Part 2

The Royal Australian Chemical Institute

Inorganic Chemistry Division Conference

IC'98

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1 – 5 February 1998

University of Wollongong

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Wollongong, New South Wales, Australia

1-5 February 1998

Written Contributions:

Posters

Continued . . . Part 2

PT 1

REACTIVITY OF AQUAPLATINUM(II) COMPLEXES TOWARD COMPONENTS OF MOBILE PHASES USED IN HPLC STUDIES

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Since the discovery of the anti-tumour properties of *cis*-diamminedichloroplatinum(II) ("cisplatin"), this complex and its hydrolysis products have been subjected to analytical and kinetic studies using reverse-phase high performance liquid chromatography (HPLC).[1-3] However, the components of the mobile phase have often been chosen without regard to their potential to displace the labile water molecules of aquaplatinum(II) complexes and coordinate to the metal ion. For example, mobile phases have been used containing phosphate,[1] carboxylates,[2] and acetonitrile.[3] Following previous work from this laboratory,[4] ^{15}N NMR has been used to study the reactivity toward platinum(II) aqua complexes of these and other substances that have been used in HPLC mobile phases. Because of such reactions, the validity of some previous HPLC studies must be called into question.

An effective mobile phase for HPLC analysis of cisplatin hydrolysis products has been developed, which contains only components which have little or no tendency to coordinate to platinum(II) in an aqueous medium: methanol, sodium dodecylsulfate (SDS), and trifluoromethanesulfonic acid. Traces of chloride present as impurity in commercial SDS interfere with the analysis, and must be removed. SDS as an "ion-pairing agent" is preferable to hexanesulfonate. Although hexanesulfonate shows only a slight tendency to displace water from aquaplatinum complexes in bulk aqueous solution, there are complicating reactions when hexanesulfonate is used in the mobile phase.

References :

1- A.Andersson, J.Fagerberg, R.Lewensohn, and H.Ehrsson, *J.Pharm.Sci.*, **85** (1996) 824
2- Z.Zhao,K.Tepperman, J.G.Dorsey, and R.C.Elder, *J.Chromatog.Biomed.Applic.*, **615** (1993) 83
3- P.T.Daley-Yates, and D.C.H.McBrien, *Biochem.Pharmacol.*, **33** (1984) 3063
4- T.G.Appleton, R.D.Berry, C.A.Davis, J.R.Hall, and H.A.Kimlin, *Inorg.Chem.*, **23** (1984) 3514

PREPARATION AND CHARACTERIZATION OF DINUCLEAR PLATINUM(III) COMPLEXES WITH NEW O-DONOR LIGANDS

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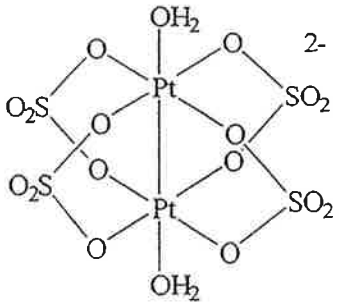
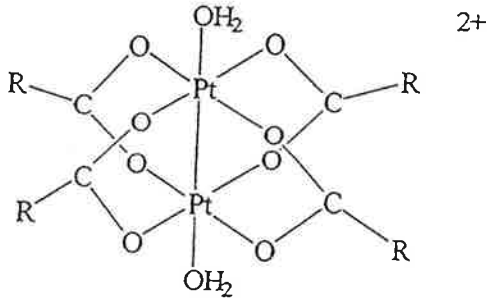
Many dinuclear platinum(III) complexes with metal-metal bonds with or without bridging ligands are now well characterized. Such dinuclear complexes containing bridging ligands form lantern shaped structures 1 .



1

The known dinuclear platinum(III) complexes with O-donor ligands e.g. $K_2[Pt_2(\mu\text{-}SO_4)_4(H_2O)_2]$[1] , $K_2[Pt_2(\mu\text{-}HPO_4)_4(H_2O)_2]$[1], $[Pt_2(\mu\text{-}CH_3COO)_4(H_2O)_2](CF_3SO_3)_2$[2], were prepared by the reaction of $[K_2Pt(NO_2)_4]$ with the appropriate acid, but have limited solubility in most solvents.The axial water molecules are labile enough for its substitution to form new compounds.



2

In the present investigation the interaction of $[K_2Pt(NO_2)_4]$ and *cis*- $[Pt(NO_2)_2(H_2O)_2]$ with a range of other bridging ligands like $RCOO^-$ ($R=C_2H_5$, C_3H_7 , C_4H_9 , CF_3) have been studied and complexes analogous to 2 have been prepared which are soluble in a wide range of solvents. ^1H and ^{195}Pt NMR and other physical techniques have been used to characterize these new compounds.

1. G.S.Muraveiskaya, G.A. Kukina, V.S. Orlava and M.A. Poraikoshits, *Dokl. Akad. SSSR.*, 226, 576, **1976;** D.P.Bancroft, F.A. Cotton, L. R. Falvello, *Inorg. Chim. Acta.*, 87, 147, **1984.**
2. T.G. Appleton, K.J.Barnham, K.A.Byriel, J.R. Hall, C.H.L.Kennard, M.T. Mathieson, K.G.Pennam, *Inorg. Chem.*, 43, 6040, **1995;** T.G.Appleton, K..A.Byriel, J.R. Hall, C.H.L.Kennard, M.T. Mathieson, *Inorg. Chem.*, 34, 5646, **1995.**

PT 3

A CONVENIENT ROUTE TO NEW DINUCLEAR PLATINUM (III) AND RHODIUM (II) COMPLEXES

G. Ade Ayoko and Trevor G. Appleton
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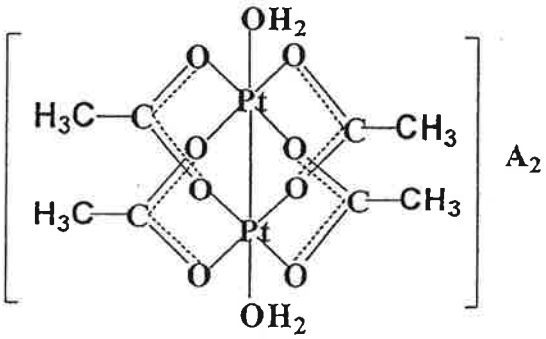
Dinuclear platinum (III) compounds, in which the two metal ions are bridged by four sulfate, hydrogen phosphate or acetate ligands[1,2], to give a "lantern structure" are now well-characterised. Of these, the acetate **(1)**, prepared by the reaction of $K_2[Pt(NO_2)_4]$ with $CH_3CO_2H/H_2O/HA$ ($A^- = CF_3SO_3^-$, ClO_4^- or NO_3^-), has the shortest Pt-Pt bond length and the smallest Pt-Pt-O(bridging ligand) angle [2].



(1)

These parameters, together with low shielding of the carboxylate carbon nuclei, were interpreted as indicating strain in the complex[2]. It is therefore reasonable to expect the complex to undergo metal-acetate bond cleavage, in the presence of suitable ligands, to give new dinuclear complexes. We describe in this poster the reactions of the acetate and of the electronically analogous but less structurally strained rhodium (II) acetate, [Rh_2 (μ-$CH_3CO_2)_4$ $(H_2O)_2$], with some N- and O-donor ligands, including 1,10-phenanthroline, 2, 2′-bipyridine, CF_3CO_2H, RPO_3H_2 (where R= CH_3, $ClCH_2$, and Ph), RSO_3H (with R= CH_3 and Cl) and $(PhO)_2P(O)(OH)$. The reactions described offer a convenient route to new platinum (III) or rhodium (II) complexes containing new N- and O-donor ligands.

References

1. Muraveiskaya, G.S., Kukina, G.A., Orlova, V.S., Evastaf'eva, O.N., Porai-Koshits, M.A. *Dokl. Akad. Nauk. SSSR* **1976**, 226, 576; Bancroft, D.P, Cotton, F.A., Falvello, L.R., Han, S., Schwotzer, W., *Inorg. Chim. Acta* **1984**, 87, 147

2. Appleton, T.G., Barnham, K.J., Byriel, K.A., Hall, J.R., Kennard, C.H. L., Matthieson, M.T., Penman, K.G., *Inorg.Chem.* **1995**, 43, 6040; 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

PT 4

CYCLIC ALKOXIDE-CARBOXYLATES OF TITANIUM(IV)

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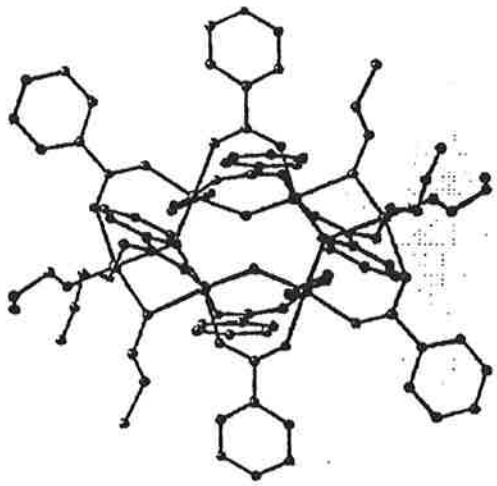
Metal alkoxides are commonly used as chemical precursors in sol-gel technology because of their ability to undergo hydrolysis and condensation reactions leading to formation of the final molecular oxide framework[1]. In practical applications carboxylic acids are often added to the alkoxide to modify the rates of hydrolysis or condensation reactions but the constitution of the carboxylate-alkoxide intermediates so produced is often unknown.

Mehrotra[2] has suggested the formula $Ti(O^iPr)_2(O_2CC_6H_5)_2$ for the product from the reaction having a 1:2 molar ratio of $Ti(O^iPr)_4$ to benzoic acid. We have re-examined this type of reaction using $Ti(O^nPr)_4$ and benzoic acid in toluene with exclusion of water and structurally characterised the product as $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(O^nPr)_8(O_2CC_6H_5)_8$, the oxo groups presumably being formed by ester elimination.



Ortep Diagram of $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(O^nPr)_8(O_2CC_6H_5)_8$

Crystalline products have also been isolated from similar reactions between $Ti(O^iPr)_4$ and $Ti(O^nPr)_4$ and pivalic or acetic acids. NMR data on such complexes will be presented. Related $Ti_6(\mu\text{-}O)_4$ alkoxide-carboxylate species have also been reported by Sanchez[3] and Mosset[4].

The formation of oxo bridges between Ti atoms prior to hydrolysis bears on the overall processes which eventually lead to the formation of TiO_2.

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[1] *Sol-Gel Science*; Brinker, C.J., Scherer, G.W., Academic Press, London, 1990.
[2] Verma, I.D., Mehrotra, R.C., *J. Prakt. Chem.*, 1959, 8, 235.
[3] Doueff, S., Dromzee, Y., Taulelle, F., Sanchez, C., *Inorg. Chem.*, 1989, 28, 4439.
[4] Gautier-Luneau, I., Mosset, A., Galy, J., *Z. Kristallogr.*, 1987, 180, 83.

