ligands, 2,2'-bipyridine, [M(bipy)₃]²⁺, and 2,2':6',2''-terpyridine, [M(terpy)₂]²⁺. In each case, there is infinite extension of the motif, as chains of [M(bipy)₃]²⁺ and as layers of [M(terpy)₂]²⁺.



[M(bipy)₃]²⁺



[M(terpy)₂]²⁺

The aryl...aryl interactions are indicated by the arrows, single ended arrows in the case of the edge-to-face interactions and double ended for offset face-to-face.

Both motifs frequently occur in high-symmetry crystal structures, hexagonal in the case of [M(bipy)₃]²⁺ and tetragonal for [M(terpy)₂]²⁺. Depending on the size and shape of the associated anions, there can be modifications to lower symmetry in each case, but the robust motif is almost always retained. The characteristics and occurrences of these concerted supramolecular motifs will be presented.

MIXED-LIGAND THIOETHER COMPLEXES OF RUTHENIUM(II)

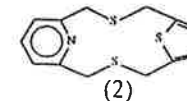
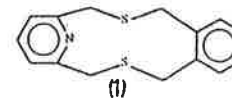
Julia M. Turnbull and Lyall R. Hanton

Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand

email: juliat@alkali.otago.ac.nz

Several mixed-ligand thioether complexes of Ru(II) have been synthesised and characterised. Two thioether ligands noxs (1) and ttp (2) were reacted with [(9S3)Ru(MeCN)₃]²⁺ to produce the coordination compounds.

¹H nmr shows the complexed ligands are coordinated quite differently to the Ru(II) centre. In the [(9S3)Ru(ttp)]²⁺ complex, the ligand ring sulfur acts as a donor atom rather than the other, more electron-donating bridging sulfur atom. These and other mixed-ligand thioether complexes of Ru(II) and Cu(I) will be presented.

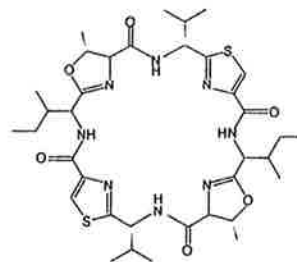


^AThe Chemistry Department, ^BThe Centre for Drug Design and Development and ^CThe
Centre for Magnetic Resonance, The University of Queensland, Brisbane 4072.

^DThe School of Chemistry, The University of Sydney, Sydney 2006.

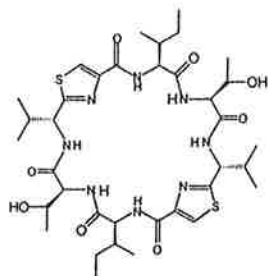
Over the last few decades, a range of cyclic peptides
have been isolated and/or synthesised and the
complexation with metal ions investigated.¹

Our interest in this field stems from the discovery
that a class of cyclic peptides containing unusual amino
acids such as aminoalkyl(oxazoline/thiazole)carboxylic
acids and D-amino acids are capable of complexing
various metals including copper and zinc. A crystal
structure of the dinuclear copper complex of one of these peptides,
ascidiacyclamide (1), also reveals the added ability of these peptides to complex carbonate
ions.² Analogues (2 and 3) of ascidiacyclamide have been synthesised to investigate the
relationship between conformation functional group and complexing ability. Complexation
studies utilising NMR and CD spectroscopy, and stability constants for zinc and calcium-
peptide complexes, will be reported.

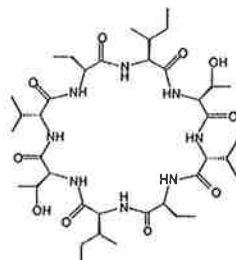


(1)

(2)



(3)



1. Karle, I. L. *Proc. Natl. Acad. Sci. USA*, **82**, 7155-7159, 1985.
2. van den Brenk, A. L.; Byriel, K. A.; Fairlie, D. P.; Gahan, L. R.; Hawkins, C. J.;
Jones, A.; Kennard, C. H. L.; Murray, K. S. *Inorg. Chem.*, **33**, 3549-3557, 1994.

W21

POSTERS

ACTIVATION OF MOLECULAR O₂ DURING THE REACTIONS OF CHROMIUM(VI/V/IV) WITH BIOLOGICAL REDUCTANTS: IMPLICATIONS FOR CHROMIUM-INDUCED GENOTOXICITIES

Peter A. Lay and Aviva Levina

School of Chemistry, University of Sydney, Sydney 2006 NSW, Australia

Chromium(VI) compounds are among the most important occupational carcinogens found
in industry. Recent studies [1] have implicated important roles for both Cr(V/IV) intermediates
and O₂ in Cr(VI)-induced genotoxicities. In the current work [2], the first systematic study on the
roles of O₂ in the reactions of Cr(VI/V/IV) with major intracellular reductants: cysteine (1),
glutathione (2), ascorbic acid (3), as well as with vitamin E analog Trolox (4), has been
performed. The reactions of 1-3 with Cr(VI) (aqueous buffer solutions, pH = 4.5-7.5, 25 °C) led
to a slow O₂ consumption (measured by a Clark oxygen electrode). The reactions of 1-3 with the
relatively stable Cr(V) and Cr(IV) 2-ethyl-2-hydroxybutanoato complexes under the same
conditions were accompanied by fast O₂ consumption. The O₂ consumption during the reactions
of Cr(VI/V/IV) with 1-3 did not lead to a significant accumulation of H₂O₂ (determined with
catalase). No significant O₂ consumption was detected for the reactions of Cr(VI/V/IV) with 4.
To reveal the mechanisms of O₂ activation, the kinetics of the Cr(V/IV) reactions with 1-4 at pH
4.5 and 7.5 were studied by stopped-flow UV-visible spectrophotometry; and the kinetic data
were processed by the global analysis method. The stoichiometries and products of these
reactions were studied by UV-visible, CD, and EPR spectroscopies. The proposed mechanisms
of O₂ activation include: oxidations of 1-4 by Cr(V/IV) to produce organic radical intermediates,
which then react with O₂ in chain processes. No evidence was found for the direct activation of
O₂ by the Cr compounds. Implications of the proposed mechanism for understanding the DNA
damage induced by the Cr(VI) + reductant + O₂ systems will be discussed.

References:

- [1] (a) Kortenkamp, A.; Casadevall, M.; Da Cruz Fresco, P.; Shayer, R. O. *J. NATO ASI Series, Ser. 2* **1997**,
26, 15-34. (b) Stearns, D. M.; Wetterhahn, K. E. *NATO ASI Series, Ser. 2* **1997**, 26, 55-72 and references
therein.
- [2] Lay, P. A.; Levina A. *J. Am. Chem. Soc.* **1998**, *120*, 6704-6714.

W22

INVESTIGATION INTO THE COORDINATION OF METAL IONS BY PENTAАЗA PENDANT-ARM MACROCYCLIC LIGANDS.

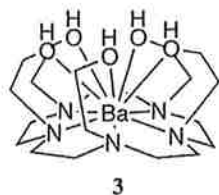
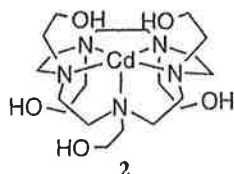
Kylie M. Tonkin*, Stephen F. Lincoln[†], and Kevin P. Wainwright*.

* Department of Chemistry, Flinders University of South Australia, GPO Box 2100, Adelaide, 5001
and [†]Department of Chemistry, University of Adelaide, Adelaide 5005.

Studies into the coordination of metal ions by pentaaza pendant-arm macrocycles has been limited, when compared with derivatives of smaller polyaza macrocyclic ligands such as cyclen. In this study the macrocycle 1,4,7,10,13-pentakis(2-hydroxyethyl)-1,4,7,10,13-pentaazacyclopentadecane (phec15), **1**, has been prepared and an investigation into its complexation properties has been undertaken.

The stability constants of several metal-ion/phec15 complexes were obtained from potentiometric studies performed in aqueous solution and indicate that complexes with stoichiometry MLH^{3+} , ML^{2+} , and $MLOH^+$ are formed. The order of stability of complexes of **1** was determined to be $Cu^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Ba^{2+}$.

¹³C nuclear magnetic resonance studies have shown that ligand **1** adopts a folded conformation when complexed with cadmium(II) as shown in structure **2**. On the other hand when complexed with larger metal ions such as barium(II), which is capable of adopting a 10 coordinate structure, **1** has a planar conformation. In the latter case, the macrocyclic ring adopts an arrangement with all five nitrogens coordinating to the central metal ion as shown by structure **3**.



This arrangement, in which all arms are projected in the same direction, is desirable in terms of the ligands potential to act as a metal ion activated molecular receptor for large molecules which have 5-fold symmetry.

REACTIONS OF IMINODIACETATE BOUND TO COBALT(III) AS A DIDENTATE LIGAND

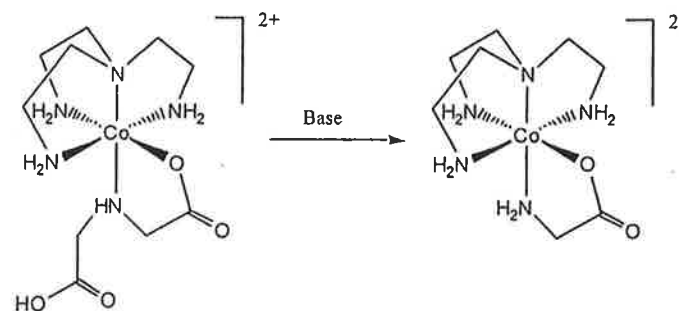
Richard M. Hartshorn

Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

Iminodiacetate (IDA^{2-}) is a potentially tridentate ligand, and there are many complexes described in the literature where it coordinates in this manner. This project was undertaken in order to explore the chemistry of complexes where this ligand is bound as a didentate ligand.

The tetradentate ligand tris(2-aminoethyl)amine (tren) was chosen to occupy the remaining four coordination sites on the cobalt(III) ion as it should be a sufficiently good ligand to minimise substitution by a tridentate ligand, while at the same time avoiding production of the diastereoisomers that would result from the use of bis(didentate) coordination in conjunction with the coordinated secondary amine of the amino acid.

This poster will describe the synthesis and reactivity of the $p-[Co(tren)(IDA)]^{2+}$ ion and related compounds. For example, treatment of the IDA^- complex with aqueous base gives rise to the $p-[Co(tren)(gly)]^{2+}$ ion, as shown below.



The low yield and production of significant amounts of cobalt(II) during the reaction may imply a mechanism involving oxidation of the ligand at the expense of the metal ion. The results of crossover studies, employing bis(1,2-diaminoethane) complexes, and other experiments, are consistent with this proposal.

SUPRAMOLECULAR ASSEMBLIES OF 1,2-DICARBADODECABORANE(12) AND CALIX[5]ARENE.

Michael J. Hardie and Colin L. Raston, Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia.

The carboranes *o*-, *m*-, and *p*-C₂B₁₀H₁₂ [1,2-, 1,7-, 1,12-dicarbododecaborane(12)] are stable icosahedral cage compounds. The C-H groups are acidic and hydrogen-bonded complexes incorporating carboranes have recently been reported [1]. *o*-Carborane can also be involved in host-guest chemistry, forming complexes with a number of different host molecules such as α -, β -, γ -cyclodextrins, diaza-18-crown-6 and cyclotrimeratrylene (=CTV) [2].

Treatment of *o*-carborane with the bowl-shaped container molecule calix(5)arene affords 1:1, 1:2 and 2:1 host-guest complexes, which display a remarkable range of supramolecular interactions. The solid state structures of the complexes have been determined from low temperature X-ray diffraction data. The supramolecular systems contain the bowl-shaped host calixarene and globular guest carborane in a ball-and-socket assembly, similar to that reported for (*o*-carborane)(CTV)₂ [2c]. Beyond this, however, the complexes show quite distinct modes of association and form entirely different nano-structures, dependent on both stoichiometry and crystallisation solvent.

(*o*-Carborane)(calix(5)arene)₂-
(dichloromethane)_{0.5}, for example, features a bowl-shaped calix(5)arene acting as a secondary host for the (*o*-carborane)(calix(5)arene) ball-and-socket as shown in Figure 1. The complex shows a number of types of supramolecular interactions such as non-classical hydrogen bonding and π stacking.

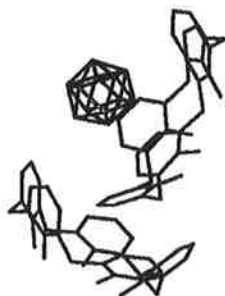


Figure 1: (*o*-carborane)(calix(5)arene)₂

- [1] M. G. Davidson, T. G. Hibbert, A. K. Howard, A. Mackinnon and K. Wade, *Chem. Commun.*, 1996, 2285.
[2] (a) A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1988, 1352; (b) P. D. Godfrey, W. J. Grigsby, P. J. Nichols and C. L. Raston, *J. Am. Chem. Soc.*, 1997, 119, 9283; (c) R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kaddour and C. L. Raston, *Angew. Chem., Int. Ed. Engl.*, 1997, 36, 504.

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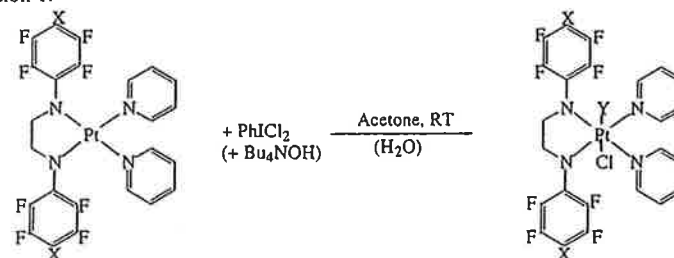
Oxidation of Organoamidoplatinum(II) Complexes with Iodobenzene Dichloride

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[N,N'-Bis(polyfluorophenyl)ethane-1,2-diaminato(2-)]dipyridineplatinum(II) complexes are easily oxidised by iodobenzene dichloride (equation 1). As shown below in brackets, mixed complexes can also be synthesised when the organoamidoplatinum(II) is in the presence of hydroxide ions when the oxidant is added.

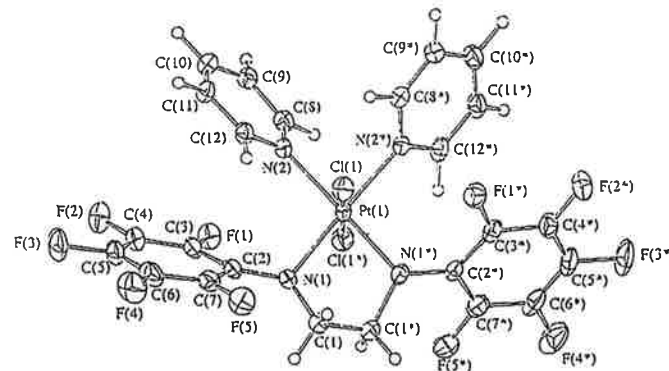
Equation 1:



Where X = H, F, Br or I and Y = Cl (or OH)

These complexes have been characterised by various spectroscopic techniques and X-ray crystal structures have been solved when X = F and Y = Cl (figure 1) and OH, and when X = H and Y = OH.

Figure 1: An Ortep diagram of *cis,trans,cis*-[N,N'-bis(pentafluorophenyl)ethane-1,2-diaminato(2-)]dichlorodipyridineplatinum(IV)



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Thermalisation of TiCl_4 with a variety of substituted phenols HOAr [$\text{Ar} = \text{C}_6\text{H}_4\text{CMe}_3$ - 4; $\text{C}_6\text{H}_3(\text{CMe}_3)_2$ - 3,5; $\text{C}_6\text{H}_2\text{Me}_3$ -2,4,6; $\text{C}_6\text{H}_3\text{Pr}^i_2$ - 2, 6; $\text{C}_6\text{H}_2(\text{CMe}_3)_2$ - 2, 6-Me - 4; $\text{C}_6\text{H}_3(\text{CMe}_3)_2$ - 2, - 2, 4; $\text{C}_6\text{H}_4\text{Ph}$ - 2 and C_{10}H_7] in hydrocarbon solvents gives high yields of the trichloromonophenoxide complexes $[\text{TiCl}_3(\text{OAr})]$ or the dichlorobisphenoxide complexes $[\text{TiCl}_2(\text{OAr})_2]$ depending on the ratio of reactants used. The complexes are monomeric in benzene and expand their coordination sphere on reacting with 4, 4'- dimethyl-2, 2'-bipyridyl (dmbipy) giving the complexes $[\text{TiCl}_3(\text{OAr})(\text{dmbipy})]$ and $[\text{TiCl}_2(\text{OAr})_2(\text{dmbipy})]$. The $[\text{TiCl}_3(\text{OAr})]$ and $[\text{TiCl}_2(\text{OAr})_2]$ complexes are the phenoxide analogues of $[\text{TiCl}_3(\text{Cp})]$ and $[\text{TiCl}_2\text{Cp}_2]$ ($\text{Cp} = \text{cyclopentadienide}$) and polymerise olefines in the presence of trimethylaluminium but with greater activity in the presence of methylaluminoxane.

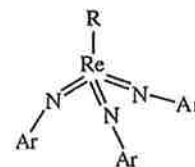
AN INVESTIGATION OF STERIC EFFECTS ON THE STRUCTURE OF Re IMIDO COMPLEXES

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The synthesis of a variety of π -loaded complexes with mixed imido ligands has been carried out (Fig.

- 1). The formation of mixed ligand complexes enables us to produce compounds with differing degrees of steric congestion.



$\text{R} = \text{Cl}, \text{Me}, p\text{-Tol}$
 $\text{Ar}, \text{Ar}' = \text{Aromatic Groups}$

Figure 1

The synthesis and reactivity of complexes of the type $\text{Re}(\text{NAr})_2(\text{NAr}')\text{R}$ will be illustrated.

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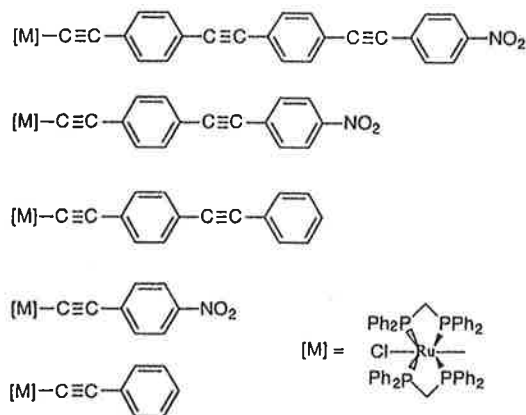
^b Cooperative Research Centre for Photonics, Laser Physics Centre,

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In nonlinear optical (NLO) materials, a logarithmic relationship is usually assumed to occur between the length of the π -conjugated system (L) and the quadratic NLO coefficient β , represented by $\beta = kL^\eta$ where η is the exponential factor and k is a constant. Semiempirical ZINDO calculations suggest that whereas polyene systems do not saturate until $n \approx 20$,¹ polyynes should saturate their NLO responses at very short conjugation lengths ($n = 2$ or 3), where n equals the number of arylyne linkages. An increase in the cubic NLO coefficient γ with chain lengthening of unsaturated organic molecules has also been observed.