Metal Complexes of Sugar based Ligands

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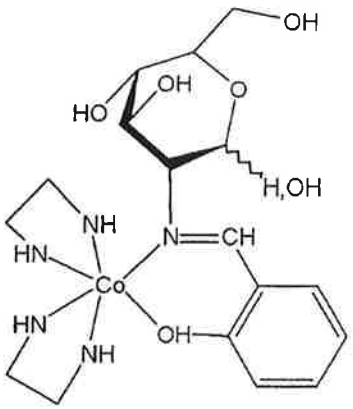
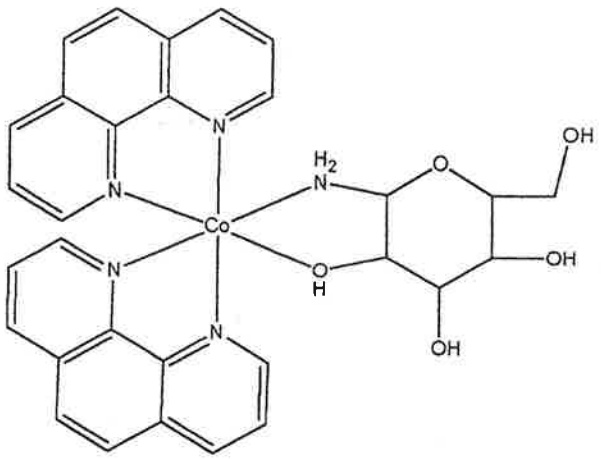
The field of sugar metal complex chemistry is still largely unexplored. This work aims to coordinate various sugar-ligands to different metals. In the field of metal drug chemistry, solubility can be a problem, particularly in the larger aromatic metal complex systems. Binding a sugar to a ligand, to create a sugar derivative, can aid in solubilising such metal complexes, thus enabling the drug to perform its proposed biological role.

This work involves the synthesis, purification and characterization of a wide number of metal complexes of sugar based ligands. As with most sugars, or sugar metal complex chemistry, purification is a major part of the process. By far the best way to purify sugar-metal complexes is by column chromatography. A range of chromatographic media has been used so far for the separation and purification of the complexes. These include Sephadex™ SP-25 (aqueous phase, dilute NaCl, or K_2SO_4), Sephadex LH-20 (organic phase, methanol) or Al_2O_3 (organic phase, acetonitrile). The recent high field 2D NMR experiments, of some of the isolated complexes, are reported.



[Co(en)$_2$gluN-sal]



[Co(phen)$_2$gluN]

The Synthesis and Characterization of α,β-[(*N,N'*-dimethyl-*N,N'*-bis(2-picolyl)-diaminocyclohexane)(dipyrido[3,2-a:2',3'-c]-6,7,8,9-tetrahydrophenazine)ruthenium(II)] Perchlorate

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[B]Department of Inorganic Chemistry, University of Sydney, Sydney, NSW 2006

[C]School of Chemistry, Macquarie University, NSW 2109

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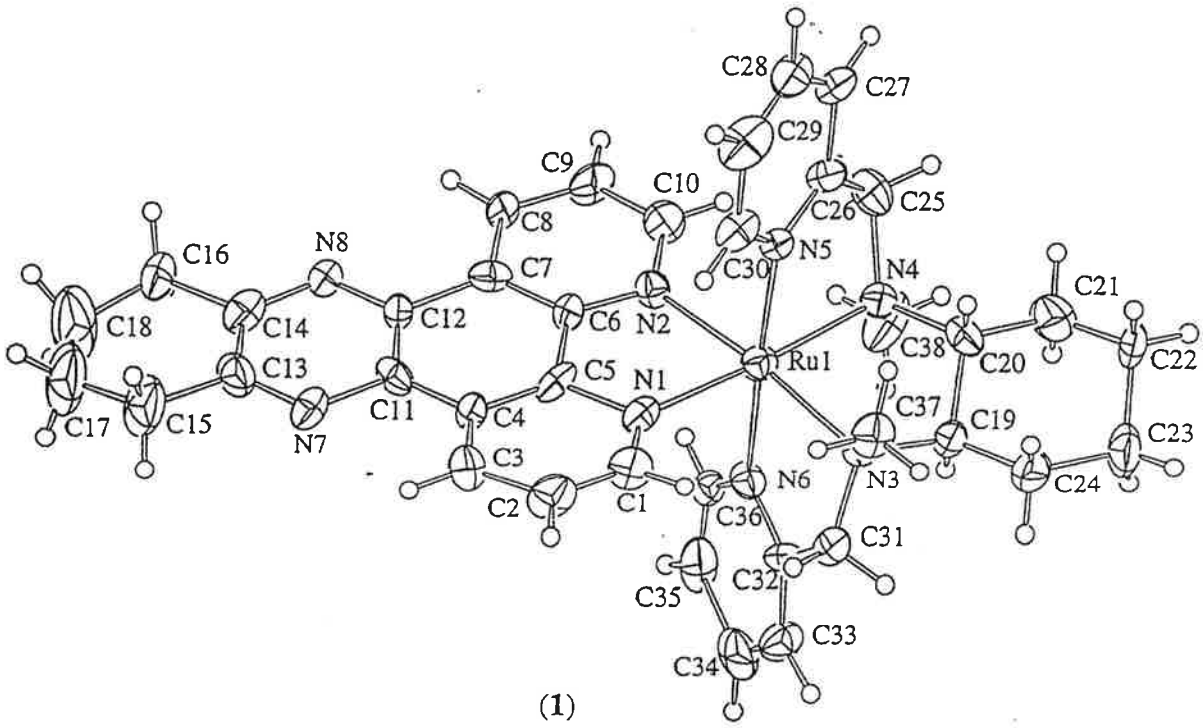
The inclusion of a N_4-tetradentate ligand into the framework of chiral metal complexes for nucleic acid structure analysis was motivated both by the synthetic flexibility that a N_4-tetradentate offers and, more importantly, the stereospecific spatial arrangement which such a molecule can adopt when coordinated to an octahedral metal ions. Ru(II) complexes of *picchxnMe*$_2$ are often obtained as mixtures of either a symmetrical α or an asymmetrical β topology on coordination. This is exemplified by the isomeric products α,β-[Ru(picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$ which require separation. The synthesis, isolation and subsequent crystal structure determination of α-[Ru(*R,R*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$ (**1**) and β-[Ru(picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$ are reported.



(**1**)

Δ-α-[Ru(*R,R*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$

SYNTHESIS AND CHARACTERISATION OF POLYAMINE COBALT(III) COMPLEXES

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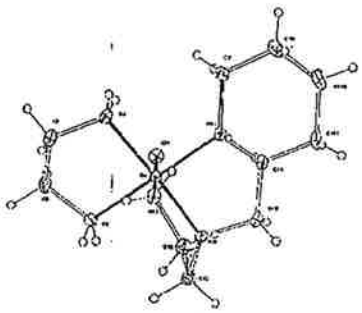
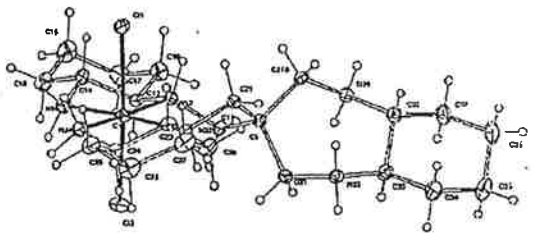
[B]Department of Chemistry, Kosin University, 149-1, Dongsam-dong, Yeongdo-gu, Pusan, 606-701, Korea
[C]School of Applied Chemistry, Curtin University of Technology, GPO Box U 1987, Perth, 6845, W.A.

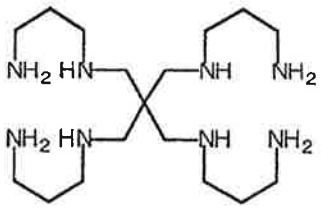
Numerous polyamines and their metal complexes by the reaction of simple amine with polyfunctional alkylating agents have been synthesised and characterised[1]. Not only the polyamine metal complexes are of interest as precursors of macrocycles[2] but therapeutic agents against several solid tumors[3]. We report herein the synthesis of some new polyamines and their Co(III) complexes by the reaction of pentaerythritol tetrabenzenesulfonate with (1R,2R)-diaminocyclohexane and 1,3-diaminopropane, glycerol tribenzenesulfonate and 1,2-diaminoethane. Major products, 2-(2-aminoethyl)aminomethyl- piperazine(**L**^{1}), 3,3-bis(2'-α-amino-1"(R),2"(R)-cyclohexylaminomethyl-1,5-diazacycloheptano[2(R), 3(R)-a]cyclohexane(**L**^{2}) and 1,11-diamino-6,6-bis(5'-amino-2'-azapentyl)-4,8-diazaundecane(**L**^{3}), have been obtained from the above reaction. X-ray crystal structures of these complexes also will be displayed.



$[Co(\mathbf{L}^1)(en)Cl]^{2+}$



$[Co(\mathbf{L}^2)Cl_2]^+$



$\mathbf{L}^3$

References

[1]. J.M. Harrowfield, Y. Kim, M. Mocerino, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., 1995, 2431

[2]. P.V. Bernhardt and G.A. Lawrance, Coord. Chem. Rev., 1990, **104**, 297

[3]. L.J. Marton and A.E. Pegg, Ann. Rev. Pharmacol. 1995, **35**, 55

PT 8

Unusual Octahedral Tetraamine complexes of Cobalt(III)

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Octahedral Co(III) tetramine complexes with simple ammonia or bidentate amine ligands are the most thoroughly studied coordination compounds. It is well known that a variation of the tetramine ligand structure in $[N_4CoXY]$ can greatly influence the rate of a large variety of reactions including catalytic processes, and even dissociation of the amine which ordinarily is extremely slow.

Although affecting ligand substitution and rearrangement rates, C-alkylation of one diamine ligand generally does not greatly influence other properties of the compounds, eg, their absorption spectra, or capacity to form complexes with particular ligands. When all methylene protons are replaced with methyl groups, producing 2,3-dimethyl-2,3-diaminobutane (tmen), steric congestion between adjacent chelates is introduced. For example, Hendry et al have observed dramatic differences between $[Co(tmen)_3]^{3+}$ and $[Co(en)_3]^{3+}$. However, we have observed unexpected chemistry for complexes containing just two (or even one) tmen ligands, eg. $[Co(tmen)(en)X_2]^{n+}$ and $[Co(tmen)_2X_2]^{n+}$. The substitutional lability of the bis(tmen) species is extraordinarily rapid for a Co(III) species, and stable species such as $[Co(tmen)_2O_2]^{+}$, previously unknown in aminecobalt(III) chemistry, can be isolated.

We have prepared a series of both conventional and unusual Co(III) tetraamine complexes for the tmen ligand. Aside from the mononuclear peroxo species, the most surprising so far has been a Co-Co dimer, and, remarkably, the chemistry is beginning to resemble that for arsine complexes of cobalt(III), exposed some 25 years ago.

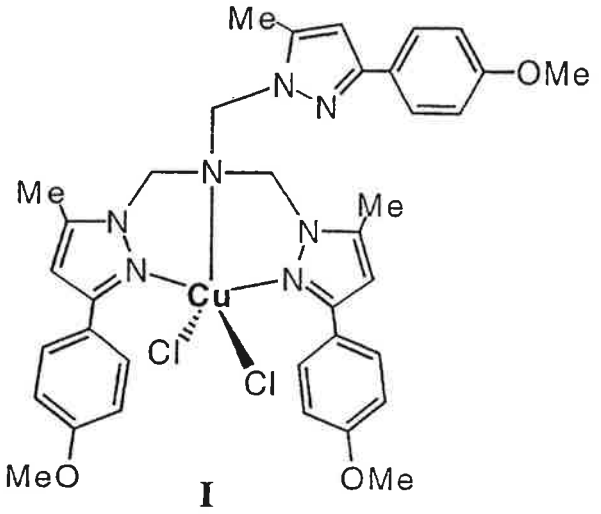
PT 9

Copper Complexes of a New Tripodal Pyrazolylamine Ligand

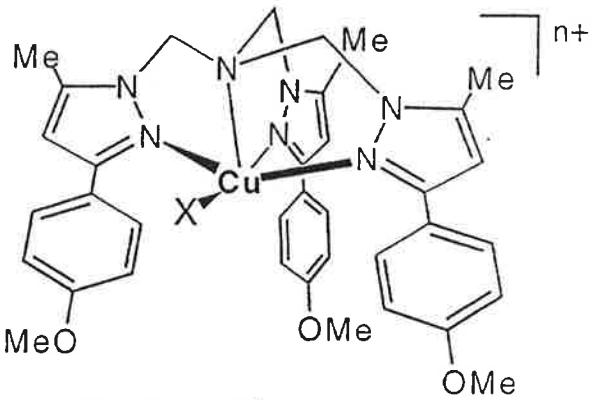
Jack Z. Chen, Natasha Karasek and Stephen B. Colbran

Department of Inorganic and Nuclear Chemistry
University of New South Wales, Sydney, 2052, Australia

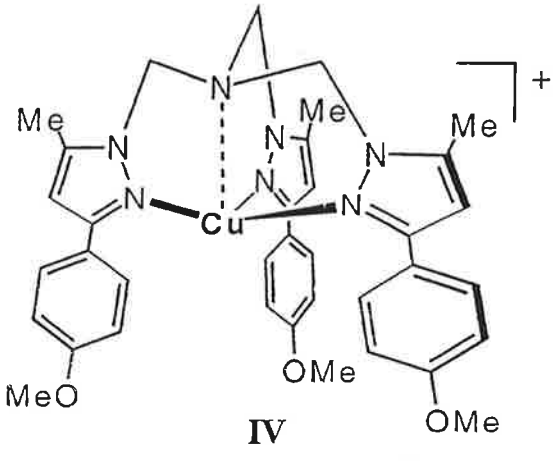
A new tripodal tris(pyrazolylmethyl)amine ligand has been synthesised in four steps beginning with 4-methoxyacetophenone. This poster will describe coordination chemistry of this new ligand with copper ions, including the unexpected reductions of **I** – **III** by tetraphenylborate anion (BPh_4^- → BPh_3 + $^1/_2$ Ph–Ph + e^-) to give **IV**. The X-ray structures of **I** – **IV** will be described.



I



II: X = Cl, n = 1
III: X = H_2O: n = 2



IV

PT 10

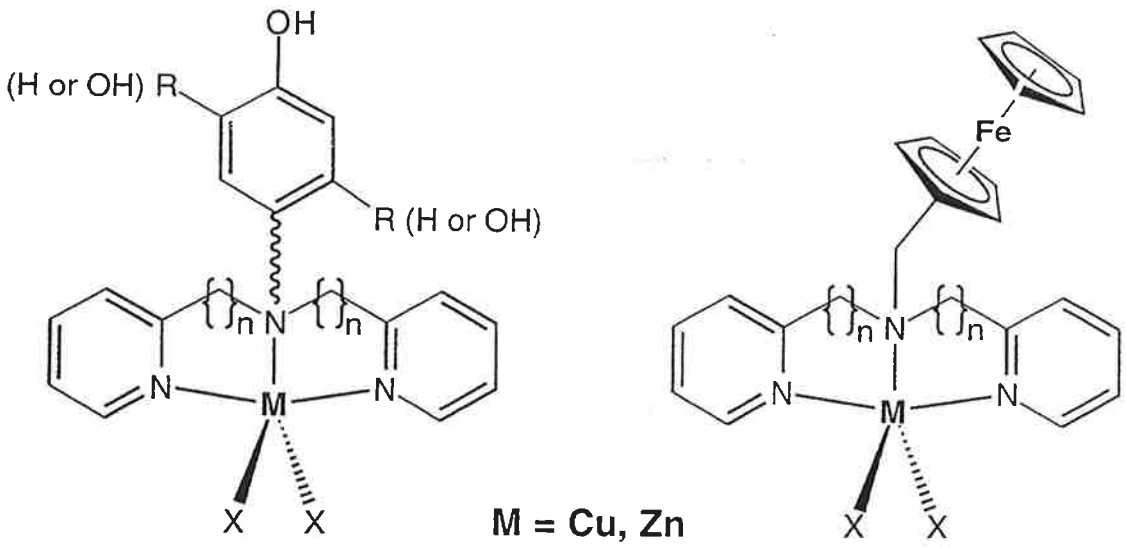
Metal Complexes of New Chelating Pyrazole and Pyridine Ligands with Oxidisable Pendants

Jack Z. Chen, Scott E. Watkins and Stephen B. Colbran

Department of Inorganic and Nuclear Chemistry
University of New South Wales, Sydney, 2052, Australia.

Mononuclear copper oxidases, *e.g.* copper amine, lysyl, galactose and glyoxal oxidases, are ubiquitous enzymes responsible for the biological oxidation of various organic substrates.[1] The active sites of these copper proteins consist broadly of a copper ion bound by histidine ligands and an associated electrochemically-active cofactor which in the listed examples is produced by post-translational modification of a specific protein residue. These oxidases act by a "ping-pong" mechanism where substrate uptake and oxidation reduces the cupric form of the enzyme and dioxygen oxidises the thus produced cuprous form of the enzyme. We have prepared several new N-donor chelating ligands with oxidisable phenolic or ferrocene pendants in order to mimic or model various facets of the biological chemistry, including (i) the copper-assisted cofactor biogenesis and (ii) the oxidation of the cuprous form of the enzyme by dioxygen. Current investigations of the coordination chemistry of copper and zinc complexes of these ligands will be presented.

[1] J. P. Klinman, "Mechanisms of mononuclear Cu proteins", *Chem. Rev.* **1996**, *96*, 2541.



PT 11

Characterisation of some complexes of TMPA and TBIMA and their derivatives

David G. Lonnon, Zhicong He and Stephen B. Colbran

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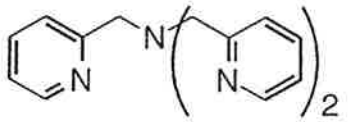
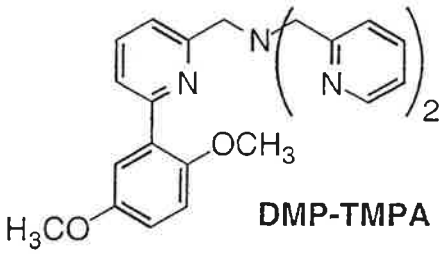
University of New South Wales, Sydney, 2052, Australia.

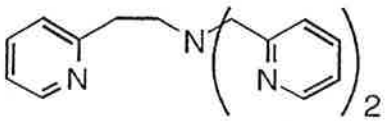
This poster will describe the preparations and structures, both in solution and in the solid-state, of selected new transition metal complexes of the tripodal, tetradentate ligands: TMPA, DMP-TMPA, EPBMPA, MPBEPA, TBIMA and Et-TBIMA.



TMPA

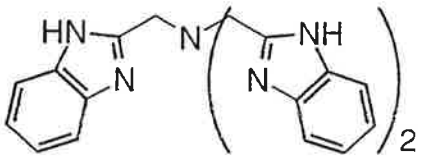


DMP-TMPA

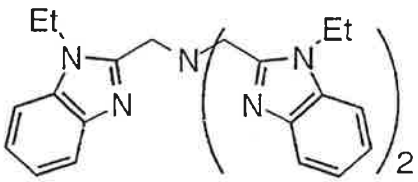


EPBMPA

MPBEPA



TBIMA



Et-TBIMA

PT 12

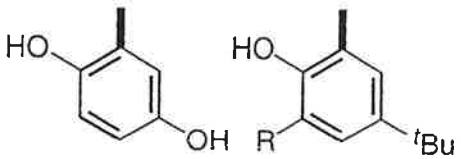
New Routes to New Derivatives of Tris(2-pyridylmethyl)amine

Zhicong He, P. J. Chaimungkalanont and Stephen B. Colbran

Department of Inorganic and Nuclear Chemistry
University of New South Wales, Sydney, 2052, Australia

Coordination complexes of the tetradentate, tripodal ligand tris(2-pyridylmethyl)amine (TPMA) 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 our research to be reported in this poster is on modification of TPMA to give novel ligands for the synthesis of new biomimetic models. Routes to new TPMA ligands, including examples with cofactor substituents, and the copper coordination chemistry of these ligands will described.

X, Y = H, Br, CH_2OH, PPh_2,



etc.

[1] L. Que, Jr. and Y. Dong, *Acc. Chem. Res.* **1996**, *29*, 190.
[2] K. Karlin *et al. Acc. Chem. Res.* **1997**, *30*, 139

PT 13

AN INVESTIGATION OF TRIS(4-BUTYL-3,5-DIMETHYLPYRAZOLYL)METHANE CHROMIUM TRICARBONYL

Nicole L. Armanasco, Murray V. Baker, Brian W. Skelton and Allan H. White

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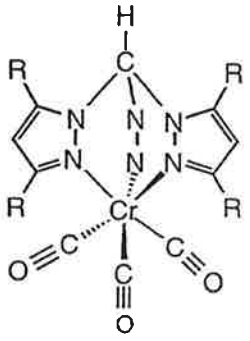
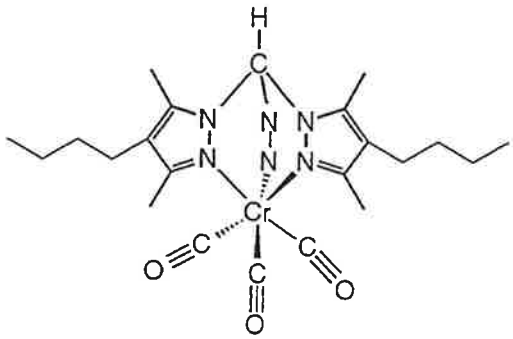
Tris(pyrazolyl)methanes are a family of neutral, tridentate nitrogen donor ligands. In their simplest form (i.e. with little or no alkyl substitution on the pyrazole ring) they form chromium tricarbonyl complexes [e.g. **(1a)** and **(1b)**] that are sparingly soluble in only highly polar organic solvents, such as DMSO and DMF. A tris(3,5-dimethylpyrazolyl)methane derivative, with the substitution of a butyl group on C4 of the pyrazole rings, has been synthesised and the resulting chromium tricarbonyl complex **(2)** is readily soluble in a range of organic solvents. The solubility of this complex in solvents such as benzene makes it possible to further investigate the behaviour of this class of compounds, in particular the lability of the tris(pyrazolyl)methane and carbonyl ligands.