The effect of chain-lengthening on the NLO responses of organometallic complexes is as yet unknown. With this in mind we have synthesized a series of complexes with a varying number of $C_6H_4C\equiv C$ - groups ($n = 0 - 2$), and have analyzed their quadratic and cubic NLO responses.



ELECTROSPRAY MASS SPECTROMETRY OF METAL INTERACTION WITH POLYAMINOALCOHOL LIGANDS

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Electrospray mass spectrometry (ESMS) is a soft ionization technique¹ that has been successful in the study of large biomolecules such as proteins and oligonucleotides² and is gaining increased application in the characterization of large of inorganic and organometallic systems^{3,4}. One of the most productive areas of investigation involving ESMS has been the detection and analysis of metal ion complexes. Applications include the study of gas phase metal ion chemistries and the formation of metal ion adducts to assist in the detection and structural elucidation of organic ligands, including those important to biochemical processes. Recently, we reported the use of ESMS to follow metal ion exchange in dinuclear macrocyclic complexes,⁵ pointing to the potential of the technique to aid mechanistic studies.

The aims of the present study were (i) to characterize polyaminoalcohol ligands such as kanamycin (L¹), neomycin B (L²), neamine (L³), 2-deoxystreptamine (L⁴), ethanolamine (L⁵) and propanolamine (L⁶) using ESMS, and (ii) to evaluate ESMS as a technique for determination metal interaction (such as Cu(II), Zn(II), Cd(II), Hg(II), Fe(II), Fe(III), Co(II) and Ni(II)) with these ligands to form metal complexes.

The preliminary results of the fragmentation patterns of the molecular ions of the complexes at different sample cone voltages and in several solvents will be discussed. Complexes detected will be described.

References

1. Fenn, J.B.; Mann, M.; Meng, C.K.; Wong, S.F.; Whitehouse, C.M. *Mass Spectrom. Rev.* 1990, 9, 37.
2. Smith, R.D.; Loo, J.A.; Edmonds, C.G.; Barinaga, C.J.; Udseth, H.R. *Anal. Chem.* 1990, 62, 882.
3. Colton, R.; Agostino, D.A.; Traeger, J.C. *Mass Spectro. Rev.* 1995, 11, 48.
4. Lau, T.C.; Wang, J.; Guevremont, R.; Siu, K.W.M. *J. Chem. Soc., Chem. Commun.* 1995, 877.
5. Sutrisno; Baran, Y.; Lawrance, G.A.; von Nagy-Felsobuki, E.I.; Richens, D.T.; Xiao, H. *J. Chem. Soc., Chem. Commun.*, 1998, submitted.

1. D.R. Kanis, M.A. Ratner and T.J. Marks, *Chem. Rev.* 1994, 94, 195-242.

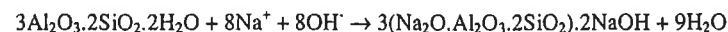
REACTIONS OF KAOLIN IN THE PROCESSING OF BAUXITE ORES

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^a School of Chemistry, University of Melbourne, Parkville, Victoria, Australia, 3052

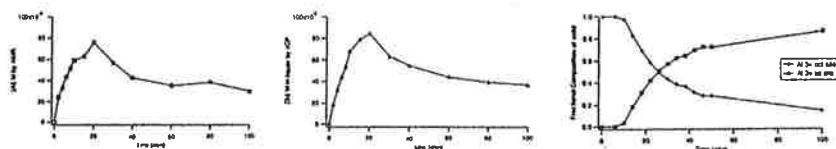
^b Comalco Research and Technical Support, Thomastown, Victoria, Australia, 3074

Bauxite ores, primarily a mixture of hydrated aluminium oxides, are refined to gibbsite ($\text{Al}(\text{OH})_3$) by dissolution in superheated concentrated sodium hydroxide and reprecipitation from the cooled liquor in the Bayer Process. The raw bauxite ore also contains iron oxides, organic materials, quartz and aluminium silicates such as kaolinite. Kaolinite undergoes reaction with caustic soda in the predesilication step of the Bayer Process resulting in the formation of an insoluble sodium aluminosilicate known as desilication product (DSP).



A major characteristic of Bayer type liquors is their ability to form supersaturated solutions of aluminate and silicate due to an imbalance of the kinetics of dissolution and the rate of crystallisation. ICP-AES and multinuclear solution NMR can be used to monitor liquor concentration changes and generic profiles of silicate and aluminate concentrations during DSP formation are characterised below.

We have also used ^{27}Al , ^{29}Si and ^{23}Na multinuclear magic angle spinning Nuclear Magnetic Resonance (MAS NMR) to obtain local structural information and quantify the transformation of kaolinite to DSP. Solid composition/time profiles have been used in combination with solution concentration/time profiles to determine the kinetics and mechanism of transformation of kaolinite to DSP.



Kinetic profiles of silicate and aluminate concentrations and solid state composition during reaction

A DETAILED STUDY OF THE DNA BINDING OF $\text{Pt}(\text{en})(\text{ibn})^{2+}$

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In order to have a better understanding of drug-DNA recognition at a molecular level, metal complexes have been widely used as DNA probes because of their structural rigidity.

Our laboratory has demonstrated that $\text{Pt}(\text{en})_2^{2+}$ (1) binds selectively at the AT regions of the minor grooves of the dodecanucleotides $\text{d}(\text{CAATCCGGATTG})_2$ and $\text{d}(\text{TCGGGATCCCGA})_2$.¹ However, due to the symmetry of the ligands, the exact binding mode of the metal complex could not be determined.

In the present study, 2D NMR spectroscopy and molecular modelling have been used to determine the structure of an asymmetric analogue, $\text{Pt}(\text{en})(\text{ibn})^{2+}$ (2), bound to $\text{d}(\text{CAATCCGGATTG})_2$. The results give a more detailed picture of the binding of the planar platinum complex and its effects on the structure of the DNA.



Abbreviations: en = ethylenediamine, ibn = isobutanediamine

¹ Franklin, C. A.; Fry, J. V.; Collins, J. G. *Inorg. Chem.* 1996, 35, 7541.

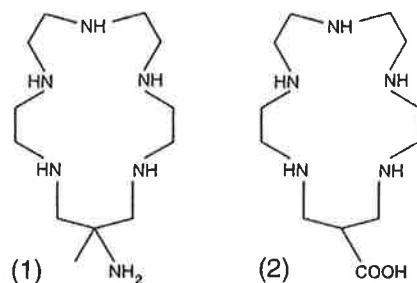
Mery Napitupulu,^a Paul V. Bernhardt,^b Geoffrey A. Lawrance^a and Gang Wei^a

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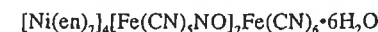
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Reports of pentaaza macrocycles with pendant arms have been quite rare. This has probably resulted from the paucity of investigations of pentaaza macrocycles of any type or else the perceived unsuitability of the large cavity for accommodation of most metal ions with simultaneous binding to the full set of donors. Pentaaza ligands with one pendant donor can in principle satisfy the coordination sphere of many metal ions, and if sufficiently flexible can encapsulate such ions effectively, a possibility probed in this study.

Copper(II)-directed condensation of the linear polyamine 3,6,9-triazaundecan-1,11-diamine (tetren) with formaldehyde and nitroethane in basic methanolic solution yields the sixteen-membered macrocyclic molecular cation (15-nitro-15-methyl-1,4,7,10,13-pentaazacyclohexadecane)copper(II). Reduction with HCl/Zn(Hg) yields the amine-pendant macrocycle (1) from this precursor as the metal-free hydrochloride salt. An analogue polyaminoacid (2) can also be prepared by a related template route.



Complexes of the hexamine (1) with cobalt(III), chromium(III) and iron(III) are reported, with the $[\text{CoN}_6]^{3+}$ complex characterised by an X-ray crystal structure analysis. This shows that the metal ion is encapsulated in the macrocycle, lying in the plane of four secondary amines, with the central secondary amine and the pendant primary amine in the *trans* (axial) sites.



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Rational design of molecular solid with desired network topology and function via an assembly of molecular building blocks attracts great attention recently. Blocks can be designed and synthesized before being assembled together through specific bonding or interaction. In addition, as the blocks are usually cooperated in the assembly, new properties may appear. By this method, we successfully designed and synthesized a new photo-functional metal-organic coordination polymer of $[\text{Ni}(\text{en})_2]_4[\text{Fe}(\text{CN})_5\text{NO}]_2\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ (en = ethylenediammine).

This compound was obtained by mixing $[\text{Ni}(\text{en})_2]\text{Cl}_2$ and $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ in water solution. X-ray diffraction shows that it is crystallized as monoclinic. $[\text{Fe}(\text{CN})_6]^{2-}$ and Ni form a one dimensional wave-like main chain along c axis. Photo-functional group of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ appends to the main chain through an Ni atom.

Photo-induced changes were firstly observed by both IR and UV-visible spectra below 200 K. IR spectrum shows that a blue light irradiation can transfer the vibration of NO in $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ from 1909 cm^{-1} to 1792 cm^{-1} . The low wavenumber side shift of $\nu(\text{NO})$ indicates the appearance of a metastable state of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ after irradiation, which can be explained by the photo-induced charge transfer from Fe to NO. The appearance of the metastable state after irradiation can also be observed by UV-visible spectrum, in which the absorbance in the range of 300 nm - 400 nm is increased. Additional experiment finds that changes in $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ affect the electronic structure of the main chain. All these changes can be recovered by a red light irradiation.

NOVEL BIS-IMIDAZOLE PALLADIUM CATALYSTS. A STUDY OF THEIR STRUCTURE BY THEORY AND PRACTICE.

Jeremy Rackham, Kingsley Cavell, Brian Yates

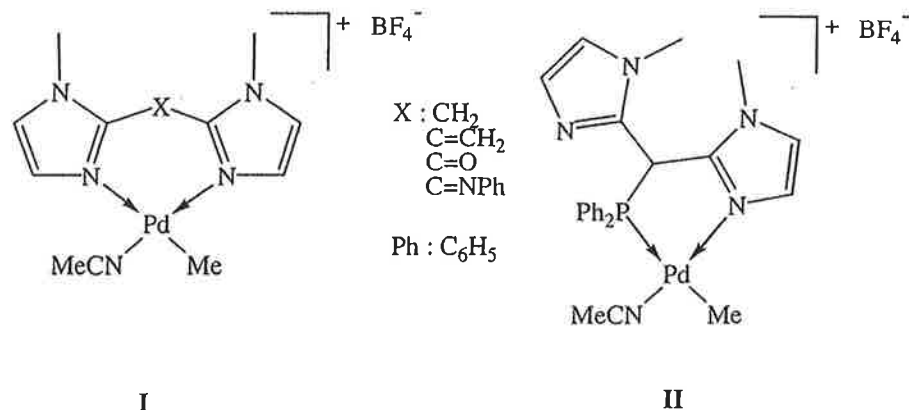
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Melvyn Kilner

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Complexes of bis-imidazoles with palladium, platinum, rhodium, zinc and iron have been known since the early 1980s.¹⁻⁹ In 1995 several new complexes of palladium were prepared by this research group which demonstrated interesting catalytic activity. The results from these complexes (I, X : CH₂, C=CH₂, C=O) ranged from decomposition with no activity (X : CH₂) to stable and reasonably active catalysts (X : C=O). The structure of the chelate, therefore, has a marked effect on catalytic activity. New catalysts (I, X : C=NH₂; II) have been prepared and catalytically tested

Since 1995, there has been an increased collaboration with a modelling group which has allowed a theoretical study of the reaction mechanism. The reaction mechanism has been modelled computationally using an *ab initio* level of theory to try to understand the results obtained, and to enable predictions to be made about the coordination of the reaction intermediates.



References:

1. Canty, A.J.; Lee, C.V. *Aust. J. Chem.* 1983, 36, 415
2. Gorun, S.M.; Papaefthymiou, G.C.; Frankel, R.B.; Lippard, S.J. *J. Am. Chem. Soc.* 1987, 109, 4244-4255
3. Byers, P.K.; Canty, A.J. *Organometallics* 1990, 9, 210-220
4. Reusmann, G.; Grehl, M.; Reckordt, W.; Krebs, B. *Z. Anorg. Allg. Chem.* 1994, 620, 199-209
5. Engelking, H.; Karentzopoulos, S.; Reusmann, G.; Krebs, B. *Chem. Ber* 1994, 127, 2355-2361
6. Grehl, M.; Krebs, B. *Inorg. Chem.* 1994, 33, 3877-3885
7. Chen, X.-M.; Xu, Z.-T.; Mak, T.C.W. *Polyhedron* 1995, 14, 319-322
8. Canty, A.J.; Traill, P.R.; Skelton, B.W.; White, A.H. *Inorg. Chim. Acta* 1997, 117-123
9. Elgafi, S.; Field, L.D.; Messerle, B.A.; Hambley, T.W.; Turner, P. *J. Chem. Soc., Dalton Trans.* 1997, 2341-2345

ZEROVALENT PALLADIUM AND NICKEL COMPLEXES OF HETEROCYCLIC CARBENES: OXIDATIVE ADDITION OF ORGANIC-HALIDES AND THE HECK REACTION.

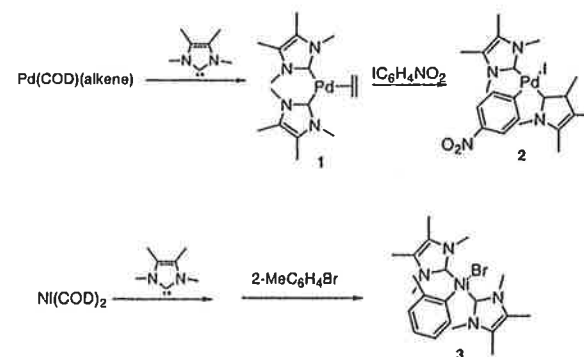
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Many transition metal catalysed processes have been shown to proceed via an initial oxidative addition to the metal, often to a d¹⁰ (Ni⁰, Pd⁰) centre stabilised by ancillary ligands. Recently, heterocyclic carbene complexes have been shown to have considerable potential as efficient catalysts for Heck (Pd) and Suzuki coupling (Pd,Ni)¹⁻⁵ and hydrosilylation (Rh),⁶ apparently owing to the stability imparted on the active species by the strong donor heterocyclic carbene ligands.

We report here the synthesis and characterisation of a number of novel zerovalent carbene complexes of Pd, and their subsequent reactions with a number of substrates to afford divalent complexes through oxidative addition. Furthermore, we present the synthesis of Ni^{II} carbene complexes via oxidative addition to Ni(tmiy)₂ and the first crystal structure of a hydrocarbylnickel complex containing heterocyclic carbene ligands **3** is reported. The stoichiometric reaction of **2** with an olefin has been studied and as a result a Pd⁰→Pd^{II} mechanism for the Heck reaction has been suggested.



- 1) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. *J. Angew. Chem.* 1995, 107, 2602.
- 2) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* 1998, 557, 93.
- 3) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* 1996, 129, 1483.
- 4) Albert, K.; Gisdakis, P.; Rösch, N. *Organometallics* 1998, 17, 1608.
- 5) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* 1998, 565, 165.
- 6) Herrmann, W.A.; Goosen, L.J.; Köcher, C.; Artus, G.R.J. *Angew. Chem.* 1996, 108, 2980.

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The Group 11 metal cyanides MCN (M = Cu, Ag, Au) consist of infinite linear chains in the solid state, with linear bridging cyanide ligands connecting the metal atoms within the chains.¹ There is essentially no chemical bonding between the chains, and this allows the binding of neutral and anionic ligands to the metal atoms in the chain. In many cases the infinite MCN structure is maintained, even when the ligand is a strong σ donor, such as PPh₃ or SbPh₃.²

In the present work, we have examined the interaction of MCN (M = Cu, Ag) with N-donor ligands L such as amines and nitriles. The MCN solids readily absorb such ligands from the liquid state to form adducts of the type described above, but with a wide variety of MCN:L stoichiometries, which result in some unusual structures. Thus, in AgCN/pyridine 10:9, every tenth Ag atom in the chain does not bear a pyridine ligand. In CuCN/MeCN 1:1 there is an MeCN ligand bound to every copper atom, but CuCN/PhCN 5:1 is shown by vibrational spectroscopy to be a one-dimensional polymer in which only every fifth copper atom in the chain is bound to a PhCN ligand.

The presence of excess ligand in the above cases does not result in the addition of further ligand molecules to the chains, so the stoichiometry seems to be a sensitive function of the binding strength of the ligand to the metal atom in the chain. The existence of regular structures in the case of high MCN/L ratios, together with the values of the $\nu(\text{CN})$ frequencies, suggest that electron density can readily be transmitted along the chains. Thus, the acceptor ability of a metal atom can be influenced by the binding of a ligand to another metal atom in the chain that is more than ten bonds away.

The structures, vibrational spectra, and possibly also the solid-state NMR spectra of the above and other related systems will be described.

¹ G. A. Bowmaker, B. J. Kennedy, J. C. Reid, *Inorg. Chem.*, 1998, 37, 3968-3974, 1998.

² G. A. Bowmaker, Effendy, J. C. Reid, C. E. F. Rickard, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 2139-2146.

Victoria M. Jones^a, F. Richard Keene^a and Louis M. Rendina^b

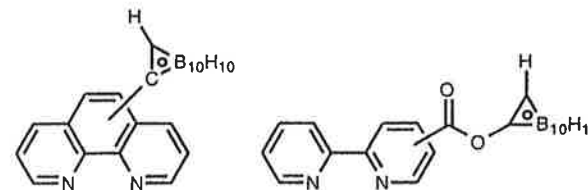
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^b Department of Chemistry, The University of Adelaide, Adelaide, SA 5005.

It has been recognised for many years that metalpolypyridyl complexes involving Ru(II) and Rh(III) can interact with DNA. The exact site and nature of this interaction remains a focal point for discussion, but it is clear that the chirality of the metal complex and the substituents on the ligands are important considerations in the design of molecules which selectively interact with DNA.¹ The fact that these complexes are able to interact with DNA makes them targets for the design of new anti-tumour reagents.

There has been a growing interest in the synthesis of boron-containing compounds for use in 'Boron Neutron Capture Therapy' (BNCT).² This technique has primarily been used to target brain tumours, but there has been a move to broaden its application to other tumours. We have been interested in determining whether boron clusters such as 1,2-carborane can be attached to a range of Ru(II) polypyridyl complexes with the ultimate aim of combining site-specific complex-DNA interaction with the BNCT technique.

This paper discusses the synthetic methodology we have employed for linking a carborane moiety to the backbone of 2,2'-bipyridine or 1,10-phenanthroline ligands.



1. M. Eriksson, M. Leijon, C. Hiort, B. Nordén and A. Gräslund, *Biochemistry*, 33, 5031-5040 (1994); R.H. Terbrugge and J.K. Barton, *Biochemistry*, 34, 8227-8324 (1995); I. Ortmans, C. Moucheron and A. Kirsch-De Mesmaeker, *Coord. Chem. Revs.*, 168, 233-271 (1998)
2. A.H. Holoway, W. Tjarks, B.A. Barnum, F. Rong, R.F. Barth, I.M. Codogni and J.G. Wilson, *Chem. Revs.*, 98(4), 1515-1562, (1998).