(1 a) R = H
(1 b) R = Me



(2)

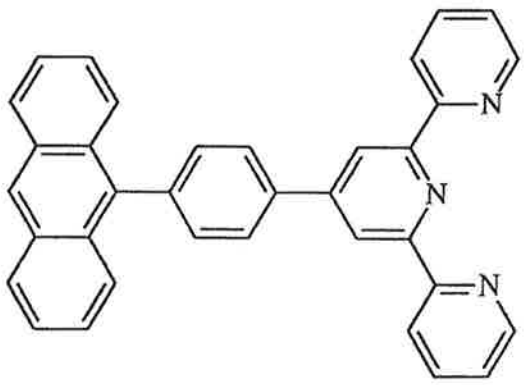
PT 14

THE SYNTHESIS AND SPECTROELECTROCHEMICAL PROPERTIES OF NOVEL TERPYRIDINE COMPLEXES OF IRON AND RUTHENIUM.

A.G.Blackman, K.C.Gordon, M.I.J.Polson
University of Otago, Dunedin
New Zealand.

Much interest has been lavished on ruthenium bipyridine complexes due to the long lifetime of the charge separated lowest excited state (a triplet metal to ligand charge transfer state). However due to the stereochemical complications of the bipyridine complexes, other polypyridyl systems are being investigated for supramolecular systems.

A novel ligand with an anthracene moiety linked to a terpyridine group via a benzene spacer has been synthesised.



The homoleptic complexes of iron, ruthenium and osmium of this ligand have been synthesised and their spectroelectrochemical properties compared to the equivalent terpyridine complexes.

PT 15

PHOSPHATE ESTER HYDROLYSIS BY THE Co(III) COMPLEX $[(abap)Co(OH)(OH_2)](ClO_4)_2$.

Allan G. Blackman, Charles R. Clark, Rachel L. Fanshawe
Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand.

The hydrolytic activity of a new tetraamine Co(III) complex towards phosphate esters has beeen investigated. We have synthesised the tripodal tetraamine ligand, abap, (N-(2-aminoethyl))-N,N-bis(aminopropyl)amine), and the Co(III) complex $[(abap)Co(OH)(OH_2)](ClO_4)_2$, which reacts relatively rapidly to hydrolyse the phosphate ester bonds in both phosphate mono- and diesters. The role of coordinated water as an internal nucleophile in the hydrolysis reactions with mono- and bis(4-nitrophenyl)phosphate will be discussed. In addition, we will report on the results of the reaction of this complex with supercoiled DNA.

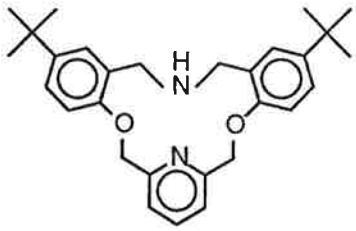
PT 16

NEW DIAZADIOXA MACROCYCLE DERIVATIVES AND THEIR INTERACTION WITH TRANSITION AND POST TRANSITION METAL IONS

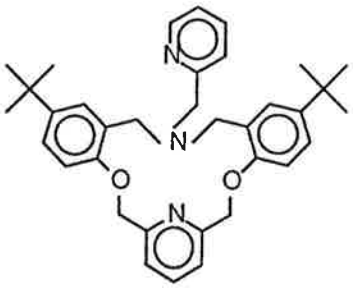
Gang Wei[A], Owen A. Matthews[B], Jy D. Chartres[B], Anthony J. Leong[B], George V. Meehan[B], Brian W. Skelton[C], Allan H. White[C] and Leonard F. Lindoy[A]

[A] School of Chemistry, The University of Sydney, NSW 2006, Australia
[B] Department of Chemistry and Chemical Engineering, James Cook University, Townsville, Qld. 4811, Australia
[C] Department of Chemistry, The University of West Australia, Nedlands, WA 6009, Australia

The Syntheses of a fourteen-membered diazadioxa-macrocyclic ligand (L^1) and its N-functionised derivative (L^2) incorporating a pendant pyridylmethyl group, have been achieved in yields of 87% and 78%, respectively.



L^1



L^2

As part of an overall project involving ligand design for metal ion recognition, we have determined the stabilities of the complexes of copper(II), zinc(II), nickel(II), cobalt(II), cadmium(II), lead(II) and silver(I) with both (L^1) and (L^2). The log K values were obtained potentiometrically in 95% methanol (I = 0.1, Et_4NClO_4, 25 ± 0.1 °C). Further details of the metal ion chemistry of both (L^1) and (L^2) with the above metal ions will be presented.

PT 17

LINKED THIAAZA MACROCYCLES AND THEIR PLATINUM/PALLADIUM CHEMISTRY

Mark. P. Lowe,* Andrew M. Groth,† George V. Meehan† and Leonard F. Lindoy*

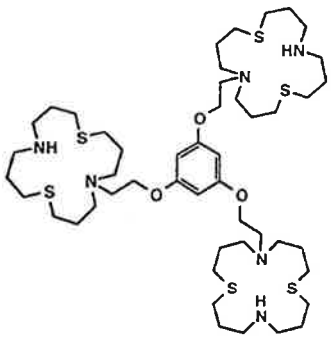
* *School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia*

† *Department of Chemistry and Chemical Engineering, James Cook University, Townsville, QLD 4811, Australia*

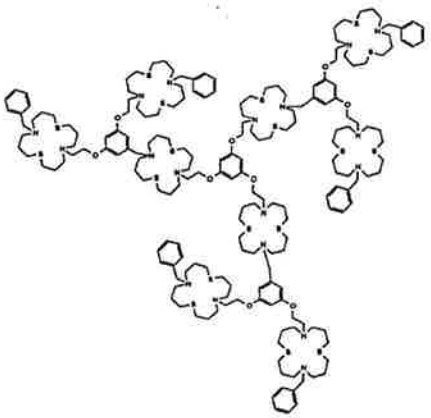
As an extension of our studies in macrocyclic chemistry, we have moved into the world of dendrimer chemistry with the synthesis of new thiaaza (N_2S_2) macrocycles linked via a central hub.[1,2] These tri-linked macrocycles form the basis of a dendrimeric core; that is, they represent a first generation (G1) dendrimer. This central core has now been successfully extended to form the second generation (G2) dendrimer containing, in all, nine N_2S_2 macrocyclic units.

The synthesis of related linked oxaaza-crowns has been reported by Shinkai and co-workers.[3,4] However, the incorporation of much softer donor atoms such as occurs in the new species reported here, makes possible an investigation of the coordination chemistry of transition and other heavy metals.

The chemistry of platinum and palladium with these new linked systems (and their monomeric model compounds) will be presented.



G1



G2

1) Groth, A.; Lindoy, L. F.; Meehan, G. V. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1553.
2) Atkinson, I. M.; Groth, A. M.; Lindoy, L. F.; Matthews, O. A.; Meehan, G. V. *Pure & Appl. Chem.* **1996**, *68*, 1231.
3) Nagasaki, T.; Ukon, M.; Arimori, S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1992**, 608.
4) Nagasaki, T.; Kimura, O.; Ukon, M.; Arimori, S.; Hamachi, I.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 75.

PT 18

LINKED CYCLAM – S_2N_2 MACROCYCLIC SYSTEMS: SYNTHESIS AND PRELIMINARY METAL ION COMPLEXATION STUDIES

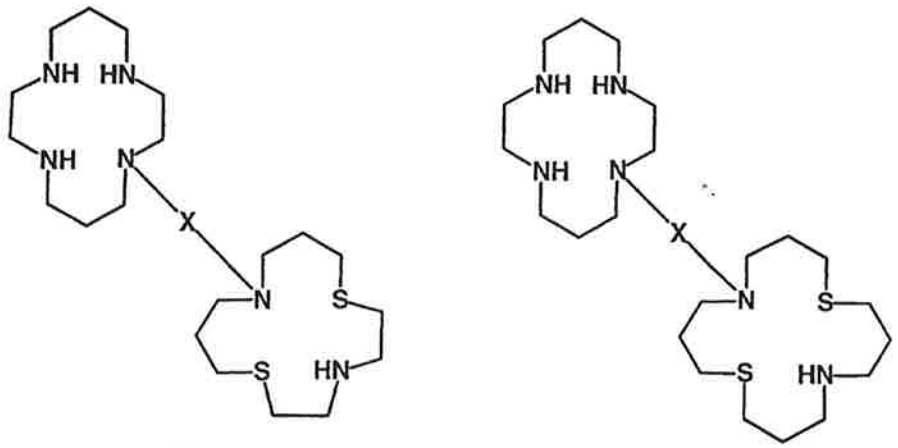
J. Chartres,[a] A. M. Groth,[a] L. F. Lindoy[b] and G. V. Meehan[a]

[a]School of Biomedical and Molecular Sciences, James Cook University, Townsville, QLD 4811

[b]School of Chemistry, University of Sydney, NSW 2006

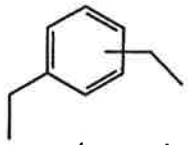
Linked macrocycles that bind simultaneously to two or more metal ions may give rise to complexes exhibiting unusual electronic, catalytic and/or redox properties. They may also provide models for the charge transfer and electron transport behaviour found in a range of metal-containing biochemical systems – as a consequence they have been studied widely.[1]

We have used a protecting group strategy developed in our laboratory[2] to prepare the new heteroditopic macrocyclic systems (**1**) and (**2**). These systems possess two distinctly different complexation sites joined by a variable linker. A preliminary investigation of the complexation of selected transition metal ions with these systems will be presented.



(1) **(2)**

—X— = —CH_2CH_2—



(*m*- and *p*-)

1. L. F. Lindoy, *Prog. Inorg. Chem.*, in press, 1998.

2. A. M. Groth, L. F. Lindoy and G. V. Meehan, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1553-1558.

PT 19

DI- AND TRI-LINKED O_2N_3 DONOR MACROCYCLES: SYNTHSIS AND COMPLEXATION WITH TRANSITION METAL IONS

Shim Sung Lee,*[1] Gang Wei,* Jin-Ho Kim, †[2] George V. Meehan† and Leonard F. Lindoy*

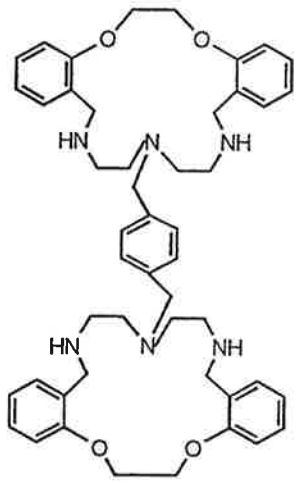
*School of Chemistry, University of Sydney, NSW 2006, Australia

†Department of Chemistry and Chemical Engineering, James Cook University, Townsville, Q. 4811, Australia

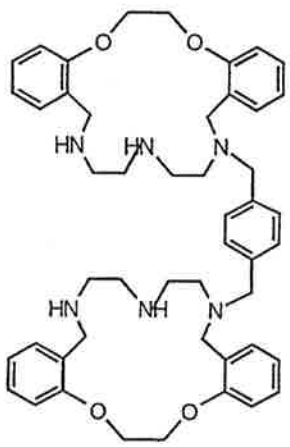
Here, we present a synthetic procedure which has allowed us to prepare a range of multi-linked macrocycles and to vary the position of the linkage joining the two cyclic units.