NOVEL PI-LIGAND EXCHANGE REACTIONS INVOLVING THREE-MEMBERED SULFUR AND PHOSPHORUS HETEROCYCLES

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Pi-ligand exchange is a well known phenomenon in organometallic chemistry,¹ but has not been observed hitherto in organic compounds. We have discovered that the three-membered heterocycle 1-methyl-1-phenylphosphiranium triflate (1) reacts with dimethylacetylene with displacement of ethylene to give the corresponding phosphirenium salt, 1,2,3-trimethyl-1-phenyl phosphirenium triflate (2).² The only other recorded exchange of ethylene on phosphorus occurs in a phosphirane-tungsten pentacarbonyl complex.³



High level ab initio calculations have revealed that insertion of the alkyne, although giving a thermodynamically favoured five-membered heterocycle, does not occur because of a relatively high energy barrier.⁴ Theoretical work indicates that similar sulfur heterocycles would also undergo pi-ligand exchange⁵ and we have experimental evidence to support the prediction.

¹ Chatt, J., Wilkins, R. G., *J. Chem. Soc.*, 1952, 2622; Boucher, H., Bosnich, B., *J. Am. Chem. Soc.*, 1977, 99, 6253.

² Hockless, C. R., McDonald, M. A., Pabel, M., Wild, S.B., *J. Organomet. Chem.*, 1996, 529, 189.

³ Marinetti, A., Charrier, C., Mathey, F., Fisher, J., *Organometallics*, 1985, 4, 2134.

⁴ Sølling, T. I., McDonald, M. A., Wild, S. B., Radom, L., *J. Am. Chem. Soc.*, 1998, 120, 7063.

⁵ Sølling, T. L., Wild, S. B., Radom, L., *paper in press*.

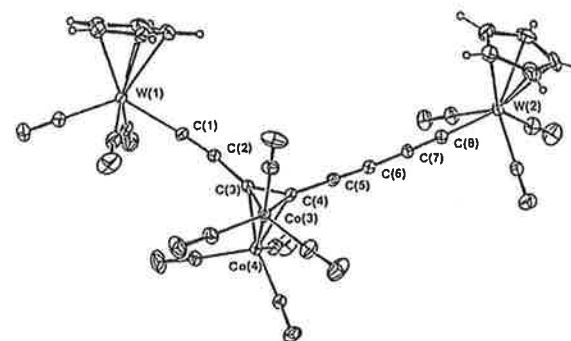
COBALT-STABILISED COMPLEXES OF THE DIMETALLATED TETRAYNE, {Cp(OC)₃W}-C≡C-C≡C-C≡C-C≡C-{W(CO)₃Cp}.

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Research into metal-capped carbon chains has assumed much interest recently, as they may be employed in useful polymeric materials with interesting electrochemical and non-linear optical properties.¹ The metal complex, {Cp(OC)₃W}-(C≡C)₄-{W(CO)₃Cp} is prepared via oxidative coupling of the diyne precursor, {Cp(OC)₃W}-(C≡C)₂-H under the mild Hay conditions.² The tetrayne reacts with Co₂(μ-dppm)(CO)₆ and Co₂(CO)₈ to produce crystalline derivatives containing one or two Co₂ moieties. X-ray structural analysis of the products has provided the first real evidence for the existence of a C₈ carbon chain in these complexes. The C₈ chain observed from the reaction of one Co₂(CO)₈ moiety with the tetrayne is shown below. Related reactions involving the tetrayne will also be discussed.



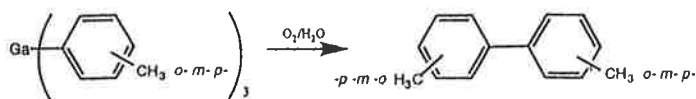
Mono-Co₂ adduct (attached to C-3, C-4 of tetrayne)

1. Y. Sun, N. J. Taylor and A. J. Carty. *Organometallics*, 1992, 11, 4293 and references therein.
2. M. I. Bruce, M. Ke and P. J. Low. *Organometallics*, 1998, 17, 3539.

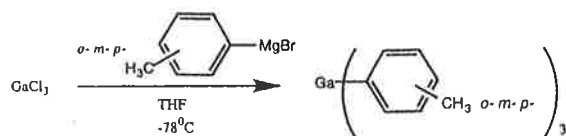
Stavroula Papadopoulos and Colin L. Raston

Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia

One of the most widely used methods for preparing biaryls is Suzuki coupling, ie, reactions involving boronic acids and esters with aryl halides, usually catalysed by $[\text{Pd}(\text{PPh}_3)_4]$.¹ A side reaction is the transfer of an aryl group from the phosphine on the catalyst to the aryl of the boronic acid.² A new synthetic methodology in biaryl synthesis is the hydrolysis of $\text{Ga}(\text{phenyl})_3$ and $\text{Ga}(o-, m-, p- \text{C}_6\text{H}_4\text{CH}_3)_3$. These reactions resulted in the formation of biaryls, with yields exceeding 70%. The aqueous layer contains an aryl-gallium oxide/hydroxide species. What becomes even more intriguing is that this reaction doesn't require a catalyst, with or without the presence of oxygen the same result is produced.



The preparation of $\text{Ga}(\text{phenyl})_3$ and $\text{Ga}(o-, m-, p- \text{C}_6\text{H}_4\text{CH}_3)_3$ initially involved beginning with gallium metal and a dialkylmercury compound via a redox transmetallation reaction. However these compounds were also found to give higher yields when prepared using GaCl_3 and reacting it with the Grignard of the aryl compound.



¹ N. Miyaara, T. Yanagi, and A. Suzuki, *Synth. Commun.*, 1981, 11, 513

² D.F. O'Keefe, M.C. Dannock and S.M. Marcuccio, *Tetrahedron Lett.*, 1992, 33, 5998

Jane E. Weder,[†] Brendan J. Kennedy,[†] Peter A. Lay,[†] Trevor W. Hambley,[†] Gary J. Foran,[#][†] School of Chemistry, University of Sydney, Sydney, NSW 2006 Australia[#] Australian National Beamline Facility, KEK-PF, OH0 1-1, Tsukuba-shi, Ibaraki-ken, Japan.

There is considerable interest in the preparation, characterization and medical use of divalent Cu(II) complexes of non-steroidal anti-inflammatory drugs (NSAIDs). This interest is due, not only to the more potent anti-inflammatory action of these complexes compared to their parent constituents, but also because of any lack of serious gastro-intestinal damage normally associated with the use of NSAIDs. Copper K-edge x-ray absorption fine structure (XAFS) measurements were recorded at room and low temperature, on the veterinary anti-inflammatory Cu(II) dimer complex of indomethacin, (1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indole-3-acetic acid = IndoH), of the formula $[\text{Cu}_2(\text{Indo})_4(\text{L})_2]$ ($\text{L} = N,N'$ -dimethylformamide (DMF), and Cu(II) acetate monohydrate, at Australian National Beamline Facility, KEK Photon Factory, Tsukuba, Japan. The bond lengths and angles of the dimeric Cu(II) cage, (Cu_2O_8) , obtained from the refinement of the solid sample XAFS data, are in excellent agreement with those obtained from crystallographic studies. The Cu---Cu vector length of 2.63 Å ($R_{\text{xafs}} = 12.3\%$) and 2.61 Å ($R_{\text{xafs}} = 12.2\%$) agrees especially well with the value of 2.630(1) Å and 2.6143(17) Å respectively, for $[\text{Cu}_2(\text{Indo})_4(\text{DMF})_2]$ and Cu(II) acetate monohydrate. In addition, the calculated Cu-ORCOO and Cu-O_{Ligand} bond lengths, in the range of 1.965 Å to 2.21 Å, are in good accordance with crystallographic data. XAFS analysis can be reliably used to simulate the co-ordination geometry of the Cu_2O_8 core of Cu(II) dimers with bridging alkanoate oxygens in solid state samples containing low percentages of Cu(II) monomer impurities.

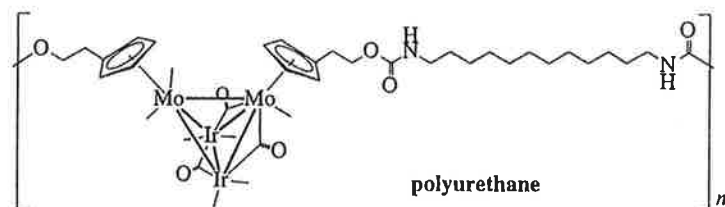
SYNTHESES, CHARACTERIZATION AND OPTICAL LIMITING PROPERTIES OF HETEROMETALLIC CLUSTER-CONTAINING POLYMERS

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^b CRC for Photonics, Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

Inorganic-organic polymers are attracting significant interest in a wide variety of applications as they provide access to new classes of polymers with unusual and potentially useful properties¹. Polymers which incorporate ligating side-chains have been utilized to complex and support metal clusters, but this usually results in clusters in more than one coordination environment. We have therefore been drawn to the possibility of incorporating clusters in the polymer backbone. Tyler and co-workers have prepared photochemically reactive polyamides, polyurethanes and polyureas containing (η^5 -C₅H₄R)₂Mo₂(CO)₆ units along the backbone². Our studies have extended these results by incorporating (η^5 -C₅H₄R)Mo units into the polymer backbone as tetrahedral Mo₂Ir₂ cluster cores, to afford structurally uniform polymer-bound mixed-metal clusters. Reaction of the cluster with a trifunctional branched organic core results in a cluster-containing dendrimer.



Efficient optical limiters are required for a range of applications in optical device protection. Clusters, along with fullerenes and phthalocyanines, have been suggested as one of the three promising classes of molecular material for detailed study³. Access to polymers with clusters in the backbone provides processable cluster-containing materials where the clusters are in uniform environments. Our structurally uniform cluster-containing polymers have exhibited optical limiting behaviour and the results of these studies will also be discussed.

1. R.B. Seymour and C.E. Carraher, *Polymer Chemistry: An Introduction*, Marcel Dekker Inc, New York, 1988, Chapter 11.
2. (a) S.C. Tenhaeff and D.R. Tyler, *Organometallics*, 1991, 10, 473
(b) S.C. Tenhaeff and D.R. Tyler, *Organometallics*, 1992, 11, 1466
(c) G.F. Nieckarz and D.R. Tyler, *Inorg. Chim. Acta*, 1996, 242, 303.
3. R. Dagani, *Chem. Eng. News*, January 1, 1996, 24.

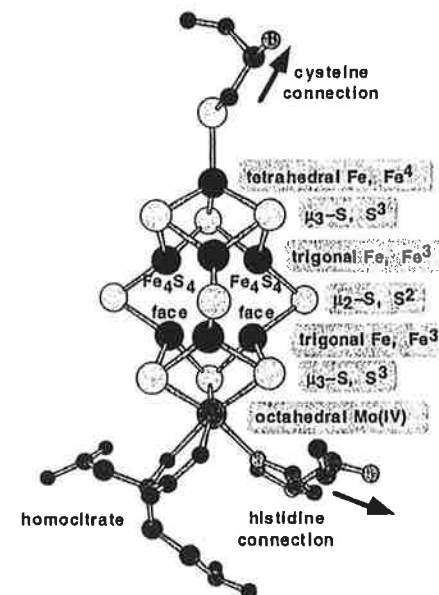
CHARACTERISTICS OF THE UNUSUAL Fe₇MoS₉ CLUSTER AT THE ACTIVE SITE OF NITROGENASE

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The enzyme nitrogenase achieves chemistry far beyond human capability in the laboratory, namely the reduction of N₂ to NH₃ under ambient conditions.

The active site for binding and reduction of N₂ is the Fe₇MoS₉(S-Cys)(N-His)(homocitrate) cluster with the following structure.



Two unusual features of this cluster are the six trigonal planar Fe atoms (Fe³), and the doubly-bridging sulfide ligands (S²). Nine atoms — (Fe³)₆(S²)₃ — forming the edge-bridged trigonal prism in the central region of this cluster, are under-coordinated. The cluster would be expected to be floppy.

The results of density functional calculations of fundamental properties of this unpredictable cluster will be presented. They include the energy-surface for distortions, the energy surface for variation of the Fe—Fe distances, and the effects of total electron population on these energy surfaces and the charge distribution. The molecular orbital spectrum of the cluster will be shown. These properties are essential factors in the mechanism of the reaction (N₂ + 8e⁻ + 8H⁺ → 2NH₃ + H₂) which is catalysed by this cluster.

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INSTITUTE OF STRUCTURAL MACROKINETICS RAS, Russia, 142432, Moscow oblast, p/o
Chernogolovka

The wide application of SiO₂ thin films in integrated circuit processing evokes an increasing interest to silanes oxidation. The branching chain nature of these reactions has been established, but the kinetic mechanisms have not been yet assigned. In our previous works charged particles formed by chemiionization have been revealed in the oxidation/chlorination of silanes in the range of 293-400K at low pressures. The concentrations of charged particles at pressures <10 torr and (DCS) ~ 5% amount to ~ 10⁹ charged units/cm³. We have also shown that constant electrical field without discharge (EF) applied before the self-ignition of silanes-oxygen mixtures reduces the amount of SiO₂ aerosol formed as well as the addition of SF₆. We used the both ways for decreasing the intensity of blackbody radiation to reveal the emission bands in the visible chemiluminescence of the rarified flames of silanes oxidation. By this means the bands ¹B₁ (0,v',0)-¹A₁ (0,v'',0) of SiH₂ and H₂SiO (¹A' - ¹A₁) have been detected. The effect of the EF on the phase formation implies that the charged particles play an important role in these reactions due to the fact that ion-molecular reactions with low activation barriers do effectively compete with those of free atoms and radicals.

The effect of the EF on the kinetical regularities such as induction periods *t*, the lower limits of the self-ignition, chemical oscillations has been also detected. The increase of the EF strength causes a decrease in *t* and an increase in the area of the occurrence of chemical oscillations; the phenomena depend on the material and the state of reactor surface. New critical phenomenon has been detected: a drastic increase in P₁ over CuSO₄ and ZnSO₄ coatings within narrow limits of EF strength. Moreover, the reactor surface coated with NaCl, "remembers" the action of the EF: after the self-ignition with the EF applied, *t* of the next self-ignition without EF is close to above *t* value. However within 5-6 subsequent ignitions the surface at least "forgets" EF action. It means that the chain branching occurs substantially on the reactor surface with the participation of charged or polarized adsorbed particles. It has been also shown that EF applied causes an increase in lower limits of flame propagation and increase in flame velocities. The effects are due to the turbulent deformation of flame zone under the action of "ionic wind". These phenomena have been used in the new method of advanced low temperature film deposition beyond the self-ignition area under afterglow conditions at 293 K. The glow discharge area was located in such a way that the Si wafers were proofed against radiation damage. The discharge was sustained by the own conductivity of the branching chain reaction. The most "large-sized" aerosol particles were "filtered" by EF and did not reach the wafers, on which the flawless film was deposited. We obtained the films with known porosity (1-10cm²) by varying the location of the discharge area. The films of this kind are useful as surface membranes of sorts for an increase in selectivity of sensors around semiconductors. The active role of the charged particles as chain carriers has not been enough considered earlier in theory. However, all the aforementioned phenomena, especially the influence of the EF on the critical conditions of low temperature branching chain process indicate that this role is more significant than it was considered previously.

W45

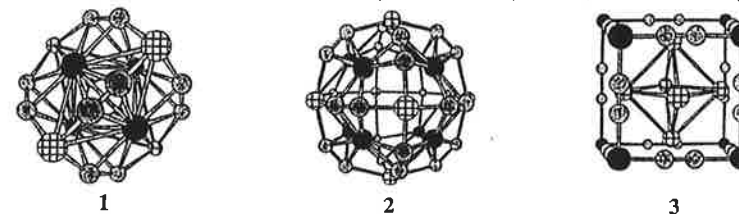
POSTERS

PLATONICALLY POLYHEDRAL METALLOCARBOHEDRENES AND METALLOFULLERENES

Ian Dance

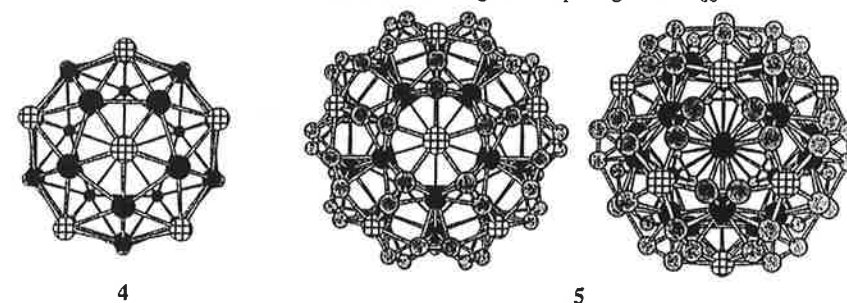
School of Chemistry, University of New South Wales, Sydney 2052.

The prototypical metallocarbohedrene, Ti₈C₁₂, has a structure 1 with T_d symmetry based on two intersecting tetrahedra of metal atoms, (M^{inner})₄(M^{outer})₄. The intersection of the inner M₄ tetrahedron and the outer M₄ tetrahedron generate six M₄ cradles, which bind the (C₂)₆.

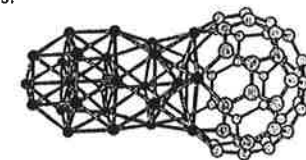


Of the five Platonic polyhedra, the tetrahedron is the dual (by vertex / face interchange) of itself. The hexahedron (cube) is the dual of the octahedron. The metal array formed by intersection of hexahedro-M₈-octahedro-M₆ supports 12 C₂ groups. Ti₁₄C₂₄ was recently observed, as its anion [L. S. Wang and H. Cheng, *Phys. Rev. Lett.*, 1997, 78, 2983-2986.]. Two of the isomeric structures for Ti₁₄C₂₄, 2 and 3, as optimised (density functional theory, DFT) are shown, with 2 very much more stable than 3.

Following this concept, the icosahedron and the (pentagonal) dodecahedron are duals. The M₁₂ + M₂₀ framework, 4, now supports 30 C₂ groups ⇒ M₃₂C₆₀. 5 is an optimised (DFT) structure for Ti₂₀V₁₂C₆₀, showing the nascent hexagons and pentagons of C₆₀.



Transition metals catalyse the formation of carbon nanotubes. The above structures demonstrate how C₂ ligands could condense to C₆ rings, and 6 (Ni₂₇C₄₀) shows one of the ideas being explored (DFT) for the mechanism of nanotube formation.



6

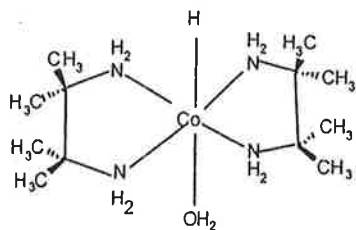
W46

Preparation and X-ray Crystal Structural Analysis of a Hydrido Tetramine Cobalt(III) Complex

A.F.M. Mokhlesur Rahman^a, W. Gregory Jackson^a, Anthony C. Willis^b and A. David Rae^b.

^aSchool of Chemistry, University College, University of New South Wales, ADFA, Canberra ACT, AUSTRALIA 2600; ^bResearch School of Chemistry, Australian National University, Canberra ACT, AUSTRALIA 0200.

Significant changes in the properties of the $[\text{Co}(\text{en})_2\text{AX}]^{n+}$ complexes are observed when all four methylene protons are replaced with four methyl groups, producing 2,3-dimethyl-2,3-diaminobutane (tmen).¹ Little attention has so far been given to the isolation and stabilisation of the unusual reaction products containing this ligand. The most unusual so far are a hydride complex and a sideways bonded peroxo complex, unprecedented in tetramine Co(III) chemistry. Such species are known, however, for arsines and phosphines as ligands.^{2,3}



The *trans* - $[\text{CoH}(\text{H}_2\text{O})(\text{tmen})_2] \text{NO}_3\text{ClO}_4$ complex is especially interesting because it contains a hydride and a labile axial aqua ligand.

The preparation, properties and X-ray crystal structure of this complex will be described.

1. P. Hendry and A. Ludi, *Helvetica Chim. Acta*, 1988, 71, 1966.
2. B. Bosnich, W.G. Jackson and S.T.D. Lo and J.W. McLaren, *Inorg. Chem.*, 1974, 13, 2605-11.
3. B. Bosnich, W.G. Jackson and S.T.D. Lo, *Inorg. Chem.*, 1975, 14, 1460-9.

A ONE-SIZE-FITS-ALL LIGAND: PORPHYRIN COMPLEXES CONTAINING BORON AND BISMUTH

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For many years the focus of porphyrin chemistry has been on transition metal complexes, but recently new examples and applications of main group porphyrin complexes have come to light. We have investigated the coordination of the porphyrin ligand to the very small, non-metallic element boron and the much larger metallic element bismuth.

Boron is too small to coordinate to all four nitrogen donors in the porphyrin cavity. Consequently, the resulting porphyrin complexes contain two boron atoms, each coordinated to only two nitrogen atoms. Two structural types have been identified, one containing an F-B-O-B-F group threaded through the porphyrin hole,¹ and the second containing a four-membered B_2O_2 ring coordinated within the porphyrin cavity.² These modes of coordination are unprecedented in porphyrin chemistry. In each case an unusual distortion of the porphyrin ligand itself is also observed.

In contrast, coordinated bismuth is much too large to reside in the hole in a porphyrin ligand. We have recently obtained the first X-ray crystal structures of bismuth porphyrin complexes which have the formula $\text{Bi}(\text{Por})\text{X}$. Each takes the form of a dinuclear arrangement of $[\text{Bi}(\text{Por})]^+$ units with the Bi atoms displaced over 1 Å from the porphyrin plane and the X⁻ anions bridging between the Bi centres.

1. Belcher, W.J.; Boyd, P.D.W.; Brothers, P.J.; Liddell, M.J.; Rickard, C.E.F. *J. Am. Chem. Soc.* 1994, 116, 8416.
2. Belcher, W. J.; Breede, M.; Brothers, P. J.; Rickard, C. E. F. *Angew. Chem., Int. Ed. Engl.* 1998, 37, 1112-1114.

Peter A. Anderson,^a Robert F. Anderson,^b Morton Z. Hoffman,^c
F. Richard Keene,^a Brett D. Yeomans^a and Bradley T. Patterson^a

^a School of Biomedical and Molecular Sciences, James Cook University, Townsville, Qld. 4811.

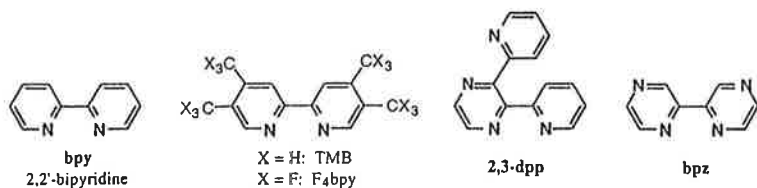
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^c Department of Chemistry, Boston University, 590 Commonwealth Ave, Boston MA 02215, USA.

Tris(bidentate)ruthenium(II) complexes based on the archetype $[\text{Ru}(\text{bpy})_3]^{2+}$ have been widely studied, mainly because of the potential use of such compounds photosensitisers in solar energy conversion. In such complexes, the π^* energy levels of the ligands may be controlled by subtle substituent variation: *e.g.* electron-withdrawing substituents will lower the π^* levels. When a ligand containing non-coordinating N-atoms (*e.g.* bpz (2,2'-bipyrazine) or dpp {2,3-bis(2-pyridyl)pyrazine}) is present, the complexes may exhibit acid-base characteristics, and pK_a studies can be used to probe the electronic characteristics of the complex.

Pulse radiolysis techniques were used to study the one-electron reduced forms of a range of polypyridyl tris(bidentate)ruthenium(II) complexes with substantially different ligand substituents. The ligands used in the study vary from electron donating (*e.g.* 4,4',5,5'-tetramethyl-2,2'-bipyridine, TMB) to strongly electron-withdrawing (*e.g.* 4,4',5,5'-tetra(trifluoromethyl)-2,2'-bipyridine, F_4bpy) in nature. Using the visible absorption spectra of the fully protonated, $[\text{RuL}_2(\text{L}'\text{H})]^{2+}$, and non-protonated, $[\text{RuL}_2\text{L}']^{2+}$ reduced forms allow an insight into the nature of the reduced species. By using a range of solutions at different pH, pK_a values for the protonated-reduced form, $[\text{RuL}_2(\text{L}'\text{H})]^{2+}$, have been determined by monitoring absorbance changes at specific wavelengths.

The results and interpretations of these studies will be discussed in this presentation.



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The selective activation of a donor-acceptor prodrug system by electromagnetic radiation could be used to deliver an active cytotoxin directly to localised tumor regions. Photoirradiation of the donor-acceptor system leads to the excitation of an electron which is transferred via a conducting linker framework to an electron acceptor unit. Reduction of the acceptor causes the release of the cytotoxin.

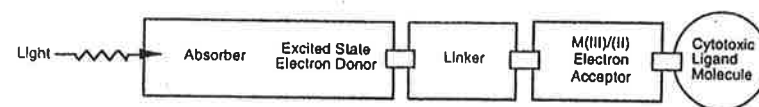


Figure 1. Schematic Diagram of Donor-Acceptor System

In order to 'tune' a donor-acceptor complex such that the cytotoxin is released within the lifetime of the charge separated state (up to approximately 1 μs) the electronic and steric effects of different coordinating ligands on the rate of ligand dissociation needs to be known in much greater detail than is presently available.

We have used pulse radiolysis to carry out the rapid reduction of model acceptor systems consisting of simple mixed diimine Co(III) complexes incorporating the ligands 2,2'-bipyridine, 1,10-phenanthroline, ethylenediamine and dipyridophenazine. Following the initial reduction a number of processes were observed leading to ligand loss. These experiments have been carried out in conjunction with structural, electrochemical and spectroscopic studies.

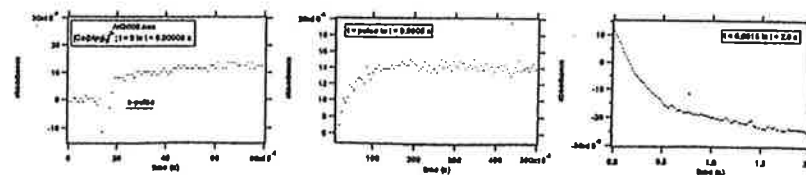


Figure 2. Processes occurring upon pulse radiolysis of $[\text{Co}(\text{bipy})_3]^{3+}$. Monitoring wavelength 305 nm; $c([\text{Co}(\text{bipy})_3]^{3+}) = 3.0 \times 10^{-5} \text{ M}$, $c(e^-_{aq}) = 2.0 \times 10^{-5} \text{ M}$; pH 7

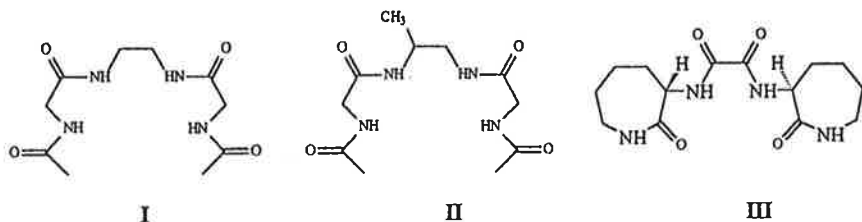
Marina Fainerman-Melnikova, Ronald R. Fenton and Peter A. Lay

School of Chemistry, University of Sydney

Sydney 2006 NSW, Australia

Cr(V) peptide complexes are potential mutagenic intermediates in the intracellular reduction of carcinogenic Cr(VI) complexes. Good models for these intermediates are complexes of Cr(V) with macrocyclic tetraamides, which are well known and biological activity of which is studied extensively¹⁻³. These complexes show high genotoxicity in both bacterial and mammalian cells. They are chemically inert, do not undergo ligand exchange reactions and can enter cells intact. They are believed to interact with DNA in direct way (such as oxo transfer, or hydrogen atom abstraction reactions, rather than formation of activated oxygen species, etc.). The preparation of the similar chiral Cr(V) chelate complexes and examination of their prospective enantioselective in genotoxicity assays might provide evidence for a direct mechanism of interaction between the DNA and Cr(V) complexes.

For these purposes the new non-macrocyclic tetraamides (2,5,10,13-tetraoxo-3,6,9,12-tetraazaquaterdecane (I), 2,5,10,13-tetraoxo-7-methyl-3,6,9,12-tetraazaquaterdecane (II), and *N,N'*-di-((S,S)-3-hexahydro-2H-azepin-2-one)oxamide (III)) were synthesised. Cr(III) and stable Cr(V) complexes, as well as complexes of some other transition metals (Ni^{2+} , Cu^{2+} and Cu^{3+} , VO^{2+}) with these ligands, were made according to published and modified methods and characterised by EPR, IR, UV-vis, ^1H and ^{13}C NMR and electrospray mass spectroscopies.



1) Collins, T. J.; Slebodnick, C.; Uffelman, E. S. *Inorg. Chem.* **1990**, *29*, 3433-3436.

2) Dillon, C. T.; Lay, P. A.; Bonin, A. M.; Dixon, N. E.; Collins, T. J.; Kostka, K. L. *Carcinogenesis* **1993**, *14*, 1875-1880.

3) Dillon, C. T.; Lay, P. A.; Bonin, A. M.; Cholewa, M.; Legge, G. J. F.; Costa, M.; Collins, T. J.; Kostka, K. L. *Chem. Res. Toxicol.* **1998**, *11*, 119-129.

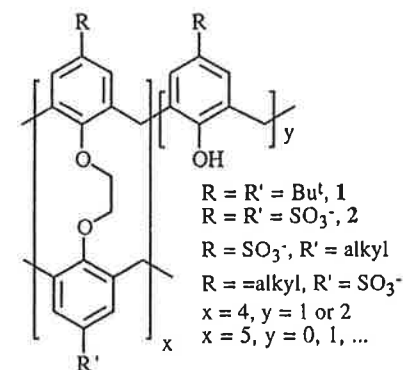
Water Soluble Divergent Receptor Molecules

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Research on divergent receptor molecules is focused on fused calixarenes to build up novel symmetrical and unsymmetrical tubular like structures, eg 1, and water soluble analogues such as 2. These molecular assemblies can function as supramolecular hosts for globular and lenticular molecules and at the same time be able to bind a wide range of metal ions. The symmetrical system $x = 4$, $y = 0$, $R = R' = \text{Bu}^t$ has been reported by Beer et al.¹



1. P. Schmitt, P. D. Beer, M.G.B. Drew and P.D. Sheen; *Angew. Chem. Int. Ed.* **1997**, *36*, No.17

CYCLODEXTRINS AND THEIR COMPLEXATION OF TRYPTOPHAN IN AQUEOUS SOLUTION

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^b Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

The coordination of a metal ion by a functionalised cyclodextrin to form a binary metalocyclodextrin and the subsequent complexation of a substrate to form a ternary metalocyclodextrin, allows the study of metal centre and cyclodextrin interactions on metalocyclodextrin stability and substrate binding.¹ A binary metalocyclodextrin is able to bind a substrate through encapsulation by the cyclodextrin annulus and by possible coordination to the metal centre. A study of the binary metallo-tetraazaalkyl-monosubstituted- β -cyclodextrins, $[M(\beta CD-X)]^{2+}$, (see Figure 1) where $M^{2+} = Ni^{2+}$, Cu^{2+} and Zn^{2+} , and of the ternary metalocyclodextrins, $[M(\beta CD-X)Trp]^+$, where Trp^- is the tryptophan ion, is reported. The protonated analogues have also been studied.

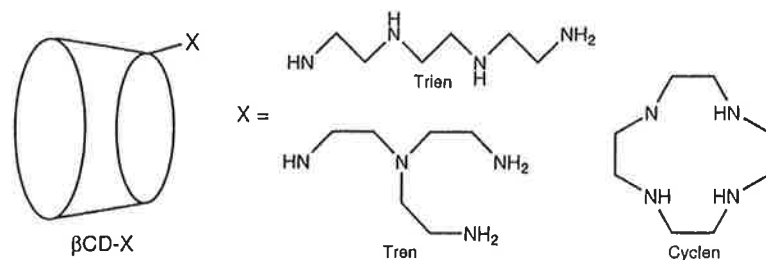


Figure 1. A schematic representation of the tetraazaalkyl-monosubstituted- β -cyclodextrins used where the cyclodextrin is represented as a truncated cone.

The complexation of (*R*)- and (*S*)-tryptophan allows a test for enantioselectivity in $[M(\beta CD-X)Trp]^+$. The complex stabilities are discussed in terms of ligand rigidity and affinity of the tryptophan guest to the cyclodextrin moiety and metal centre.

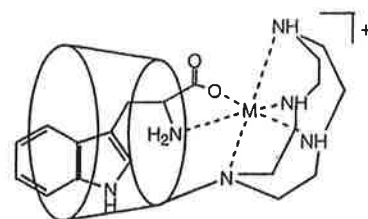


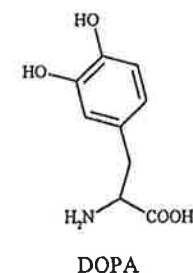
Figure 2. A schematic representation of $[M(\beta CD-X)Trp]^+$ where $X = Cyclen$

¹ C.A. Haskard, C.J. Easton, B.L. May and S.F. Lincoln., *Inorg Chem.*, 1996, **35**, 1059-1064.

1. Division of Inorganic Chemistry, School of Chemistry, University of Sydney, NSW 2006.

2. The Heart Research Institute, 145-147 Missenden Road, Camperdown, Sydney, NSW 2050.

Chromium(VI) has been shown to be a common cause of occupational cancers. The major carcinogenic and mutagenic species are proposed to be Cr(V) and Cr(IV) intermediates in the reduction of Cr(VI) to stable Cr(III) compounds. The reduction of Cr(VI) by some biological reductants (eg. ascorbate, glutathione and hydrogen peroxide) has been studied previously, and genotoxic Cr(IV/V) species have been detected. A further source of reductants *in vivo* are oxidised proteins which contain hydroperoxide and DOPA (3,4-dihydroxyphenylalanine) groups. Oxidised proteins are present in cells at higher concentrations than H_2O_2 *in vivo*, but their interaction with Cr(VI) has not been investigated. Here we report the study of Cr(VI) reduction by model DOPA compounds (catecholamines) and oxidised proteins.



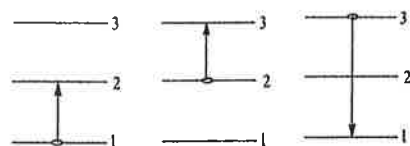
We have utilised EPR spectroscopy to observe the formation of a number of Cr(V) species during reduction of Cr(VI) by catecholamines and substituted catechols (eg. DOPA, dopamine, catechol). The stability of the Cr(V) species varies considerably, and depends on the nature of the reducing catechol(amine), the pH and the reactant ratio. Parallel experiments with plasmid DNA show that the Cr(VI)/catechol(amine) reactions produce species that interact with DNA to yield nicked DNA. This work provides preliminary evidence for a further mechanism of Cr(VI) reduction to produce potentially carcinogenic species *in vivo*.

RARE EARTH DIMERS AS CANDIDATES FOR UPCONVERSION

Paul V. Bernhardt, Bernadine M. Flanagan and Mark J. Riley

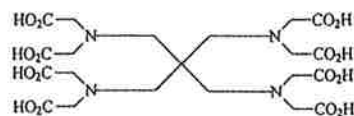
Department of Chemistry, University of Queensland, Brisbane, 4072, Australia.

There is a good deal of interest in developing an inexpensive laser, which works in the blue region of the visible spectrum. One way of doing this is to use a readily available red semi-conductor laser as the energy source and to pump a laser active material to a higher energy in sequential steps. This is blue energy upconversion.

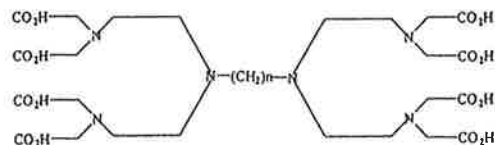


Proximate trivalent lanthanide ions are capable of energy transfer and it is anticipated that this will lead to upconversion. Systems are being investigated in which it is possible to control the distance between the two rare earths. This will make it possible to see how internuclear separation affects energy transfer in the dimer.

The system being studied with smallest distance between the lanthanide ions is based on pentaerythritol tetraamine.



The system below allows one to increase the internuclear distance using a bridge where $n = 2, 3, 4$ or 5 .



Upon synthesis of these ligands, chelation of trivalent lanthanide ions will be carried out. Lanthanides of choice include Er(III) and Yb(III). The upconversion properties of these ligands will be studied.

Synthesis and Characterisation of Optically Active Cage Complexes from Mixed Trisdiamine Cobalt Complexes

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Various hexamine cage complexes of the form $[M(N_6)]^{n+}$ have been synthesised and characterised via a template reaction [1,2]. They are interesting in their extraordinary kinetic and thermodynamic stability, redox property and many other useful properties[3]. The syntheses and characterisation of optically active cages (Figure 1) formed from L- and D-[Co(en)₂(R,R-chxn)]³⁺ and [Co(en)(R,R-chxn)₂]³⁺ via template reactions are presented. Their spectroscopic, electrochemical properties and crystal structure will be represented.