Two different approaches were used to prepare the symmetrical *p*-xylyl-linked, bis(O_2N_3-macrocycle) ($\mathbf{L^1}$). The first of these involved the direct reaction of α,α'-dibromo-*p*-xylene with two equivalents of diprotected diethylenetriamine followed by a bis-cyclisation reaction. After chromatography on silica gel, protonated $\mathbf{L^1}$ from the remaining mixture of products as its hexafluorophosphate salt was obtained. The second approach involved the use of the symmetrical di-*tert*-butyloxycarbonyl (BOC) protected parent macrocycle as a precusor. The N-protection reaction of the single ring O_2N_3-macrocycle can, in principle, yield up to five possible N-protected species whose relative yields will be vary with the ratio of reactants employed. The separation of the two desired di-BOC-protected macrocycle isomers in preparative scale was successfully accomplished by column chromatography on silica gel. These have been employed to prepare the isomeric di-linked, $\mathbf{L^1}$ and $\mathbf{L^2}$, and also the tri-linked, $\mathbf{L^3}$.

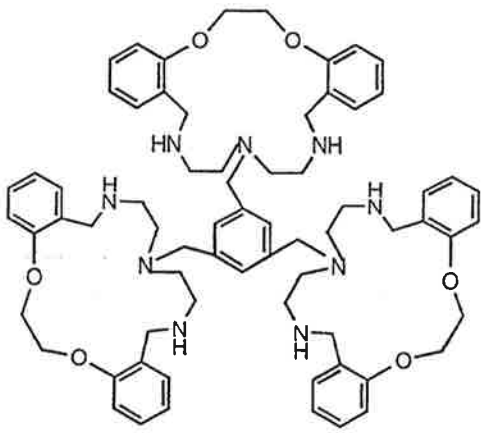
We also report the characteristics of the solid complexes and the stablity constants of the complexes with some transition metal ions in solution.



$\mathbf{L^1}$



$\mathbf{L^2}$



$\mathbf{L^3}$

[1] Permanent address, Department of Chemistry, Gyeongsang National University, Chinju 660-701, S. Korea.
[2] Permanent address, Department of Chemistry, Kangwon National University, Chuncheon 200-701, S. Korea.

PT 20

NEW MACROCYCLIC AND MACROBICYCLIC LIGANDS FOR METAL ION RECOGNITION

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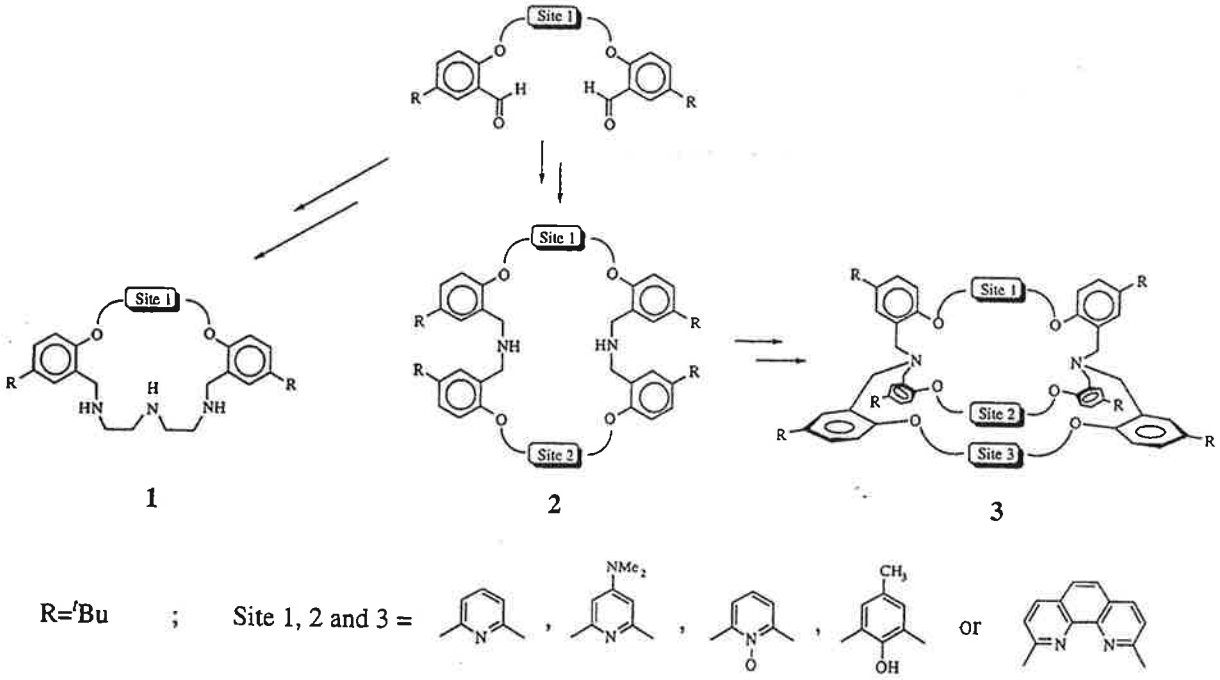
[a]School of Biomedical and Molecular Sciences, James Cook University, Townsville, QLD 4811
[b]School of Chemistry, University of Sydney, NSW 2006

Over recent years considerable effort has been directed towards the design and synthesis of new macrocycles in order to investigate their interaction with transition and post-transition metal ions.[1] As a development on our previous studies,[2,3] we now report the synthesis of a range of new macrocyclic and macrobicyclic ligands, **1 - 3** (**Scheme 1**). The pKa and preliminary metal binding studies on these new ligands will also be presented.



Scheme 1

1. L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge **1989**.

2. K. R. Adam, S. P. H. Arshad, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, B. J. McCool, M. McPartlin, B. A. Tailor and P. A. Tasker, *Inorg. Chem.* 1194, *33*, **1994**.

3 (a) R. J. A. Janssen, L. F. Lindoy, O. A. Matthews, G. V. Meehan, A. N. Sobolev and A. H. White, *J. Chem. Soc., Chem. Commun.*, 735, **1995**.
(b) M. - A. Ahearn, J. Kim, A. J. Leong, L. F. Lindoy, O. A. Matthews and G. V. Meehan, *J. Chem. Soc., Dalton Trans.*, 3591, **1996**.
(c) I. M. Atkinson, A. R. Carroll, R. J. A. Janssen, L. F. Lindoy, O. A. Matthews and G. V. Meehan, *J. Chem. Soc., Perkin Trans. 1*, 295, **1997**.

PT 21

MOLECULAR RECOGNITION AND CHEMICAL ACTIVATION OF HYDROQUINONES BY MACROCYCLIC GUESTS

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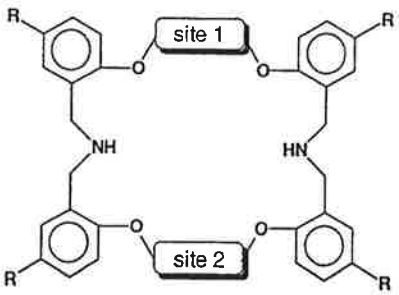
*School of Chemistry The University of Sydney, NSW, 2006, Australia

†Department of Chemistry and Chemical Engineering, James Cook University, Townsville, Qld, 4811

Selected small ring macrocycles such as (**1**) have been demonstrated to form complexes with metal ions.[1] As an extension of this study, larger rings have been prepared that may incorporate small molecules in their cavity. For example, it has been demonstrated that (**2**) and (**3**) can act as receptors for hydroquinone and its substituted derivatives. NMR studies confirm that these macrocycles form 1:1 complexes with individual hydroquinones in CD_2Cl_2 or $CDCl_3$.



(1) - site 1 = site 2 = CH_2CH_2, R = H
(2) - site 1 = site 2 = p-xylyl, R = *tert* butyl
(3) - site 1 = site 2 = 2,5 dimethoxy p-xylyl, R = *tert* butyl

Complementary hydrogen bonding between the phenolic protons and the two benzylic nitrogen atoms is indicated and π stacking interactions involving the ring xylyl groups may perhaps also contribute to the observed complexation. In the presence of oxygen, the above ring promotes the oxidation of hydroquinones to benzoquinones in non-polar solvents. The respective products are not bound by the macrocycle and the respective oxidations are thus catalytic. For the most studied system, the oxidation of 2,5-di-*tert*-butylhydroquinone (**2**) has been shown to approximate Michaelis–Menten kinetics.

1. M. Ahearn, J. Kim, A. J. Leong, L. F. Lindoy, O. A. Matthews, and G. V. Meehan, *J. Chem. Soc., Dalton Trans.*, 1996, 3591-94.

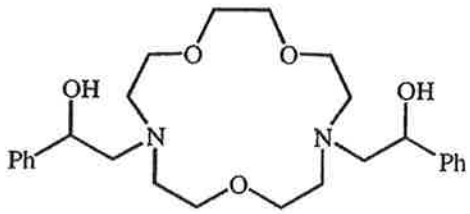
PT 22

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

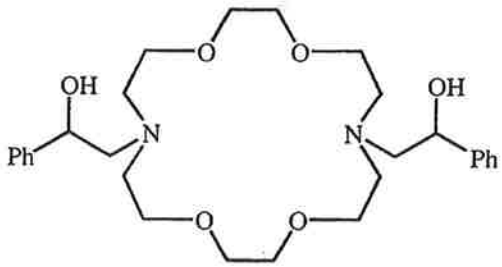
Lee C. West and Stephen F. Lincoln

Department of Chemistry, 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) (Fig. 1) .



BPHE-C21



BPHE-C22

Fig. 1. *R*-BPHE-C21 and *R*-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 divalent alkaline earth, transition and heavy metal ions are discussed . The results from the titration study 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.

PT 23

INVESTIGATION AND SYNTHETIC STUDIES TOWARDS LEAD (II) SPECIFIC FLUORESCENT PROBES.