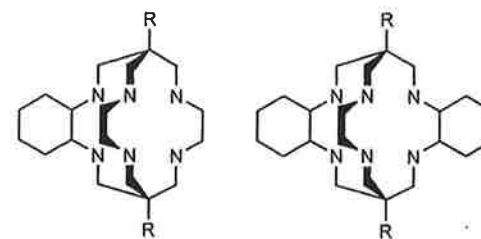


Figure 1

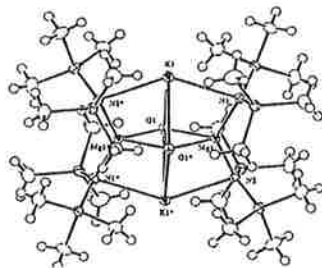
References

- [1] A.M. Sargeson, *Chem. Br.*, **15** (1979) 23
- [2] G.A. Bottomley, I.J. Clark, I.I. Creaser, L.M. Engelhardt, R.J. Geue, K.S. Hagen, J.M. Harrowfield, G.A. Lawrance, P.A. Lay, A.M. Sargeson, A.J. See, B.W. Skelton, A.H. White and F.R. Wilner, *Aus. J. Chem.*, **47** (1994) 143
- [3] A.M. Sargeson, *Coord. Chem. Rev.*, **151** (1996) 89

Amide Ring Systems

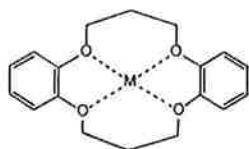
A.R. Kennedy^a, R.E. Mulvey^{a*}, C.L. Raston^b, B.A. Roberts^{a,b}, R.B. Rowlings^a^aUniversity of Strathclyde, Glasgow, G11XL, UK.^bMonash University, Clayton Victoria Australia 3168

In an exciting new development in mixed group 1 / magnesium amide chemistry, we have recently published several unprecedented macrocyclic amide ring systems of Li and Na, which incorporate a central oxide or peroxide dianion^{1,2}. Continuing on from this study, we have managed to extend the scope of this research, expanding the ring systems to include the larger alkali metal, Potassium.

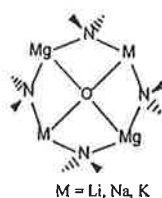


Main group metal amides are well known as being archetypal moisture- and oxygen-sensitive and are thus always studied under an inert atmosphere. However, here we have utilised dioxygen to produce novel eight-membered $[N_4M_2Mg_2]$, heterobimetallic ring systems incorporating oxide $[O^{2-}]$ and/or peroxide $[O_2^{2-}]$ central dianions of general formula, $[(R'_2N)_4M_2Mg_2(O_2)_x(O)_y]$, where $R'_2N = N(SiMe_3)_2$ or $Me_2C(CH_2)_3(Me)_2CN$ and $M = Li, Na, K$. Interestingly, these complexes can be regarded as antithetical 'crown-ether' complexes where the Lewis acid-Lewis base positions have been reversed in comparison to conventional crown ethers.

Crown-Ether Complex

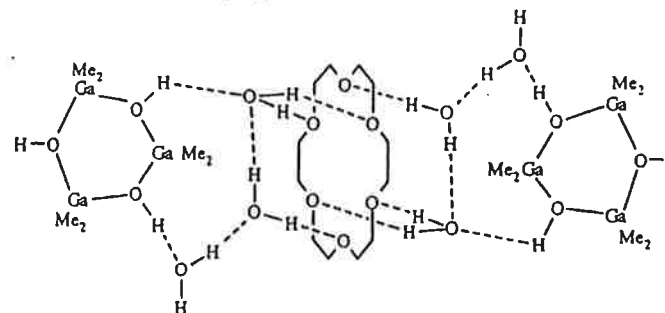


"Inverse"

¹ Kennedy, A.; Mulvey, R.; Rowlings, R.; *J. Am. Chem. Soc.*, 1998, 120, 7816² Kennedy, A.; Mulvey, R.; Rowlings, R.; *Angew. Chem. Int. Ed. Engl.*, in pressAlexander Drljaca, Paul D. Croucher, Stavroula Papadopoulos and Colin L. Raston
Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia

The chemistry of group 13 alkyl compounds has been extensively studied and have applications as precursors to semiconductor materials.^{1,2} However, relatively few studies on oxide-hydroxide chemistry of gallium have been obtained. The first organogallium-oxo compound reported was $[t\text{-BuGa}(\mu_3\text{-O})]_9$ ³ and the only known cyclic trimer hydroxy derivative of gallium, is $[t\text{-Bu}_2Ga(\mu-OH)]_3$.⁴ Only recently has the largest galloxane hydroxide been isolated, $Ga_{12}t\text{-Bu}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4$.⁵

In addressing the difficulties associated with isolated the intermediates formed during the hydrolysis of substitutionally labile alkyl metal compounds from aqueous solution we use a crown ether to promote supramolecular complexation and crystallisation. The reaction of trimethylgallium with water in the presence of 18-crown-6 affords an alkyl μ -hydroxo bridged Ga(III) trimer in solution and the solid, isolated as the hydrogen bonded assembled supermolecule $\{[(CH_3)_2Ga(\mu-OH)]_3 \cdot 3H_2O\}_2 \cdot 18\text{-crown-6}$.

¹ A.H.Cowley and R.A.Jones, *Angew. Chem., Int. Ed. Engl.*, 1989, 28, 1208 and references therein.² A.H.Cowley, B.L.Benac, J.G.Ekerdt, R.A.Jones, K.B.Kidd, J.Y.Lee and J.E.Miller, *J. Am. Chem. Soc.*, 1985, 110, 6248.³ M.B.Power, J.W.Ziller and A.R.Barron, *Organometallics*, 1992, 11, 2783.⁴ D.A.Atwood, A.H.Cowley, P.R.Harris, R.A.Jones S.U.Koschmieder, C.M.Nunn, J.L.Atwood and S.G.Bott, *Organometallics*, 1993, 12, 24.⁵ C.L.Landry, C.J.Harlan, S.G.Bott and A.R.Barron, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 1201.

SYNTHESIS OF AMINO ACID DERIVATIVES AS EFFECTIVE ORAL IRON CHELATORS

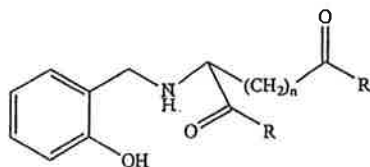
K. W. Loh and J. Ranford

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 117600

Iron overload represents a serious clinical problem in patients with thalassemias and other refractory anemias. The only iron-chelating agent currently in clinical use is Desferriamine (DFO). The mode of administration by prolonged subcutaneous infusions is quite cumbersome. Thus, the limitations have prompted an extensive search for economically and therapeutically more effective iron-chelating compounds. [1-2]

As part of this research, effort has been directed towards the synthetic preparation of orally active iron chelating drugs with emphasis on the synthesis of N-(2 hydroxybenzyl) amino acids and peptides. These compounds are chosen as they are biologically compatible, economical and have a high affinity for iron.

L-Aspartic and L-Glutamic acids form reduced Schiff bases with salicylaldehyde (see diagram) possessing nitrogen and oxygen donor groups that have high affinities for a hard acid like Fe(III).



Where R = OH, O-alkyl, O-phenyl, N-glycyl; n = 1, L-Aspartic acid; n = 2, L-Glutamic acid

The complexes obtained were characterized by NMR, FT-IR and electronic spectroscopies. Microanalyses showed that the ligands formed complexes with Fe(III), Cu(II) and Zn(II) in a 1:1 ratio. The stability constant of the ligands and their complexes were determined potentiometrically. The single-crystal structure of Zn(II) with the L-Aspartic acid analogue has been solved.

1. R. J. Bergeron, G. M. Brittenham, *The Development of Iron Chelators for Clinical Use*, CRC Press: Boca Raton, FL, 1994.
2. Y. Hara and M. Akiyama, *Inorg. Chem.*, 1996, 35, 5173.

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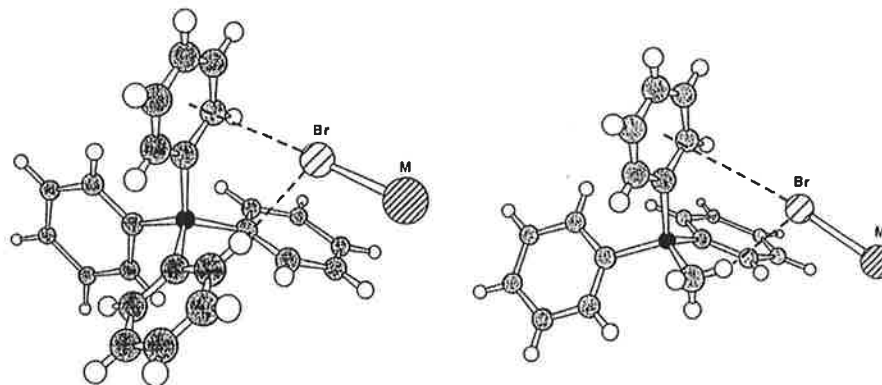
INORGANIC SUPRAMOLECULAR MOTIFS FOR MOLECULES WITH PHENYL AND BROMINE SURFACES

Marcia Scudder, Caitlin Horn and Ian Dance

School of Chemistry, University of New South Wales, Sydney 2052.

There is a favourable contribution to crystal packing whenever phenyl rings approach to form edge-to-face or face-to-face interactions. A concerted multiple embrace occurs in the 6PE (also known as the SPE, the sextuple phenyl embrace)^{1,2} where six of these attractive interactions occur together. This ubiquitous motif has been found to occur between cations such as Ph₃PR⁺. In particular, the 6PE is extremely prevalent in complexes where R = Ph, i.e. in those containing Ph₄P⁺.

However, in those structures where the anions are metal complexes with terminal or bridging Br atoms, it is possible for the Br atoms to approach the cation in such a way as to disrupt some or all of the inter-cation phenyl embraces. In those cases where R is not Ph, but an alkyl group, it is possible for the Br atom to approach the cation more closely, however, in either case, there appears to be a prevalent motif where the Br atom is situated over one of the phenyl rings, and in addition, is conveniently located to take part in a reasonably linear C-H...Br weak hydrogen bonds.



Variations in multiple phenyl embraces will be discussed for a variety of bromometallates, with particular emphasis on the group of complexes of [CuBr₂]⁻.

1. I. Dance and M. Scudder, *J. Chem. Soc. Chem. Commun.*, 1995, 1039-40.
2. I. Dance and M. Scudder, *Chem. Eur. J.*, 1996, 2, 481-6.

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Joseph P. Morral,^a Andrew M. McDonagh,^a Mark G. Humphrey,^a Marek Samoc,^b Barry Luther-Davies,^b Inge Asselberghs,^c André Persoons,^c Stephan Houbrechts,^d Tatsuo Wada,^d and Hiroyuki Sasabe^d

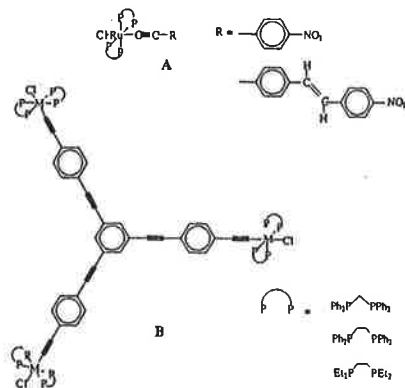
^a Department of Chemistry, ANU, Canberra, ACT 0200, Australia

^b Cooperative Research Centre for Photonics, Laser Physics Centre, Research School of Physical Sciences and Engineering, ANU, Canberra, ACT 0200, Australia

^c Centre for Research on Molecular Electronics and Photonics, Laboratory of Chemical and Biological Dynamics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

^d Nano-Photonics Materials Laboratory, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako-shi, Saitama 351-01

Both dipolar and octopolar compounds may display significant second- and third- order nonlinear optical response.¹ Although the effect of varying a number of structural components upon NLO merit has been probed, the importance of co-ligand variation at the metal is as yet unclear. A series of systematically varied dipolar and octopolar complexes incorporating bidentate ligands have now been synthesised. Synthetic procedures for these compounds, and their electrochemical, linear optical, quadratic and cubic NLO and thermal properties will be presented.



¹ a) I.R. Whittall, A.M.McDonagh, M.G. Humphrey, and M. Samoc, *Adv. Organomet. Chem.*, (42), 1998, 291; b) I.R. Whittall, A.M.McDonagh, M.G. Humphrey, and M. Samoc *Adv. Organomet. Chem.*, (43), 1998, 349.

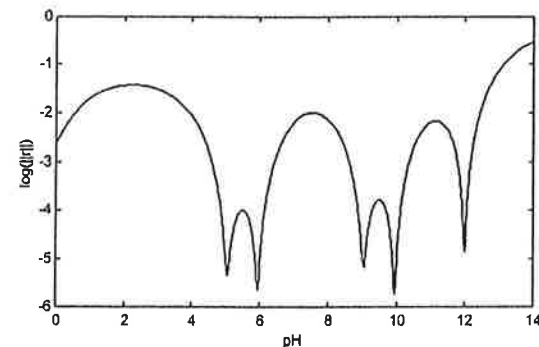
Non-Linear Parameter Fitting via Iterative Target Factor Analysis

P. Jandanklang, M. Maeder

Chemistry Department, University of Newcastle, Callaghan, NSW, 2308, Australia

Modern instrumentation in analytical chemistry provides data that can be analyzed with new computational techniques. For example, HPLC with a diode-array detector yields a 2-dimensional matrix of data. Target Factor Analysis is one of many chemometrics methods that is employed as a tool for extracting the hidden important information in complex data, e.g. the existence of the particular compounds in reaction processes or in overlapping peaks in chromatography.

The development of Target Factor Analysis for parameter fitting, namely **Target Transformation Fitting, TTF**, is the aim of this work. The idea of TTF is to search for mathematical functions (vectors) which can be represented by linear combinations of the unknown concentration profiles of components. This is done via factor analysis of the original measurement. The suspected function is tested on the abstract multidimensional data space based on the Target Factor Analysis algorithm. The following figure represents the result of TTF applied to a computer generated spectrophotometric titration of a pentaprotic acid with pK_a values of 5, 6, 9, 10 and 12. It is clear that all pK_a values are correctly detected. The standard non-linear fitting program is also used to improve the fitting of the parameters.



The TTF combined with a non-linear parameter fitting algorithm has been successfully applied to kinetics systems, chromatographic studies, equilibrium systems and NMR-measurements.

STUDIES OF THE BIOCHEMICAL INTERACTIONS OF COPPER AND ZINC POTENTIAL ANTI-INFLAMMATORY DRUGS.

Carolyn T. Dillon,* Trevor W. Hambley,* Brendan J. Kennedy,* Peter A. Lay,* Jane E. Weder,* Qingdi Zhou,* John R. Biffin† and Hubertus L. Regtop.†

* School of Chemistry, University of Sydney, NSW, 2006, Australia.

† Biochemical Veterinary Research Pty Ltd., Braemar, NSW, 2575, Australia.

[Cu₂(indo)₄] (indo = indomethacin) is a non-steroidal anti-inflammatory drug commonly used by veterinarians for the treatment of horses and dogs. Its use is preferred over indomethacin because indomethacin produces severe gastric ulcerations that can ultimately lead to death, particularly in dogs. The aim of this work is to investigate the metabolism of [Cu₂(indo)₄] to understand why it is a less toxic, yet more effective anti-inflammatory agent than indomethacin. To date, studies in this laboratory have been performed to characterise the abovementioned copper drug [1]. Work has also commenced on the preparation and characterisation of [Zn₂(indo)₄] complexes as anti-inflammatory drugs. The interest in these complexes stems from the knowledge that Zn possesses anti-ulcerogenic effects [2]. Previous studies have shown that [Zn₂(indo)₄] induces less ulcers than indomethacin yet exhibits a similar indomethacin bioavailability profile to that following treatment with free indomethacin [2].

The subject of this work involves investigations of the cellular interactions of these drugs. Results of permeability studies, cytotoxicity studies, DNA interactions and the superoxide dismutase activities of these complexes will be discussed with regard to their anti-inflammatory properties.

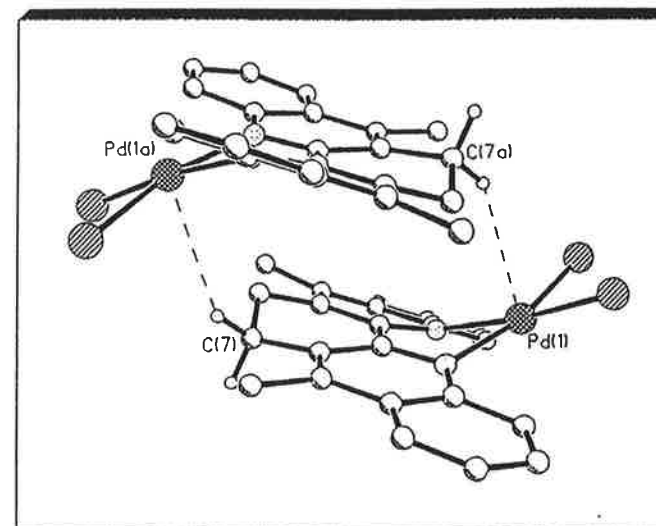
1. Weder, J. E.; Hambley, T. W.; Kennedy, B. J.; Lay, P. A.; MacLachlan, D.; Bramley, R.; Delfs, C. D.; Murray, K. S.; Moubaraki, B.; Warwick, B.; Biffin, J. R.; Regtop, H. L. Anti-inflammatory dinuclear copper(II) complexes with indomethacin. Synthesis, magnetism and EPR spectroscopy; crystal structure of the N,N-dimethylformamide adduct. *Inorganic Chemistry*, 1998, submitted.
2. Singla, A. K.; Mediratta, D. K.; Pathak, K. Bioavailability of indomethacin from zinc-indomethacin complex. *International Journal of Pharmaceutics*, 1990, 60, 27-33.

TRANSITION METAL COMPLEXES OF NON-PHOSPHINE BIDENTATE LIGANDS

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Activation of the saturated carbon-hydrogen (C-H) bond in alkane or alkyl groups present both a fundamental and practical challenge to chemists. It has been found that certain transition metal complexes can break normally inert hydrogen-carbon bonds. Development of reagents capable of selective transformation of C-H bond to form more reactive functionalised molecules is a recent and a relatively unexplored area of research.¹ Our work has focused on the design of potential metal catalyst complexes with chelating ligands. Chelating ligands can concurrently stabilize intermediates and provide an active site on the metal more effectively than monodentate ligands. Surprisingly there are only a few examples of the application of metal complexes with chelating ligands in this field, especially non-phosphine based bidentate ligands. We are investigating the saturated carbon-hydrogen bond activation by transition metal complexes with nitrogen donor bidentate ligands.



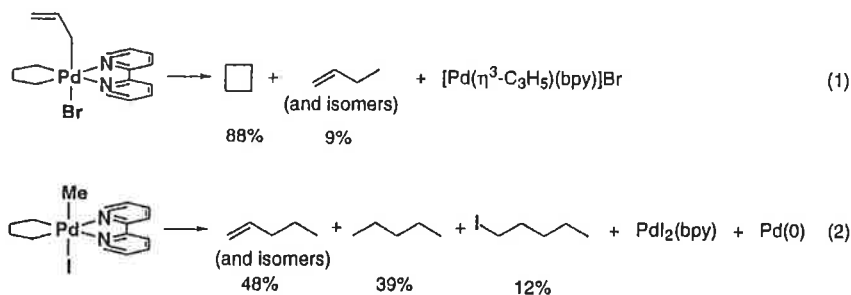
In this work, so far, a series of novel non-phosphine bidentate ligands which contain a pyridine ring, and the symmetrically substituted bispidinones were synthesized.² Metal complexes of the ligands were prepared with palladium and platinum.