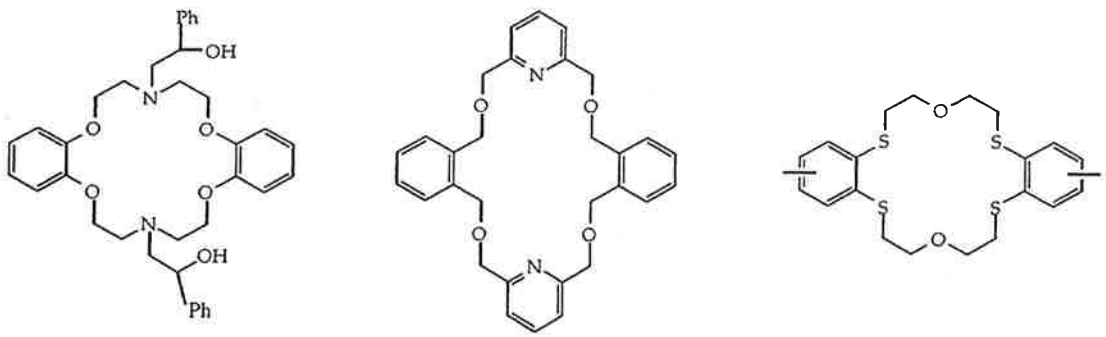
D.Caiazza, S.F.Lincoln and A.D.Ward

The Chemistry Department, The University of Adelaide, Adelaide, S.A. 5005

Lead is the most abundant of the naturally occurring heavy metals. Evidence for the toxicity of lead and its adverse effects on the environment and human health has been widely reported in the literature for centuries.

Industrial utilization of lead and its compounds continue to be major contributors of lead contamination of humans and the environment today. Thus, investigations into the development of efficient screening methods for lead levels in biological and water samples have been of considerable interest.

In this paper the development of lead (II) specific fluorescent probes is reported. A series of crown ethers (Figure 1), have been synthesised and investigated for their ability to complex heavy metal ions, in particular lead (II) ions. For these compounds to be of use in biological systems, the ligands must be non-fluorescent in the free state but highly fluorescent as the ligand-metal complex. Selectivity and specificity of the ligands with certain heavy metal ions were determined using potentiometric methods, fluorescence spectroscopy, electrospray ionisation mass spectrometry and abinitio molecular modelling calculations.



(1) (2) (3)

FIGURE 1

SUPERCHIRAL MACROCYCLIC LIGANDS AS MOLECULAR RECEPTORS

Jennifer M. Weeks†, Stephen F. Lincoln† and Kevin P. Wainwright‡

†*Department of Chemistry, The University of Adelaide, Adelaide, SA 5005.*
‡*Department of Chemistry, The Flinders University of South Australia, GPO Box 2100.*

Superchiral molecules occur when chiral subunits in one enantiomeric form are linked together and their spatial or stereochemical requirements impose an additional chirality over the secondary structure of the molecule. This additional chirality is termed *superchirality.*

A range of superchiral 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]

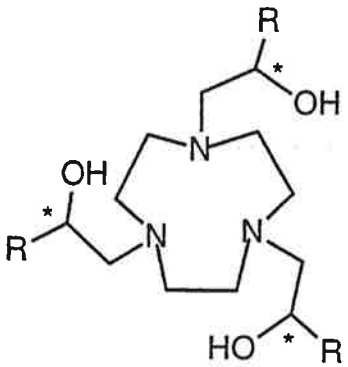


Fig. 1. Λ*S*-thpc9 (R = CH_3) Λ*S*-thpec9 (R = Ph) and their alkali metal ion complexes assume single diastereomeric conformation in solution.

The pendant arms were found to adopt the *syn* configuration, and for the case where R = Ph, the phenyl rings form a basket-like hydrophobic cavity which may act as a host for smaller molecules. The shape and size of this molecular basket can be diversified by variation of the R group, the macrocycle and the coordinated metal ion. The superchiral nature of the molecules should result in substantial selectivity to form a range of molecular baskets selective for a variety of guests.

1. Enantiomerization in Pendant Arm Triaza Macrocyclic Alkali Metal Complex Ions. S.L. Whitbread, J. M. Weeks, P. Valente, M. A. Buntine, S. F. Lincoln and K. P. Wainwright, *Aust. J. Chem.*, **1997**, *50*, 853-856.

PT 25

TOWARDS METAL ION ACTIVATED MOLECULAR RECEPTORS: DIASTEREOMERIC PENDANT ARM LIGAND ALKALI METAL COMPLEXES: EQUILIBRIUM, KINETIC AND MOLECULAR ORBITAL STUDIES

Sonya L. Whitbread,† Peter Valente,‡ Mark A. Buntine,† Philip Clements,† Stephen F. Lincoln† and Kevin P. Wainwright‡

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

Δ-1, 4, 7, 10-Tetrakis((*R*)-2-hydroxy-2-phenylethyl)-1,4,7,10-tetraazacyclododecane (Δ*R*-thpec12) and its eight-coordinate alkali metal complexes, Δ[M(*R*-thpec12)]$^+$, are unusual in existing predominantly as single square antiprismatic Δ diastereomers in dimethylformamide in labile equilibria as shown in Fig. 1. These equilibria require a double inversion at each nitrogen, and the corresponding Λ diastereomers are not observed. A similar chiral preference is observed for the methyl analogues.[1]

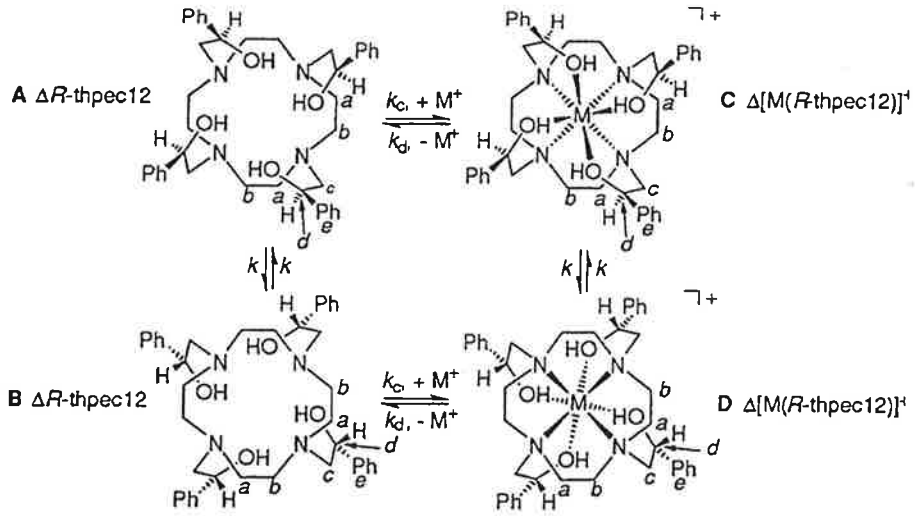


Fig. 1. **A** and **B** are equivalent forms of the Δ*R*-thpec12 diastereomer and **C** and **D** are equivalent forms of Δ[M(*R*-thpec12)]$^+$. In both pairs, ^{13}C NMR shows *a* and *b* to exchange between different environments while *c*, *d* and *e* exchange between equivalent environments. For Δ*R*-thpec12, *k* (298.2 K) = 46300 ± 1800 s^{-1}, $\Delta H^{\ddagger}$ = 40.8 ± 0.4 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = -18.8 ± 1.7 J K^{-1} mol^{-1}. For Δ[Na(*R*-thpec12)]$^+$, *k* (298.2 K) = 98 s^{-1}, $\Delta H^{\ddagger}$ = 46.1 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = -52.2 J K^{-1} mol^{-1}.

Molecular orbital calculations show the parallel square oxygen and nitrogen planes to delineate the square antiprismatic structure of Δ*R*-thpec12 and Δ[M(*R*-thpec12)]$^+$ where the bowl defined by the four phenyl groups of Δ*R*-thpec12 becomes increasingly shallow as the M$^+$ radius increases from Na$^+$ to Cs$^+$ and the four oxygens move further apart. This systematic variation may offer an avenue for the development of metal ion activated molecular receptors.

1. 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 - 6134.

TWO STAGE ENCAPSULATION OF EUROPIUM(III) BY AN OCTADENTATE PENDANT ARM MACROCYCLIC LIGAND

Peter Valente,† Stephen F. Lincoln‡ and Kevin P. Wainwright†

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

The gadolinium(III) magnetic resonance imaging reagents and the luminescent europium(III) and terbium(III) complexes used as biochemical probes have focused considerable attention on the chemistry of lanthanide(III) macrocyclic complexes.[1] However, little is known about the complexation process wherein the lanthanide(III) ion is complexed by the macrocyclic ligand. We have extended our pendant arm macrocylic ligand complexation studies[2] to include the lanthanide(III) ions, and for the first time demonstrate the early complexation of the Eu^{3+} ion by the pendant arms prior to its full complexation and encapsulation by the ligand (Fig. 1)

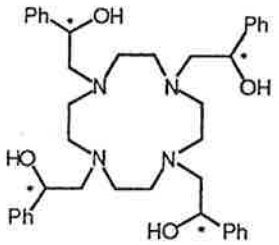

Fig. 1. Δ*R*-thpec12 assumes a single diastereomeric conformation in solution, which is retained in its complex ions. The asterisks indicate the chiral centres.

This is exemplified by some of our ^{13}C nmr studies which show that the diastereomeric ligand, Δ-1,4,7,10-tetrakis((*R*)-2-hydroxy-2-phenylethyl)-1,4,7,10-tetraazacyclododecane, Δ*R*-thpec12, Figure 1) complexes Eu^{3+} in two major steps:

$$Eu^{3+} + 2\Delta R\text{-thpec12} \xrightarrow{\text{fast}} [Eu(\Delta R\text{-thpec12})_2]^{3+}$$

$$[Eu(\Delta R\text{-thpec12})_2]^{3+} \xrightarrow[\text{slow}]{k} [Eu(\Delta R\text{-thpec12})]^{3+} + \Delta R\text{-thpec12}$$

where k(298.2 K) = 8.0 x 10^{-7} s^{-1}, $\Delta H^{\ddagger}$ = 118.2 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 230 J K^{-1} mol^{-1} in acetonitrile. In $[Eu(\Delta R\text{-thpec12})_2]^{3+}$, Eu^{3+} is thought to be bound by the four hydroxy groups of each Δ*R*-thpec12 ligand; and in $[Eu(\Delta R\text{-thpec12})]^{3+}$, Eu^{3+} is bound by the four amine nitrogens and the four hydroxy groups of Δ*R*-thpec12 which encapsulates it. Other Ln^{3+} ions also form both types of complexes.

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 - 6134.

PT 27

OLIGONUCLEAR COPPER(II) COMPLEXES OF ALL SHAPES AND SIZES

Paul V. Bernhardt

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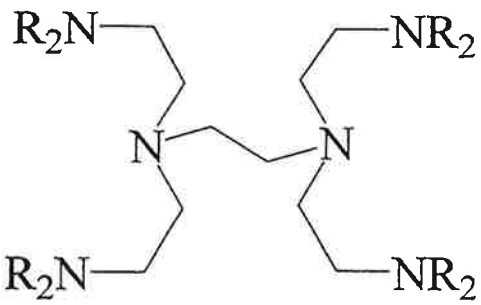
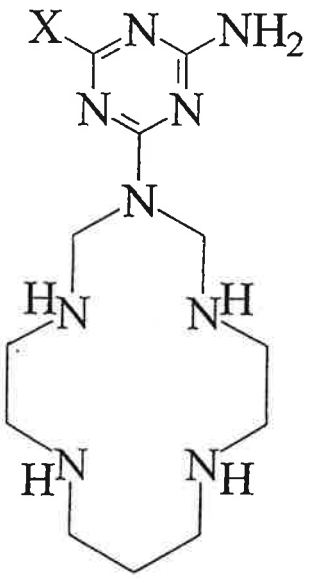
Recent results from our group have revealed that the preference for mono- or oligonulcear complexation may be modulated by subtle modification of the ligand structure. A variety of structural forms have been identified comprising 2:1, 2:2 and 3:1 metal:ligand complexes. Most of these studies have focused upon complexes of Cu^{II} and the lability of this metal ion has resulted in some remarkable, and sometimes unexpected, structures. Some of these structures closely resemble those found in biological systems such as multicopper oxidases.



R = H

R = CH_3



X = NH_2

X = OH

PT 28

CADMIUM(II), MERCURY(II), LEAD(II), ZINC(II), COPPER(II), and NICKEL(II) COMPLEXES with MIXED DONOR (O, N and S) 12-MEMBERED MACROCYCLIC LIGANDS

Sebastian T. Marcus,[A] Lawrence R. Gahan,[A] Paul V. Bernhardt[A] and Trevor W. Hambley[B]

[A]Chemistry Department, The University of Queensland, Brisbane 4072.
[B]School of Chemistry, The University of Sydney, Sydney, NSW 2006.

We are interested in 12-membered ring macrocyclic ligands containing four heteroatoms, with at least one heteroatom being nitrogen. The macrocycles studied include 4-oxa-10-thia-1,7-diazacyclododecane ([12]aneN_2OS), 4,10-dioxa-7-thia-1-azacyclododecane ([12]aneNO_2S), 4-oxa-1,7,10-triazacyclododecane ([12]aneN_3O), 4-thia-1,7,10-triazacyclododecane ([12]aneN_3S), 4,7,10-trioxa-1-azacyclododecane ([12]aneNO_3), and 1,4,7,10-tetraazacyclododecane ([12]aneN_4).

Potentiometric, spectrophotometric and ligand-ligand competition titrations have been employed to obtain stability constants in aqueous solutions for the ligands with lead(II), mercury(II), cadmium(II), zinc(II), nickel(II), and copper(II). Crystal structures of some of the metal complexes have been obtained. Thermodynamic functions ($\Delta H°$ and $\Delta S°$) for the reaction of nickel(II) with 12-membered macrocyclic ligands have been determined (25 °C, I = 0.1 mol.dm^{-3}).

PT 29

TITANIUM(IV) COMPLEXES OF N_2O_2 MACROCYCLES AND SCHIFF BASES AND N_2O_3 TRIPODAL LIGANDS

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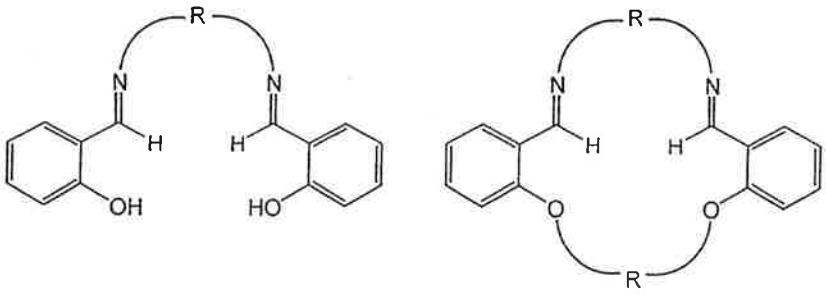
[A] Molecular Design and Synthesis Group, Department of Chemistry, University of Western Sydney Macarthur, PO Box 555 Campbelltown NSW 2560.

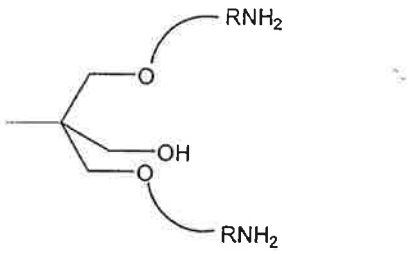
[B] Universität of Tübingen, Röntgenweg 15, Tübingen 72076 Germany.

[C] Radiopharmaceuticals Division, ANSTO, Menai NSW 2234.

This presentation describes the synthesis of a number of titanium(IV) complexes with a variety of N_2O_2- and N_2O_3-donor ligands. The work presented focuses on the use of ligands containing four and five donor atoms that are able to coordinate to titanium. [1]



N_2O_2-donor ligands under investigation



N_2O_3-donor ligands under investigation

The sensitivity of titanium(IV) complexes to moisture has been extensively reported in the literature. [2] This renders such complexes difficult to synthesise, handle and characterise. One of the many aims of this work has been to investigate and understand the mechanism of hydrolysis in these titanium complexes. We are able to report here some complexes which are resistant to hydrolysis.

Our work has made use of molecular modeling for the analysis and design of these ligands and the complexes that arise from their reaction with titanium. This modeling, along with comparison of our spectral data, has provided insights for predicting the most favourable binding modes of the ligands.

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[1] For example: Alexander, J.J, *Annual Reports in Inorganic and General Syntheses*, **1974**, 130.
[2] For example: Friedrich, S., Gade, L.H., Li, W-S, and McPartlin, M., *Chem. Ber.*, **1996**, *129*, 1287.

TITANIUM(IV) AND ZIRCONIUM(IV) COMPLEXES OF SOME N_2O_2 DONOR MACROCYCLES

Gary R. Bowman, Trevor D. Bailey, David Clarke, Melissa Helm, Robyn L. Crumbie and Christopher L. Whicker.

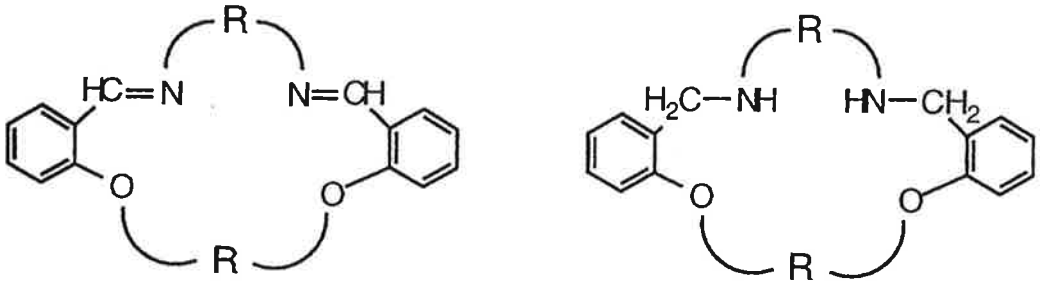
Molecular Design and Synthesis Group

Department of Chemistry

University of Western Sydney, Macarthur

P.O. Box 555 Campbelltown NSW 2560

The metal ion recognition by macromolecular donor molecules is a rapidly developing area of interest for coordination chemists. This presentation describes the results of some synthetic work involving macrocycles of the type shown below and their interaction with titanium and zirconium.



R = various alkyl and aryl groups

The structure and design of the macrocycles have been based on the work of Lindoy and coworkers[1]. Sodium Borohydride reduction of the imine portion of the original macrocycle yields amine nitrogen donors in the product. In addition, the loss of the double bonds has a dramatic effect on the properties of the new macrocycle. The structure becomes significantly more flexible and the hydrogens of the amine groups are able to be deprotonated to potentially enhance coordination.

We are particularly interested in the binding modes of these macrocycles with the metal ions, titanium(IV) and zirconium(IV). Reactions of various starting materials of titanium and zirconium with the imine and amine type macrocycles have yielded a range of products. We have used nmr and molecular modelling to study and compare the syntheses of the macrocycles and the titanium and zirconium complexes.

1. Armstrong, L. F. and Lindoy, L. F., *Inorg. Chem.*, **14**, 1975, 1322

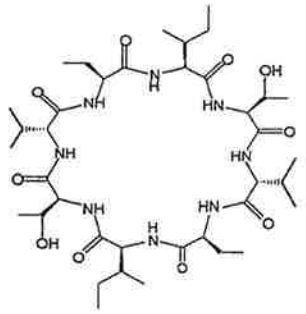
INVESTIGATION OF THE INTERACTION OF METAL IONS WITH CYCLIC OCTAPEPTIDES

Rodney M. Cusack,[A] John Abbenante,[B] David P. Fairlie,[B] Lawrence R. Gahan,[A] Lisbeth Grøndahl,[A] Trevor W. Hambley,[D] Graeme R. Hanson.[C]

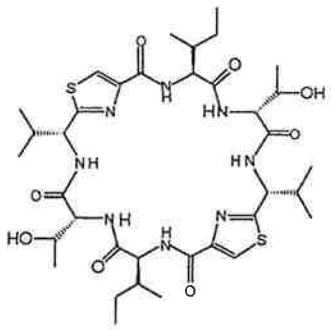
[A] Chemistry Department, [B] 3D Centre, and [C] Centre for Magnetic Resonance The University of Queensland, Brisbane, Australia 4072.

[D] The School of Chemistry, The University of Sydney, Sydney, Australia 2006.

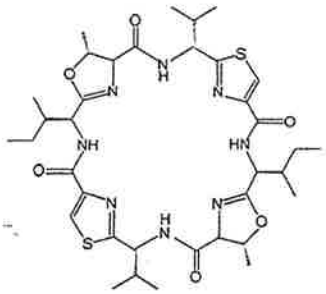
In the last few decades, a number of cyclic peptides containing unusual amino acids, such as aminoalkyl(oxazoline/thiazole)carboxylic acids, N-methyl- and D-amino acids, have been isolated from various marine organisms. It is known that these peptides are capable of forming metal complexes, eg. ascidiacyclamide (**3**) binds two copper ions in the presence of a carbonate bridge.[1] To investigate the relationship



(1)



(2)



(3)

between conformation, presence of functional groups and metal binding potential, a number of analogues of ascidiacyclamide have been synthesised (eg. **1** and **2**). A comparison between both synthetic and naturally occurring cycles demonstrates a wide variety of conformations in the solid state and in solution.[2] Studies of the metal complexes formed with these peptides have been carried out utilising ^{1}H NMR and EPR spectrometry and CD and UV-vis spectrophotometry. We will report our initial evaluations of the stability constants of some of these cyclic peptide-metal complexes.

1. 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.*, 1994, **33**, 3549-3557.
2. Abbenante, G.; Fairlie, D. P.; Gahan, L. R.; Hanson, G. R.; Pierens, G. K.; van den Brenk, A. L. *J. Am. Chem. Soc.*, 1996, **118**, 10384-10388.

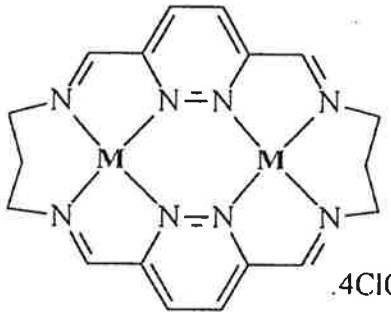
PT 32

Synthesis and Electrochemical Investigation of a Cobalt and Zinc Pyridazine Macrocycle.

Sally Brooker, Robert J. Kelly and Paul Plieger.