1. Bruce A. Arndtsen, Robert G. Bergman, T. Andrew Mobley, and Thomas H. Peterson, *Acc. Chem. Res.*, 1995, 28, 154.
2. Adolf Gogoll, Helena Grennberg, and Andreas Axen, *Organometallics*, 1997, 16, 1167.

Allan J. Canty,^a Jason L. Hoare,^a Noel W. Davies^b and Peter R. Traill^a
^aSchool of Chemistry and ^bCentral Science Laboratory, University of Tasmania, Hobart, Tasmania, Australia 7001

Decomposition mechanisms for metallacyclopentane complexes have been explored because of the involvement of such metallacycles in catalysis. The relatively recent development of organopalladium(IV) chemistry,¹ and emerging views that this oxidation state may play a key role in some catalytic processes involving palladium,² has prompted us to examine the synthesis and decomposition of pallada(IV)cyclopentanes.

We report here that pallada(IV)cyclopentanes complexes may be accessed via oxidative addition of alkyl halides to Pd(II) precursors, and that decomposition occurs predominantly by reductive elimination via C-C coupling to give Pd(II) species that are stable (e.g. eq 1) or which undergo further decomposition (e.g. eq 2). Product analysis from decomposition of mixtures of PdX(C₄H₈)R(bipy) and PdX(C₄D₈)R(bipy) suggest that decomposition of intermediate Pd^{IV}CH₂CH₂CH₂CH₂Me species (eq 2) occurs via β-elimination (to give pentenes) and protonation (to give pentanes), and that formation of butenes in eq 1 occurs by intermolecular hydride transfer processes. Parts of this work have been reported.³


 1. Canty, A.J. *Acc Chem Res*, **1992**, *25*, 83.

 2. For example, Yoneyama, T.; Crabtree, R.H. *J Mol Catal A*, **1996**, *108*, 35.

 3. Canty, A.J.; Hoare, J. L.; Davies, N. W.; Traill, P. R. *Organometallics*, **1998**, *17*, 2046.

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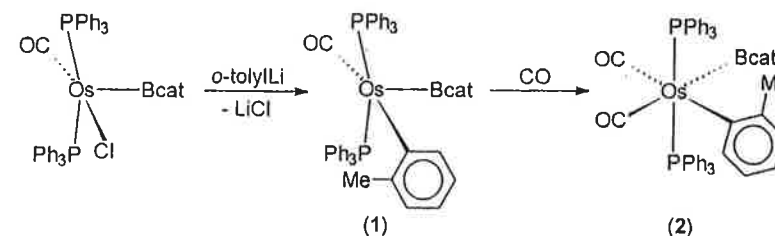
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OSMIUM ARYL, BORYL COMPLEXES

Clifton E. F. Rickard, Warren R. Roper, Alex Williamson and L. James Wright

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Reaction of Os(Bcat)Cl(CO)(PPh₃)₂ (cat = 1,2-O₂C₆H₄) with *ortho*-tolyl lithium in benzene at 5°C affords five-coordinate Os(Bcat)(*o*-tolyl)(CO)(PPh₃)₂ (1) as a bright yellow solid in good yield. Treatment of 1 with carbon monoxide or *para*-tolylisocyanide gives the six-coordinate derivatives, Os(Bcat)(*o*-tolyl)(CO)₂(PPh₃)₂ (2) or Os(Bcat)(*o*-tolyl)(CO)(CN-*p*-tolyl)(PPh₃)₂ (3) respectively, in which the boryl and aryl ligands are mutually *cis*.



Complexes 2 or 3 reductively eliminate *ortho*-tolylBcat in CHCl₃ solution at room temperature to give OsCl₂(CO)₂(PPh₃)₂ and OsCl₂(CO)(CN-*p*-tolyl)(PPh₃)₂ respectively. Complexes 2 and 3 may serve as models for an intermediate in the borylation of arenes by CpFe(CO)₂(Bcat) as reported by Hartwig.¹ The decomposition reactions of 2 or 3 in benzene solution provide convenient routes to "Os(CO)₂(PPh₃)₂" or "Os(CO)(CN-*p*-tolyl)(PPh₃)₂". Indeed, reactions of 2 or 3 with B₂cat₂ in benzene yield Os(Bcat)₂(CO)₂(PPh₃)₂ or Os(Bcat)₂(CO)(CN-*p*-tolyl)(PPh₃)₂ respectively. Reaction of 2 with HBcat or C₂Cl₄ yields Os(Bcat)H(CO)₂(PPh₃)₂ or Os(CCl=CCl₂)Cl(CO)₂(PPh₃)₂. Carbonylation of Os(Bcat)Cl(CO)(PPh₃)₂ affords the six-coordinate complex Os(Bcat)Cl(CO)₂(PPh₃)₂.² This complex reacts with *ortho*-tolyl lithium or phenyl lithium to give Os(Bcat)(*o*-tolyl)(CO)₂(PPh₃)₂ (4) or Os(Bcat)(Ph)(CO)₂(PPh₃)₂ (5) respectively, in which the boryl and aryl ligands are mutually *trans*. Complex 4, therefore, is a structural isomer of 2. It is much more robust than 2 and shows no tendency to decompose even in refluxing benzene. However, on irradiation with a 1000W tungsten lamp in refluxing benzene, the orthometallated complex [Os(C₆H₄PPh₂)H(CO)₂(PPh₃)] is formed.

 (1) K. M. Waltz, X. He, C. Muhoro and J. F. Hartwig, *J. Am. Chem. Soc.*, **1995**, *117*, 11357.

 (2) G. J. Irvine, *PhD Thesis*, The University of Auckland, 1996.

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STABILITY CONSTANTS OF TWO MODIFIED β -CYCLODEXTRINS

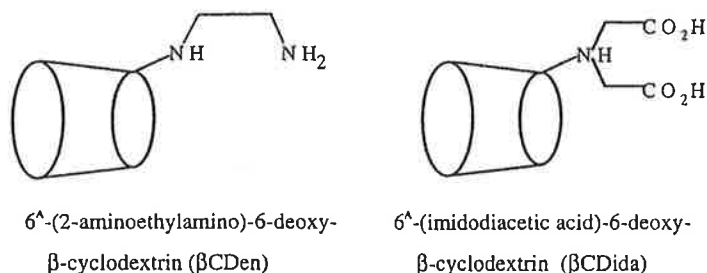
Melissa A Sandow[†], Stephen F Lincoln[†], Christopher J Easton[‡]

[†] Department of Chemistry, The University of Adelaide, Adelaide, SA 5005.

[‡] Department of Chemistry, Australian National University, Canberra, ACT 2601.

Cyclodextrins are naturally occurring cyclic oligosaccharides, usually composed of either six (α CD), seven (β CD) or eight (γ CD) α -1,4-linked-D-glucopyranose units. They are able to bind a wide variety of substrates and by modifying the cavity of the cyclodextrin this binding may be enhanced¹. In this study two different modifications of the cavity have been made and the stabilities of a range of complexes have been studied.

Fig 1



The stability of complexes were investigated in a pH titration study using the above modified cyclodextrins (Fig 1). Initially the formation of the metalocyclodextrins with $M = \text{Zn}^{2+}$, Co^{2+} , Cu^{2+} and Ni^{2+} was investigated. This was followed by the formation of the ternary complexes, using the metalocyclodextrins and either the (*R*)- or (*S*)- tryptophan anions. Finally the host-guest interactions of the modified cyclodextrins with (*R*)- or (*S*)- tryptophan and phenylalanine anions were calculated. Both the preparative chemistry and the complex chemistry associated with these systems will be discussed.

1. Brown, S. E.; Coates, J. H.; Easton, C. J.; Lincoln, S. F. *J. Chem. Soc. Faraday Trans.*, 1994, 739-743.

NOVEL COMPLEXES FOR NON-LINEAR OPTICS INCORPORATING THE ALKYNILBENZALDEHYDE LIGAND.

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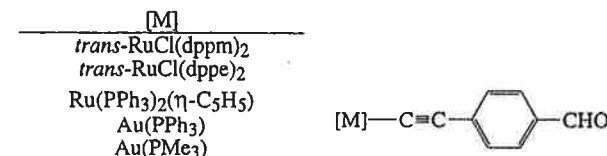
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Organometallic molecules with a donor-bridge-acceptor composition, where the bridge is an arylalkynyl group, may have significant quadratic and cubic nonlinear optical (NLO) responses.¹ Our studies have probed the effect of varying the ligated metal centre and the bridging unit, but we have not thus far examined the impact on NLO response of acceptor group replacement. We have now synthesized complexes incorporating a different acceptor group, namely the 4-alkynylbenzaldehyde ligand, of interest not only in their own right, but for their potential as precursors to bimetallic and ene-linked complexes. The syntheses and nonlinear optical properties of these complexes and related vinylidene complexes will be presented.



1. (a) I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, *Organometallics* 1995, 14, 3970. (b) I.R. Whittall, M.G. Humphrey, A. Persoons, S. Houbrechts, *Organometallics* 1996, 15, 1935. (c) I.R. Whittall, M.G. Humphrey, M. Samoc, J. Swiatkiewicz, B. Luther-Davies, *Organometallics* 1995, 14, 5493. (d) A.M. McDonagh, I.R. Whittall, M.G. Humphrey, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 1996, 519, 229. (e) A.M. McDonagh, I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 1996, 523, 33. (f) A.M. McDonagh, M.P. Cifuentes, I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, D.C.R. Hockless, *J. Organomet. Chem.* 1996, 526, 99. (g) I.R. Whittall, M.G. Humphrey, A. Persoons, S. Houbrechts, D.C.R. Hockless, *Organometallics* 1996, 15, 5738. (h) I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, *Angew. Chem. Int. Ed. Engl.* 1997, 36, 370. (i) I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G.A. Heath, D.C.R. Hockless, *J. Organomet. Chem.* 1997, 549, 127. (j) I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, A. Persoons, G.A. Heath, D.C.R. Hockless, *Organometallics* 1997, 16, 2631. (k) S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamasa, J. Gimeno, I.R. Whittall, M.G. Humphrey, *SPIE*, 2852, 1996, 99. (l) I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, D.C.R. Hockless, *J. Organomet. Chem.* 1997, 544, 189. (m) R.H. Naulty, M.P. Cifuentes, M.G. Humphrey, S. Houbrechts, C. Boutton, A. Persoons, G. Heath, D.C.R. Hockless, B. Luther-Davies, M. Samoc, *J. Chem. Soc., Dalton Trans.*, 1997, 4167. (n) I.R. Whittall, M.G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid, D.C.R. Hockless, *J. Organomet. Chem.* 1997, 544, 277. (o) R.H. Naulty, A.M. McDonagh, I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, G. Heath, D.C.R. Hockless, *J. Organomet. Chem.*, in press. (p) S. Houbrechts, C. Boutton, K. Clays, A. Persoons, I.R. Whittall, R.H. Naulty, M.P. Cifuentes, M.G. Humphrey, *J. Nonlinear Opt. Phys. Mater.*, 1998, 7, 113. (q) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.*, 1998, 42, 291. (r) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.*, 1998, 43, 349.

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Polydentate ligands containing N-donor heterocyclic rings have played an important role in the development of coordination chemistry and continue to be of widespread interest, particularly centered upon complexes of diimine-type ligands, such as 2,2'-bipyridine, 1,10-phenanthroline and bis(o-pyridyl)amine¹. In this work, we describe the synthesis and characterization of ruthenium(II) polypyridyl-phosphine complexes, with general formula *cis*-[RuCl(bpa)₂(L)]PF₆, where L = triphenylphosphine, ethyldiphenylphosphine, *p*-tolylidiphenylphosphine, triphenylarsine and bpa = bis(o-pyridyl)amine. The complexes were obtained from *cis*-[RuCl₂(bpa)₂].2H₂O and were isolated in solid state. All the species were characterized by elemental analysis, cyclic voltammetry, conductivity measurements, UV-Vis, NMR and IR spectroscopies.

The precursor *cis*-[RuCl₂(bpa)₂].2H₂O (bpa = bis(o-pyridyl)amine) was obtained by heating a mixture of RuCl₃.3H₂O, LiCl and bpa at 140°C in ethylene glycol for 48 hours. The reaction of *cis*-[RuCl₂(bpa)₂].2H₂O with an excess of phosphine or arsine ligand gave a series of Ru(II) mentioned complexes. The ³¹P{¹H} NMR spectra of these complexes, measured in CH₂Cl₂, showed only singlets (δ 40-44 (ref. H₃PO₄)), confirming the presence of coordinated phosphine groups. In CH₂Cl₂, cyclic voltammetry of these complexes showed a one-electron, chemically reversible wave corresponding to the Ru^{III}/Ru^{II} couple. The E_{1/2} values for these complexes are in the range 0,66 – 0,68 V (versus Ag/AgCl). Conductivities of these complexes vary from 100 to 134 ohm⁻¹ cm² mol⁻¹ in acetone. Values for a 1:1 electrolyte in the solvent are 100-140 range, and thus the data are in good agreement with the compositions of these complexes.

(1) Queiroz, S.L.; Batista, A.A.; Oliva, G.; Gambardella, M.T.do P.; Santos, R.H.A.; MacFarlane, K.S.; Rettig, S.J. and James, B.R. *Inorg. Chim. Acta* 1998, 267, 209.

Acknowledgments : The author acknowledges grants from FAPESP.

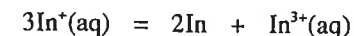
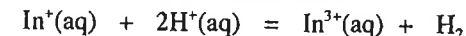
Low-valent indium in aqueous solutions

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Solutions containing indium in low-valent states can be produced by anionic oxidation of the metal in aqueous media or by the action of an indium/mercury amalgam. In⁺ may attain a concentration of up to 10⁻³ mol L⁻¹. The product is a strong reductant and potentially useful as such, although little is known of the particular species or its interaction with ligands. Modes of decay of the indium(I) cation include oxidation by water or acid to form In³⁺(aq), and disproportionation:



The presence of halogen acids, HCl, HBr or HI slows the rate of oxidation, apparently because of the stabilising effect of halide as a ligand for the low-valent species. Freshly prepared HCl and HBr solutions of indium continue to evolve hydrogen, even when no trace of metal remains, which provides further evidence of low-valent indium. With these facts in mind, we have examined a recent report of ambient-temperature formation of crystalline indium monohalides from aqueous media,¹ e.g. InBr as an orange-red solid. Our investigations suggest that the solution precursor may not be In⁺(aq), but instead it may be the dinuclear indium(II) species In₂⁴⁺ in the form of bromide complexes akin to those long known for gallium.^{2,3}

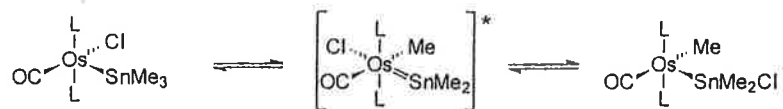
1. R. Dronskowski, *Inorg. Chem.* 33, 5960 & 6201 (1994).
2. C.A. Evans and M.J. Taylor, *Chem. Commun.* 1201 (1969).
3. L.A. Woodward and M.J. Taylor, *J. Inorg. Nucl. Chem.* 27, 737 (1965).

NOVEL INTERCHANGE OF LIGANDS BETWEEN OSMIUM AND TIN IN COORDINATIVELY UNSATURATED OSMIUM STANNYL COMPLEXES

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Photolysis of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ in benzene/toluene in the presence of $(\text{CH}_2=\text{CH})\text{SnMe}_3$ for seven minutes provides a deep red solution which contains the coordinatively unsaturated $\text{Os}(\text{II})$ complex $\text{Os}(\text{SnMe}_3)(\text{Cl})(\text{CO})(\text{PPh}_3)_2$.¹ Treatment of this solution with NaS_2CNR_2 provides the expected coordinatively saturated complexes $\text{Os}(\text{SnMe}_3)(\eta^2\text{-S}_2\text{CNR}_2)(\text{CO})(\text{PPh}_3)_2$ (1; $\text{R}=\text{Me}$; 2; $\text{R}=\text{Et}$) in good yield. These feature the dithiocarbamate ligand bound in a bidentate fashion to the osmium centre. However, we have now found that treatment of the red solution with NaO_2CR yields the complexes $\text{Os}(\text{SnMe}_2\text{OC}(\text{O})\text{R})(\text{Me})(\text{CO})(\text{PPh}_3)_2$ (3; $\text{R}=\text{H}$; 4; $\text{R}=\text{Me}$; 5; $\text{R}=\text{Ph}$). Here a methyl group has migrated from tin to osmium and the carboxylate ligand bridges across the Os-Sn bond. The geometry at the tin centre closely resembles that found in base stabilised stannylene complexes. These results suggest that in solution $\text{Os}(\text{SnMe}_3)(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ might be in equilibrium with the corresponding coordinatively unsaturated dimethylchloro stannyl complex, perhaps via an intermediate stannylene complex. ($\text{L}=\text{PPh}_3$)



Addition of the Lewis base, pyridine, gives the stannyl complex $\text{Os}(\text{SnMe}_2\text{Cl})(\text{Me})(\text{CO})(\text{py})(\text{PPh}_3)_2$ (6), which results from interchange of Cl and Me between the osmium and tin. Compound 6 reacts with NaS_2CNR_2 to give $\text{Os}(\text{SnMe}_2\text{SC}(\text{S})\text{NR}_2)(\text{Me})(\text{CO})(\text{PPh}_3)_2$ (7; $\text{R}=\text{Me}$; 8; $\text{R}=\text{Et}$), where the ligand bridges across the Os-Sn bond in analogous fashion to carboxylate examples. Compounds 7 and 8 can also be prepared by treatment of 4 with dialkyldithiocarbamate.

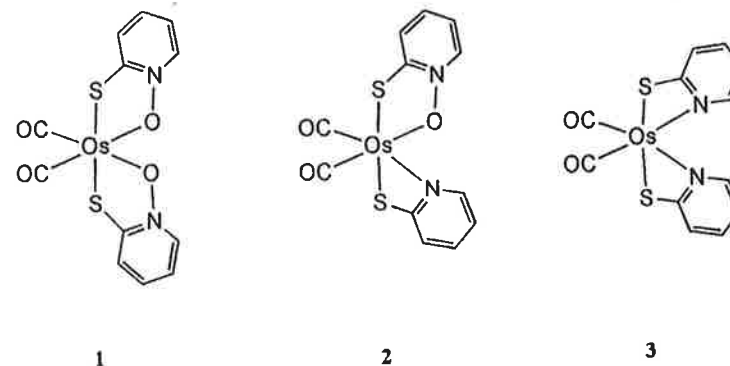
1) P. D. Craig, K. R. Flower, W. R. Roper and L. J. Wright, *Inorg. Chim. Acta*, 1995, **240**, 385

STEPWISE TRANSFORMATION OF 1-HYDROXYPYRIDINE-2-THIONE INTO *N*-OXIDE AND THIOAMIDE LIGANDS IN OSMIUM COMPLEXES

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The reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with excess 1-hydroxypyridine-2-thione in the presence of Me_3NO yielded three mononuclear osmium complexes $\text{Os}(\text{CO})_2(\eta^2\text{-SC}_3\text{H}_4\text{N}(\text{O}))_2$ (1), $\text{Os}(\text{CO})_2(\eta^2\text{-SC}_3\text{H}_4\text{N}(\text{O}))(\eta^2\text{-SC}_3\text{H}_4\text{N})$ (2), and $\text{Os}(\text{CO})_2(\eta^2\text{-SC}_3\text{H}_4\text{N})_2$ (3). The pyridinethione *N*-oxide-ligated triosmium complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\eta^2\text{-S-C}_3\text{H}_4\text{N}(\text{O}))$ (4) has been found as the first intermediate, which was subsequently converted to $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-}\eta^2\text{-}\eta^1\text{-SC}_3\text{H}_4\text{N}(\text{O}))$. The stepwise degradation of the triosmium complex 4 to the mononuclear complexes 1–3 as well as the transformation of 1-hydroxypyridine-2-thione into the coordinated *N*-oxide and thioamide ligands have also been examined.



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Over recent years there has been interest in the synthesis of open-framework metal phosphonates due to their potential applications in the areas of sorption, ion exchange, catalysis and sensors. To date the majority of research in this area has focussed on the synthesis and characterisation of divalent-, trivalent- and tetravalent-metal phosphonates, in particular those of zirconium. With some exceptions, metal ions in these lamellar systems are octahedrally coordinated with the organophosphonate moieties directed into the interlayer space.

Research into the phosphonates of the p-block Group-III metals has focussed on aluminium, with some recent interest in gallium. In this work the first layered indium phosphonate compounds, as well as an indium phosphinate and arsonate, have been synthesised at high temperature and pressure from aqueous solutions of indium(III) chloride tetrahydrate and the corresponding phosphorus or arsenic containing acid. The resulting compounds were characterised by elemental analysis, FTIR, TGA, powder XRD, ^{31}P , and ^{13}C MAS NMR. The properties of these compounds, the majority of which conform to the formula $\text{In}(\text{O}_2\text{X}(\text{O})\text{R})(\text{OX}(\text{OH})(\text{O})\text{R})\cdot\text{H}_2\text{O}$ (where R is CH_3 , C_6H_5 or $\text{C}_6\text{H}_5\text{CH}_2$ when X is P, R is C_6H_5 when X is As), will be outlined in this paper.

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The development of complexes that mimic the structural and/or the functional properties of enzymes that hydrolyse phosphate ester bonds in such molecules as DNA or RNA is generating considerable interest. It has been reported¹ that at the active sites of these metalloenzymes pendant protein functional groups such as carboxyl, alcohol and imidazole, and the metal centres are located in close proximity and act in concert to promote nucleophilic substitution at the phosphate group. Since many of these enzymes have been found to have two or more unsaturated metal centres at the active sites, the development of low molecular weight metal complexes which mimic the properties and function of metalloenzymes have attracted much attention.

Our own studies have focused on the metal complexes of polynucleating ligands derived from the small macrocycle 1,4,7-triazacyclononane. In particular, the bis- and tris-(1,4,7-triazacyclononane) ligands and their pendant arm carboxylate derivative (figure 1). An attractive feature of these ligands is they bind strongly to many metal centres whilst leaving one or more coordination sites available for coordination of substrates or for generation of nucleophiles capable of promoting hydrolytic reactions. The complexes will be studied for their ability to promote the hydrolysis of phosphate esters.

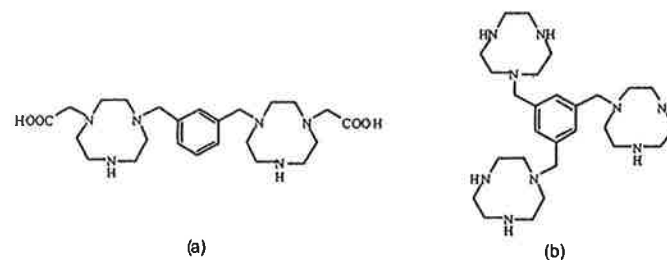


Figure 1 Example of a bis(1,4,7-triazacyclononane) ligand with carboxylate arms (a) and a tris(1,4,7-triazacyclononane) ligand (b).

References

1. Kimura, E., *Progress in Inorganic Chemistry*, 1994, 443.

NITROGEN AND OXYGEN MIXED DONOR MACROCYCLES

INCORPORATING BENZYL PENDANT ARMS:

SYSTEMS SHOWING SILVER(I) SELECTIVITY

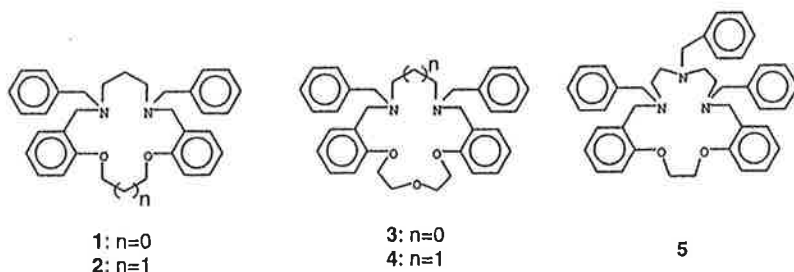
Jeong Kim,^{*†} Tania Strixner,[#] Gang Wei,[†] Brendan R. Rumbel,[†] Leonard F. Lindoy[†]

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Macrocyclic ligands incorporating pendant arms attached to nitrogen donor atoms have been the subject of much study in recent years. In the context of metal-ion discrimination studies, we have investigated the effects of N-benylation of a series of mixed oxygen-nitrogen donor macrocycles on their metal binding properties. Thus, starting from the corresponding secondary-amine containing precursors, we have synthesised the series of benzylated derivatives given by 1 to 5. We have also investigated the binding constants for the cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II) and silver(I) complexes of each of the above ligand types by potentiometry in 95 percent methanol.



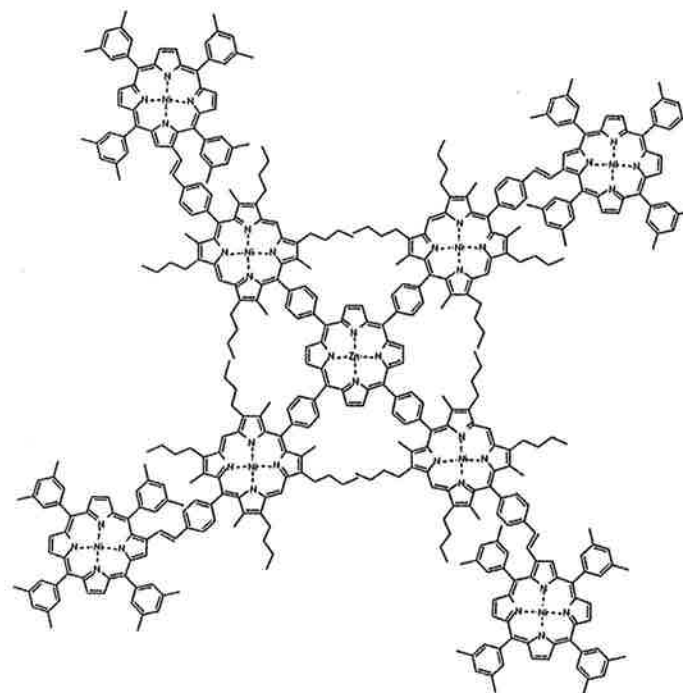
Compared with the corresponding complexes of the (unsubstituted) parent macrocycles, N-benylation generally resulted in the lowering of complex stability, as expected from steric effects involving the bulky substituents. However, for the silver(I) complexes of 3 and 5, comparable log *K* values to those for the corresponding parent rings were obtained. This unexpected behaviour has been probed using ¹³C induced chemical shift measurements.

Ligands 3 and 5 were demonstrated to act as ionophores for the selective transport of silver(I) across bulk chloroform membranes (in the presence of equimolar concentrations of the other six metal ions mentioned above).

COOKING UP MIXED-METAL AND MIXED-PORPHYRIN LINEAR TRIMERS, PENTAMERS AND PANCAKE NONAMERS

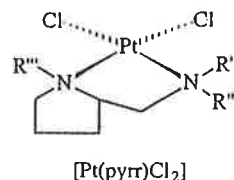
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The synthesis of the appropriate porphyrinic aldehydes leads efficiently to the synthesis of large mixed-metal and mixed-porphyrin molecules. These large photoactive molecular systems are easily fabricated by employing a combination of Wittig chemistry and acid catalysed pyrrole-aldehyde type condensation reactions on porphyrinic aldehydes.

We have been using the chiral platinum complexes [Pt(ahaz)Cl₂] (ahaz = 3-aminohexahydroazepine) and [Pt(pyr)Cl₂] (pyr = 2-aminomethylpyrroline) and its derivatives to probe the mechanisms of both their anti-cancer activity and toxic side-effects. As a part of this work we have identified and quantified the adducts formed when these complexes bind to DNA and have observed substantial stereoselectivity and enantioselectivity in the adduct profiles.



The enantiomers of each complex can form two orientational isomers of the GpG adduct when they bind to DNA; one with the primary amine directed toward the 5' direction and the other with it orientated toward the 3' direction. We do indeed observe two isomers in digests of DNA treated with either *R*- or *S*-[Pt(ahaz)Cl₂]. For the *R* enantiomer the two isomers form in approximately equal amounts, accounting for 9 and 12% of the platinum bound to the DNA. In contrast, for the *S* enantiomer the isomers form in different amounts, accounting for 7 and 30% of the platinum. High resolution 2D NMR spectroscopy is being used to identify the isomers; preliminary assignment of the most abundant isomer, combined with molecular modelling, shows it has the orientation which results in fewest non-bonded contacts with the DNA. It exists in two forms in solution: with the guanine H8s in a head-to-head or head-to-tail orientation. Variable temperature 1D NMR spectra have been analysed and simulations performed to obtain the rate of exchange of the sugar backbone between the two forms.

Similar studies are now being carried out for the [Pt(mepyr)Cl₂] complexes: preliminary studies on the binding of the *S*-enantiomer to a dinucleotide show it to form four isomers, resulting from two orientational isomers for each chirality at the exocyclic nitrogen. Molecular modelling studies show similar total strain energies for all four isomers.

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POSTERS

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As part of a continuing program, XAFS data in the range $0 \leq k \leq 16.3 \text{ \AA}^{-1}$ have been obtained from frozen aqueous solutions (10 K) of horse heart Fe(II) and Fe(III) cytochrome *c* (cyt *c*), and of nitrophorin in its native Fe(III) state and as the Fe(II)-NO and Fe(III)-NO adducts. The latter adducts are used by blood sucking insects (*Rhodnius prolixus*) to transport NO to the blood of the host animal where it is used as a vasodilator.

The structures of the Fe sites have been refined using both single-scattering (SS) and multiple-scattering (MS) analyses. The XAFS MS analyses yield more precise Fe-ligand bond lengths (estimated error $0.02 - 0.03 \text{ \AA}$) than those determined previously from X-ray crystal data for cyt *c* (estimated errors $\geq 0.1 \text{ \AA}$). For both forms of cyt *c*, the Fe-N(pyrrole) distances are 1.98-1.99 \AA and the Fe-N(imidazole) distances 1.98-2.00 \AA . The Fe-S(methionine) distance of Fe(II) cyt *c* (2.29 \AA) is shorter than for Fe(III) cyt *c* (2.33 \AA), although the values are not significantly different. The small changes in bond lengths are consistent with the fast electron transfer of cyt *c*.

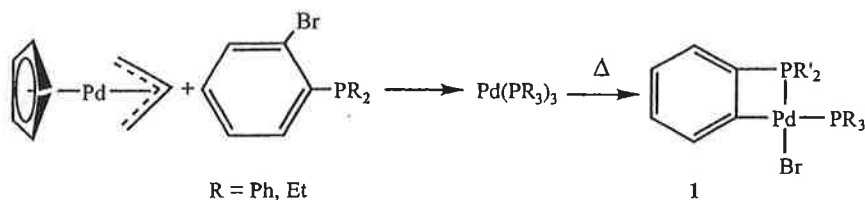
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SYNTHESIS AND CHEMISTRY OF PALLADACYCLES BASED ON
THE LIGANDS $\text{PR}_2(\text{C}_6\text{H}_4)$.

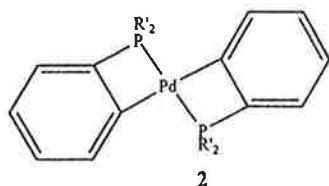
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There has been much recent interest in the chemistry of five membered palladacycles, due to their ability to catalyse the Heck reaction much more efficiently than previous catalytic mixtures¹. The activity of these species has led to a reassessment of the catalytic cycle involved in this reaction². Little work has been produced on four membered palladacycles, such as **1**, with only one example reported. We will discuss alternative routes to the synthesis of four membered palladacycles, with the most useful shown below.



The chemistry of these species will be presented, as well as studies on their catalytic behaviour. Attempts to produce a bis(cyclometallated) Palladium complex, such as **2**, will also be described.



¹ W.A. Herrmann, C. Brossmer, C.P. Reisinger, T.H. Riermeier, K. Ofele & M. Beller, *Chem. Eur. J.*, 1997, 3, 1357; B.L. Shaw, S.A. Perera & A. A. Staley, *Chem. Commun.*, 1998, 1361..

² B.L. Shaw, *New J. Chem.*, 1998, 77.

THE FIRST CRYSTAL STRUCTURES OF
BISMUTH(III) PORPHYRIN COMPLEXES

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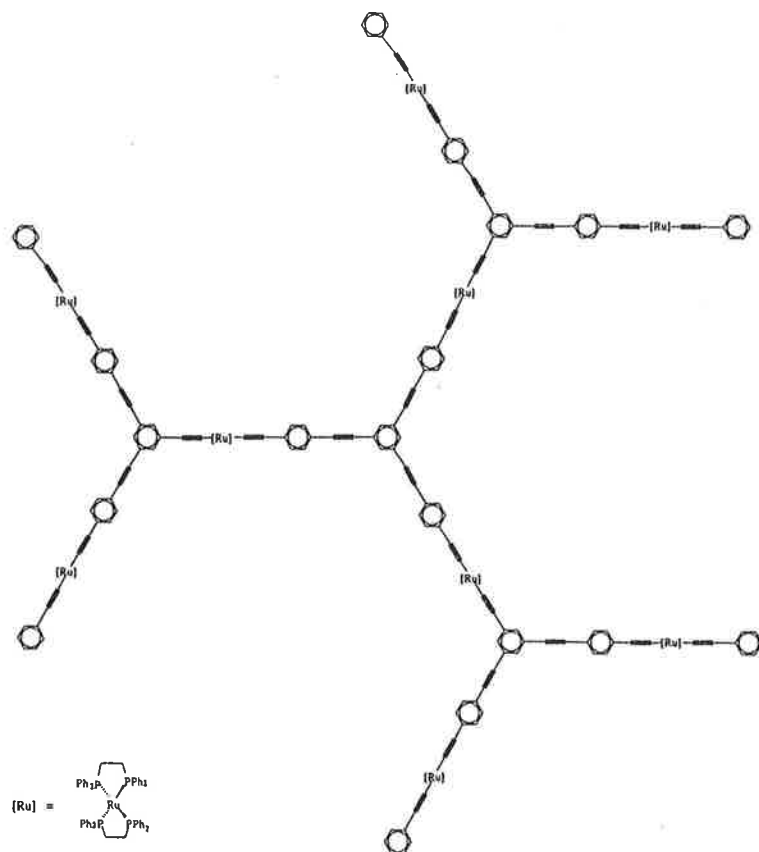
The chemistry of porphyrin complexes of the main group elements has been developed only recently, and a variety of applications have been investigated. The general order of stability of Group 15 porphyrins in oxidation state III is $\text{Bi}^{\text{III}} > \text{Sb}^{\text{III}} > \text{As}^{\text{III}} > \text{P}^{\text{III}}$. Among these, only Bi(III) porphyrins have been crystallographically characterised, as detailed below.

Here we demonstrate the synthesis and crystal structure of some $\text{Bi}(\text{Por})\text{X}$ complexes where Por = tetra-*p*-chlorophenylporphyrin or tetra-*p*-tolylporphyrin and $\text{X} = \text{NO}_3^-$, I^- or Br^- . The nitrate and the iodide complexes were prepared by reacting bismuth(III) nitrate or iodide with the porphyrin free base in refluxing pyridine. The bromide complex was unexpectedly obtained from the reaction of $(\text{C}_6\text{H}_5)_3\text{BiBr}_2$ with the porphyrin base in pyridine, presumably by a reductive process. The green compounds were recrystallised from $\text{CH}_2\text{Cl}_2/\text{ethanol}$.

The molecular structure of these compounds show that the four coordinate Bi^{III} ion protrudes from the porphyrin N_4 plane by more than 1 Å, and exhibit a dinuclear arrangement of $[\text{Bi}(\text{Por})]^+$ units where the X^- anions bridge between the Bi atoms. The iodide and the bromide complexes have more symmetrical molecular structures than that of the nitrate complex.

Further details of the synthesis and characterisation of the new bismuth porphyrin complexes will be presented, including UV-visible and NMR spectroscopic data.

Few examples of organometallic dendrimers with metal centres in each layer (rather than just at the periphery) have been reported. We have recently prepared the illustrated alkynylruthenium dendrimer using the metal centre as the reactive site for dendrimer growth. A convergent synthetic technique was utilized in which a core containing ligated Ru-Cl centres was coupled to three dendrimer 'wedges', each containing a terminal acetylene, to yield a dendritic organometallic complex with acetylide linkages. The synthetic methodology, used for the first time to prepare complexes of this size and geometry, will be presented.



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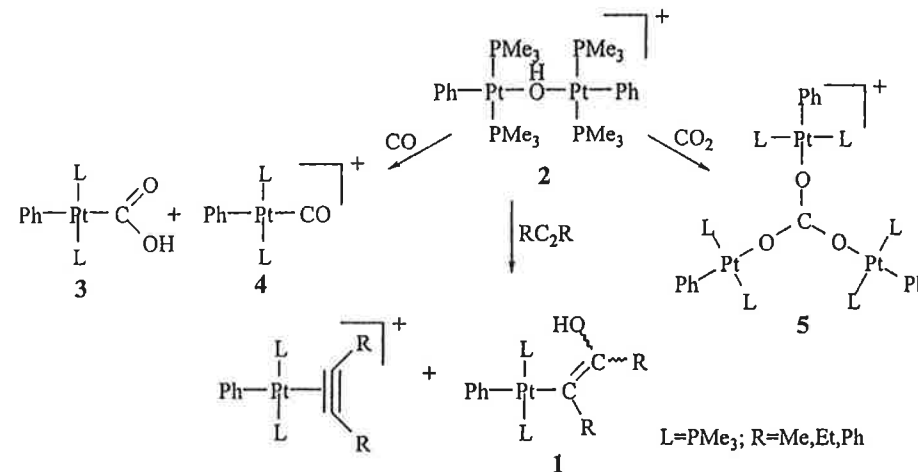
ORGANOPLATINUM(II) HYDROXO COMPLEXES

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The insertion of alkenes (dimethyl maleate, tetrafluoroethene) has been reported to take place into the Pt-OH bonds of Pt(II) hydroxo complexes of the type *cis*-[PtMe(OH)L₂] (L₂ = 2PPh₃, dppe, pdmp) to give hydroxyethyl complexes,¹ whereas complexes of the type *trans*-[PtPh(OH)L₂] (L = PPh₃, PEt₃) have been shown to add alkynes to give σ -enol complexes analogous to 1.² In an attempt to extend the range of alkenes/alkynes which insert into Pt-OH bonds, as well as determining the importance of the *cis/trans* geometries in these complexes, several compounds containing phosphines of low steric bulk such as PMe₃ or dmpe have been prepared, including the dinuclear complex *trans*-[(PtPh(PMe₃)₂)₂(μ -OH)](SO₃CF₃) (2). The reactivity of these complexes towards alkenes and alkynes has been investigated and the mechanisms for the formation of the insertion products (ie. external OH⁻ attack versus migratory insertion) will be discussed.

The novel bridged hydroxo complex 2 has proved to be a versatile and reactive starting material. For example, reaction with CO gives a 1:1 mixture of the hydroxycarbonyl complex (3) and the cationic mononuclear carbonyl complex (4), whereas it reacts with CO₂ to give a trinuclear μ -carbonato complex (5). Mechanisms for these reactions will be proposed.



1.(a) Bryndza, H.E. and Tam, W. *Chem. Rev.* **1988**, *88*, 1163 (b) Bennett, M.A. *et al. J. Am. Chem. Soc.* **1995**, *117*, 8335; erratum: *J. Am. Chem. Soc.* **1996**, *118*, 6528.

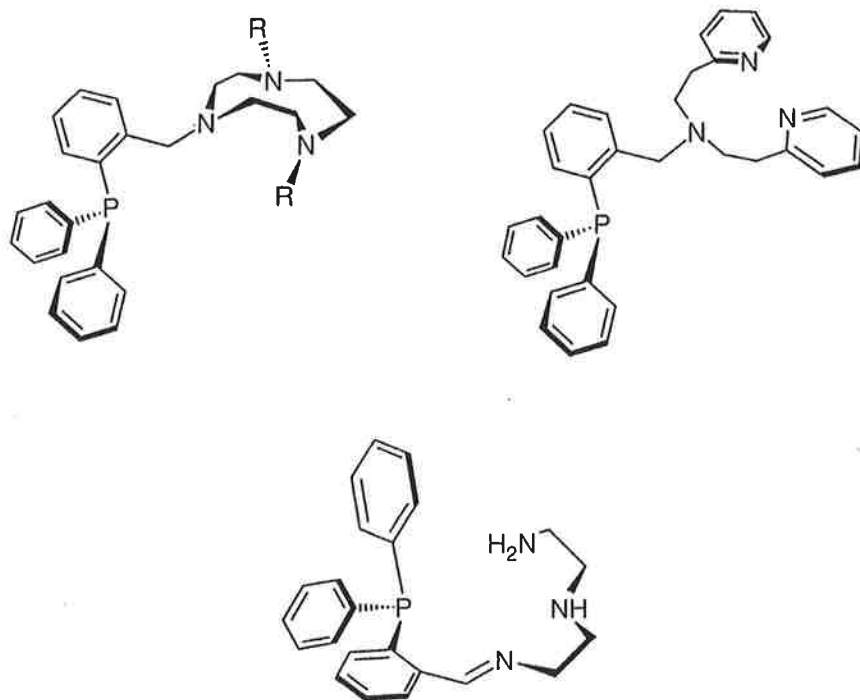
2. Jin, H. *Ph.D. Thesis*, The Australian National University, 1990.

W82

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University of New South Wales, Sydney, 2052, Australia

Ligands capable of stabilising multinuclear transition metal complexes with binding domains for both dioxygen and an organic substrate have potential biological and catalytic relevance. The synthesis of several new phosphine ligands with triazacyclonane, bispyridylethylamine and diethylenetriamine substituents and their metal complexes will be described. The "soft" phosphine centre was chosen because of the extensive transition metal chemistry of phosphines which includes many catalytically active complexes. The "hard" N-donor binding domains were selected because simple transition metal complexes of these have been demonstrated to bind and activate dioxygen. Work towards the synthesis of heteronuclear dimers and trimers of these ligands will also be discussed.



Sequence Selectivity of Cisplatin: Intra- and Interstrand Binding Kinetics of Cisplatin to DNA.

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The anticancer properties of cisplatin are believed to arise from its binding to intracellular DNA, inducing a conformational change. Platination is concentrated at intrastrand GpG (65%) and ApG (25%) sites, and is also seen at low levels at intrastrand GpNpG and interstrand G-G positions. Bifunctional binding is not observed at GpA sites.

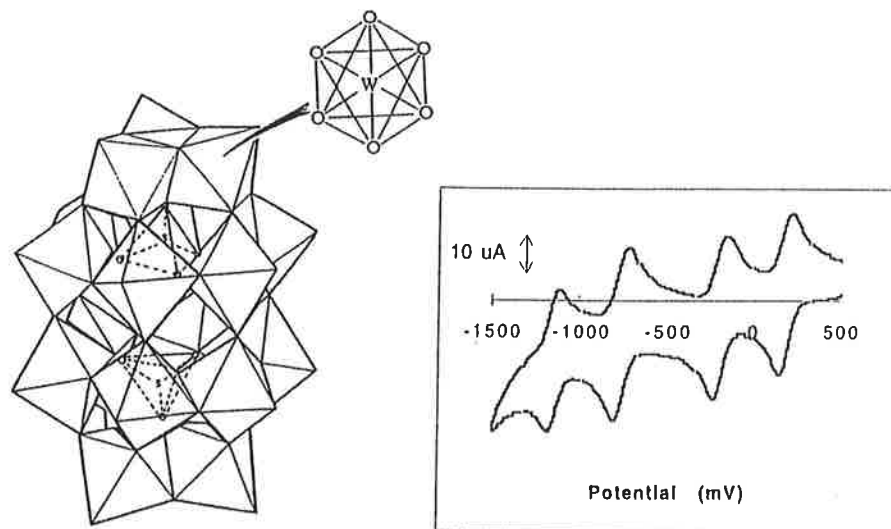
Recently, we reported a [¹H, ¹⁵N] HSQC 2D NMR spectroscopic of the kinetics of the reaction of cisplatin with two 14-base pair defined duplex oligonucleotides bearing, either an intrastrand ApG or GpA site.¹ Our results showed a slower rate of monofunctional formation for GpA relative to ApG and a dramatically slowed rate of closure to form a Pt-GpA chelate relative to Pt-ApG. Interestingly, the diaqua form of cisplatin did not exhibit a slower rate of platination, although closure was slowed, with the GpA oligonucleotide.

The technique has now been extended to a study of the rates of reaction between cisplatin and two 14-mer duplex oligonucleotides d(AATTATGCATAATT) and d(AATTAACGTTAATT), where the preferred bifunctional adduct is, in each case, a 1,2-*interstrand* G-G adduct, differing only in the direction of the crosslink. Rates of reaction are compared with those of similar oligonucleotide sequences, and the influence of the rate of platination on the product distribution is explored.

¹ Davies, M. S.; Berners-Price, S. J.; Hambley, T. W. *J. Am. Chem. Soc.*, 1998, In press.

The hetero-atom X in polyoxoanion clusters, $[X_xM_yO_z]^{n-}$, determines the anionic charge. For example, X = Si^{IV}, P^V or S^{VI} in the tungsten(VI) Dawson anions $[X_2W_{18}O_{62}]^{n-}$ leads to n = 8, 6 or 4, respectively. The progressive decrease in anionic charge leads to positive shifts in reduction potentials allowing redox activity to be photo-induced. This aspect has been explored recently in the $[S_2Mo_{18}O_{62}]^{4-}$ system.^{1,2}

The new heteropolyoxotungstate $[S_2W_{18}O_{62}]^{4-}$ has now been isolated. It exhibits the Dawson structure (D_{3h} point symmetry) and a spectacular redox chemistry (see figures below).

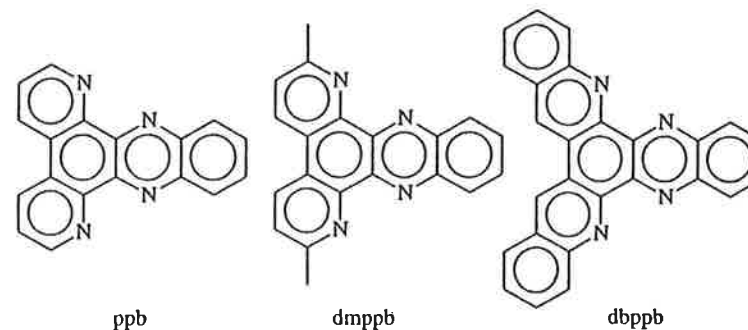


SYNTHESIS AND SPECTROELECTROCHEMISTRY OF A NEW SERIES OF RIGID PHENANTHROLINE-TYPE LIGANDS

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University of Otago

Metal complexes with polypyridyl ligands are the subjects of furious research because of their potential in solar energy harvesting, molecular device technology and as chemical sensors. An area of interest in the development of molecular devices is the control of intersite communication through bridging ligands. Such communication is manifest in the level of charge delocalisation when the complex is oxidised or reduced and in the rate of interchromophoric energy transfer between moieties on either side of the bridging ligand. We have synthesized a series of rigid highly conjugated polypyridyl ligands that we believe will facilitate effective intermetal communication. The ligands are based on diprydilphenazine (ppb)



The osmium(II) mononuclear and heteronuclear osmium(II)/rhenium(I) complexes have been characterized and their spectroelectrochemical properties investigated.

The bimetallic complexes have shown a remarkable ease of reduction with the first and second reductions being localized on the bridging ligand.

¹ A. M. Bond, D. M. Way, R. G. Compton, J. Booth, J. C. Eklund and A. G. Wedd, *Inorg. Chem.*, 1995, 34, 3378.

² D. M. Way, J. B. Cooper, M. Sadek, T. Vu, P. J. Mahon, A. M. Bond, R. T. C. Brownlee and A. G. Wedd, *Inorg. Chem.*, 1997, 36, 4227.

Intercalation Reactions with Lamellar Manganese (III, IV) Oxide

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Manganese oxides having good electrochemical performance are attractive as cathode materials for lithium batteries because manganese has economic and environmental advantages over compounds based on cobalt and nickel.

Birnessite is a lamellar manganese dioxide based on octahedral MnO_6 units, with stoichiometry $\text{AMnO}_2 \cdot x\text{H}_2\text{O}$, where A is an alkali metal cation ($\text{A} = \text{K}, \text{Na}, \dots$) intercalated between the layers of MnO_6 octahedra.

Using both ion exchange (1) and acid-base reactions (2) it is possible to intercalate a monolayer of alkylammonium salts of different chain length. We are particularly interested in the intercalation of long chain alkylammonium ions (n : carbon number = 10, 12, ..., 18). For each chain we have a different interlayer spacing, giving a d-spacing increase of 1.27 Å per $-\text{CH}_2$ group (3).

We have shown that thermal treatment of the monolayer phase produces a bilayer structure, with an increase of 2.8 Å per $-\text{CH}_2$ group. The rate and the temperature of the monolayer to bilayer transition varies with n .

A novel polyaniline birnessite hybrid phase has been prepared via the exfoliation of reduced bilayer and monolayer hexadecylammonium structures.

REACTION KINETICS AND MECHANISM OF FORMATION OF $[\text{MnW}_6\text{O}_{24}]^{8-}$ BY HYPOCHLOROUS ACID OXIDATION OF $\text{Mn(II)}_{\text{aq}}$ IN THE PRESENCE OF TUNGSTATE

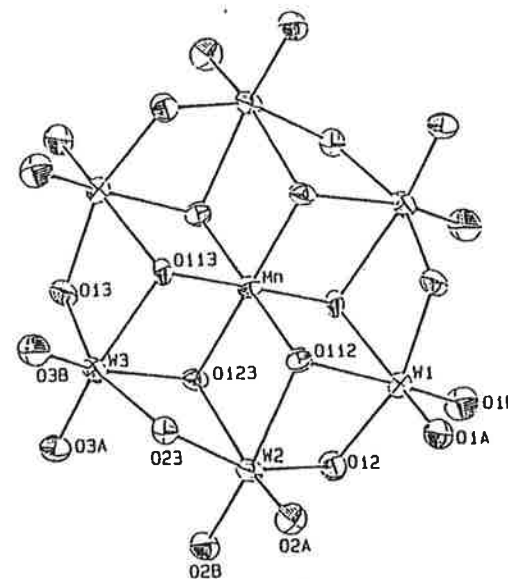
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email: annette@paracelsus.newcastle.edu.au

Oxidation of Mn(II) by HOCl in weakly acidic solution, in the presence of tungstate, gives $[\text{MnW}_6\text{O}_{24}]^{8-}$. The kinetics of oxidation was found to exhibit solution autocatalytic behaviour, and followed an expanded rate expression consisting of two terms:

$$+d[\text{MnW}_6\text{O}_{24}^{8-}]/dt = k_{\text{AC(1)}}[\text{Mn}^{2+}][\text{MnW}_6\text{O}_{24}^{8-}][\text{HWO}_4]^{-2}[\text{OCl}^-] \\ + k_{\text{AC(2)}}[\text{Mn}^{2+}][\text{MnW}_6\text{O}_{24}^{8-}][\text{HWO}_4]^{-2}[\text{HOCl}]$$

where $k_{\text{AC(1)}}$ and $k_{\text{AC(2)}}$ are $1.7(1) \times 10^{15}$ and $6.9(4) \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25.0 °C and are the autocatalytic rate constants for the OCl^- and HOCl pathways, respectively. A mechanism involving the formation of a transition state based on a partially built Mn(IV) -centred Keggin structure is proposed. The structure of $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$, which contains the product species, is also reported. The $[\text{MnW}_6\text{O}_{24}]^{8-}$ ion exhibits a standard Anderson structure with six octahedral tungstate edge-sharing units surrounding the central manganese, with all metals in a common plane.



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Layered manganese dioxides, birnessites, have been studied by cyclic voltammetry and Raman spectroscopy. Electrochemical polarisations have been carried out using two types of electrode coatings; thin film and a thicker birnessite/graphite/Teflon composite.

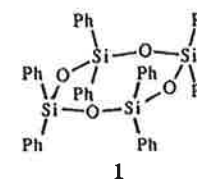
Raman spectroscopy shows heterogeneous phase transformation of hydrogen birnessite to Mn_2O_3 at high negative potentials. The addition of Li^+ in working solution leads to intercalation of Li^+ ions and a change of electrochemical behaviour of the birnessites to reversible reduction-oxidation of MnO_2 . Under these conditions the Raman spectra do not show "structural collapse" to Mn_2O_3 .

Polarisation data for amine salts and for aniline are comparable for those of Li^+ where intercalation has occurred. Cyclic voltammetry in organic solution also demonstrates the absence of any phase transformation and points to the reversible behaviour of birnessites.

A good correlation of electrochemical and spectroscopy results has been obtained.

Self Assembly of Fullerene C_{60} and a SiloxaneIan Grey,^a Michael J. Hardie,^b Tim Ness,^b and Colin L. Raston^b^aCSIRO Division of Minerals, Clayton, Melbourne, Victoria, 3168 Australia.^bDepartment of Chemistry, Monash University, Clayton, Melbourne, Victoria 3168 Australia

Rigid concave surfaces such as Ni(II) macrocycles¹ and cyclotrivaltylene² can bind globular molecules including P_4S_3 , *o*-carborane, and C_{60} and C_{70} . The binding of such molecules which have curvature complementarity will be favoured entropically over the binding of solvent molecules. Moreover, there is no pre-organisational energy requirement of the rigid receptor molecule prior to complexation with a globular molecule. Octaphenylcyclotetrasiloxane, **1**, has a rigid core and several concave surfaces. We find that it forms a 1:1 complex with C_{60} and this complex has been characterised using X-ray diffraction data.



1. P. C. Andrews, J. L. Atwood, L. J. Barbour, P. J. Nichols, and C. L. Raston, *Chem. Eur. J.*, 1998, 4, 1384.

2. R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kaddour, C. L. Raston, *Angew. Chem.*, 1997, 109, 520. *Angew. Chem., Int. Ed. Engl.*, 1997, 36, 504; J. L. Atwood, M. J. Barnes, R. S. Burkharter, P. C. Junk, J. W. Steed, C. L. Raston, *J. Am. Chem. Soc.*, 1994, 116, 10346; J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.*, 1996, 1449.

AN ADVANCED INORGANIC EXPERIMENT FOR CORRELATION OF INFRARED
VIBRATIONAL MODES WITH DESCENT OF SYMMETRY IN SOME SULPHATO
MULTIAMMINECOBALT(III) COMPLEXES

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In order to illustrate principles taught in Applications of Symmetry and Group Theoretical Concepts to Vibrational Spectroscopy in Inorganic Chemistry 3, we searched for a suitable experiment to correlate descent of symmetry from T_d , to C_{3v} and C_{2v} , with changes in vibrational modes in oxoanions in metal complexes. Numerous literature methods on different oxoanions systems were tried and they were not always suitable or reliable for an undergraduate experiment.^{1,2,3}

This Experiment synthesizes the well known complexes $[Co(NH_3)_6]_2(SO_4)_3$, $[CoSO_4(NH_3)_5]Cl$ and $[Co_2(NH_2)(SO_4)(NH_3)_8]Cl_3$ in order to correlate the descent in symmetry of T_d , C_{3v} and C_{2v} sulphates with ν_1 , ν_3 and ν_4 IR vibrational modes. Viable synthetic procedures for these complexes were developed and the nature of the bridged C_{2v} sulphato complex confirmed by a time dependant 1H NMR study of the deuteration of *axial* and *equatorial* amines.

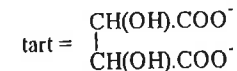
References

1. Ribas, J., Casabo, J. and Coronas, J.M., *J.Chem.Ed.* 1977, 54, 321.
2. Nakamoto, K., *Infrared and raman spectra of inorganic and coordination compounds*, 4th edn Wiley. 1986.
3. Hezel, A., and Ross, S.D., *Spectrochim. Acta*, 1968, 24A, 985

NOVEL WERNER COMPLEXES: SYNTHESIS AND STRUCTURAL STUDIES

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Novel Werner complexes $Co(NH_3)_6Cl.Cr_2O_7.H_2O$ (1), $Co(NH_3)_6Cl.SeO_4.3H_2O$ (2), and $Co(NH_3)_6Cl.(tart).H_2O$ (3) where



have been synthesized by reacting hexammine cobalt(III) chloride with appropriate salts in aqueous medium. Their structures were established by single-crystal X-ray crystallography.