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

The reaction of 3,6-diformylpyridazine and 1,3-diaminopropane in the presence of $Pb(ClO_4)_2.6H_2O$ gives the macrocycle **1**[1]. Subsequent transmetallation of **1** with $Zn(ClO_4)_2.6H_2O$ or $Co(ClO_4)_2.6H_2O$ gives the macrocycles **2** and **3** respectively. The synthesis and electrochemistry of these two products will be discussed.



1. **M** = Pb^{2+}
2. **M** = Zn^{2+}
3. **M** = Co^{2+}

1. S.Brooker and Robert J. Kelly, *J. Chem. Soc., Dalton Trans.*, 1996, 2117.

Preparation of, and Growth Inhibition Studies on Oligomeric 16-, 24-, and 32-Membered Benzazocine Macrocycles

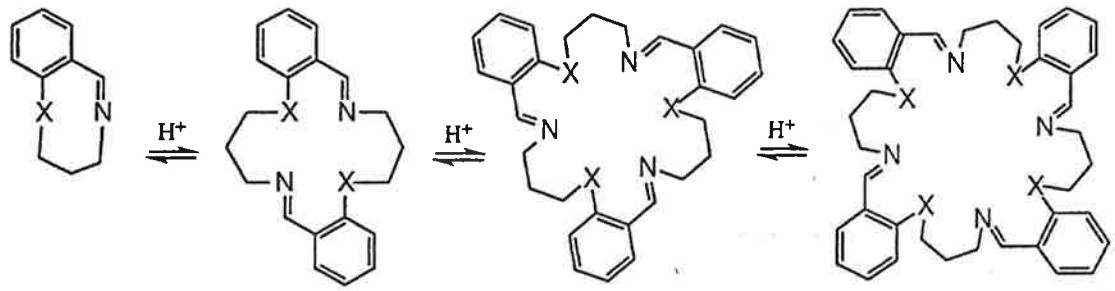
PT 33

Silvina Rainone[a], Gerhard F. Swiegers[b], Lorraine Webster[a], S. Bruce Wild[c]

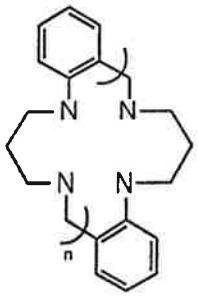
[a] *Research Division, Peter MacCallum Cancer Institute, East Melbourne, VIC 3002, Australia*
[b] *Department of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia*
[c] *Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia*

Acid-catalysed re-arrangements of benzazocines **1** (X = NH, O, S) result in the spontaneous formation of thermodynamic mixtures of oligomeric 16- , 24-, and 32-membered macrocycles **2-4** (X = NH, O, S) in weakly acidic solution. The position of this equilibrium is dependent on entropic or solubility effects and can be manipulated to selectively obtain **2**, **3**, or **4** (X = NH, O).[1,2] Chemical reduction of the isolated benzazocines gives the corresponding, kinetically inert polyamine oligomers **5-7** which differ from each other in ring size but not empirical formula.

In-vitro growth inhibition studies have been performed on **5-7** against human and animal cancer cell lines. The results indicate a significant and successive increase in activity (per unit amine) in the order **5** < **6** < **7**, suggesting a cooperative effect.



1 **2** **3** **4**



5 (n = 1)
6 (n = 2)
7 (n = 3)

1. D. C. R. Hockless, L. F. Lindoy, G. F. Swiegers, S. B. Wild *Perkin Trans. 1* in press.
2. P. A. Gugger, D. C. R. Hockless, G. F. Swiegers, S. B. Wild *Inorg. Chem.* **1994**, *33*, 5671.

PT 34

PLATINUM(II) DIRECTED TEMPLATE SYNTHESES OF 14-MEMBERED MACROCYCLES

Hong Xiao,[A] Geofferey A. Lawrance,[A] Trevor W. Hambley,[B] and Peter Turner[B]

[A]*Department of Chemistry, The University of Newcastle Callaghan, NSW 2308*
[B]*School of Chemistry, The University of Sydney, NSW 2006*

The metal-directed synthesis of a range of pendent-arm macrocycles with copper(II), nickel(II), palladium(II),[1] and gold(III)[2] ions are well studied; however, related research reports about platinum(II) - directed template complexes are rare. Both the nitrogen and mixed sulfur-nitrogen donor platinum(II) macrocycles using bis(ethane-1,2-diamine)- and (3,7-dithianonane-1,9-diamine)-platinum(II) complexes as precursors for formaldehyde and nitroethane condensation reactions in basic condition have been synthesised, and well characterised by x-ray crystal structure analysis, element analysis, electronic and n.m.r. spectroscopy, and cyclic voltammetry.

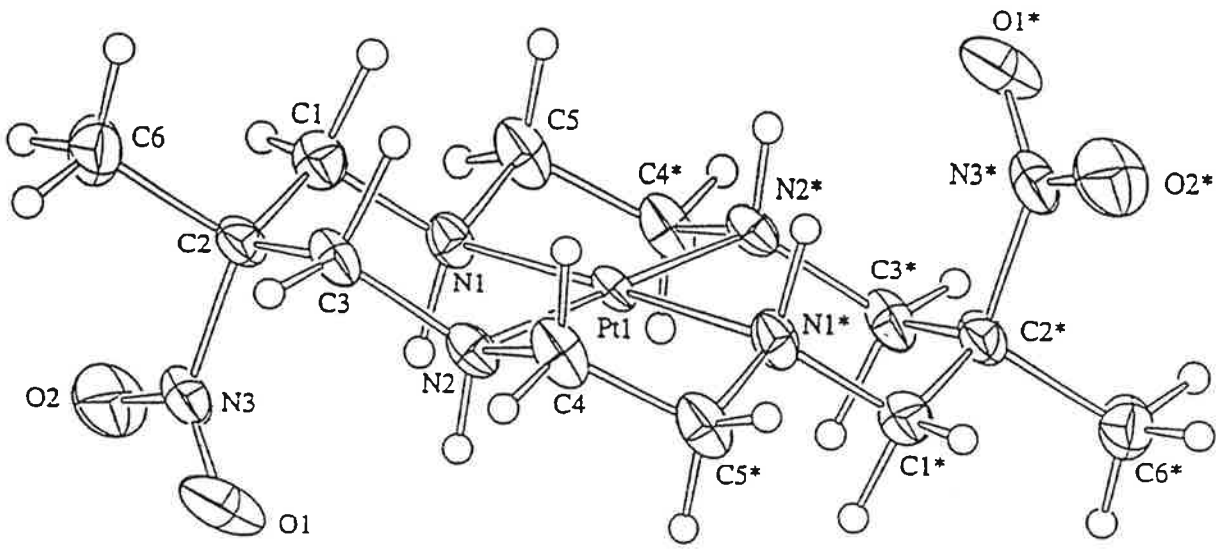


Fig. 1 View of the [Pt(dino[14]mac)] cation, showing the atom numbering

References

1. M. Rossignoli, C.C. Allen, T.W. Hambley, G. A. Lawrance and M. Maeder, *Inorg. Chem.*, 1996, **35**, 4961.

2. M. Rossignoli, P.V. Bernhardt, G. A. Lawrance and M. Maeder, *J. Chem. Soc., Dalton Trans.*, 1997, 323.

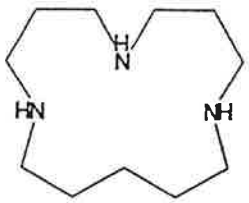
PT 35

Structural Studies on Triazamacrocyclic Complexes: Structures of bis-isothiocyanato(1,5,9-triazacyclopentadecane)nickel(II) hydrate $[Ni(tapd)(NCS)_2]\cdot H_2O$ and bis-isothiocyanato(1,5,9-triazacyclopentadecane)cobalt(II), $[Co(tapd)(NCS)_2]$

Hollie Inwood, Olga P. Gladkikh and David C. Weatherburn

School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand.

A number of years ago we reported the structure of a copper(II) complex $[Cu(tapd)Br]ClO_4$ of the ligand 1,5,8-triazacyclotetradecane (tapd) which was of interest because it contained an eight-membered chelate ring (Graham *et.al. Inorg. Chim. Acta* **178**, (1990) 227). The complex was unusual in that the copper(II) was 4-coordinate with a geometry best described as distorted tetrahedral and the 8-membered chelate ring was disordered. We have now extended these investigations to include nickel(II) and cobalt(II) complexes of this ligand.



Crystal structures of $[Ni(tapd)(NCS)_2]H_2O$ **1** and $[Co(tapd)(NCS)_2]$ **2** have been determined. **1** is monoclinic, $P2_1/n$, a 10.587(5), b 14.605(8), c 11.960(5)Å, β 98.77(4)° and the structure was refined to a conventional R_1 of 0.0477 (wR_2 0.134 F^2) for 4202 independent reflections. **2** is orthorhombic Pnma with a 16.059(5), b 9.514(3), c 11.513(6)Å and the structure was refined to R_1 of 0.0623 (wR_2 0.1366) for 1788 independent reflections. Both complexes have 5-coordinate metal ions. The nickel(II) ion has distorted square pyramidal geometry and the cobalt(II) ion has a distorted trigonal bipyramidal geometry. In both complexes the 8-membered chelate ring is ordered, and there are agostic interactions between the middle CH_2 group of the 8-membered ring and the metal ion.

PT 36

Pentadentate Macrocyclic Ligands and their Cobalt(III) Complexs

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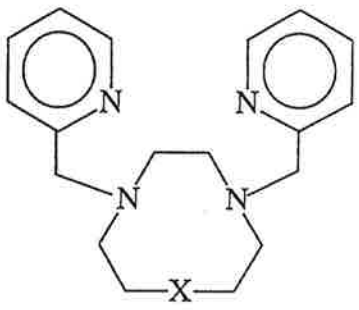
School of Chemistry
University College (UNSW)
Australian Defence Force Academy
Canberra, ACT 2600, Australia

Abstract

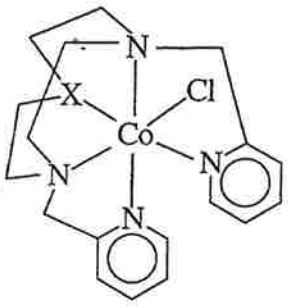
New macrocyclic ligands——1-heteroatoms-4,7-diazacyclonane with two pendant pyridine arms have been prepared——$Py_2[9]aneN_2O$, $Py_2[9]aneN_2S$ and $Py_2[9]aneN_2Se$.

Their unsym-$[Co(N_5X)Cl]^{2+}$ complexes have been prepared and characterised.

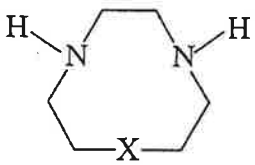
The following precursor macrocyclic ligands——$[9]aneN_2O$, $[9]aneN_2S$ and $[9]aneN_2Se$ have been prepared by a variety of methods.



$Py_2[9]aneN_2X$



Unsym-$[Co(N_5X)Cl]^{2+}$



$[9]aneN_2X$

X = O, S and Se

PT 37

Quinquidentate Ligands of Aza-, Oxa- and Thia-Heteroatoms and their Cobalt (III) Complexes

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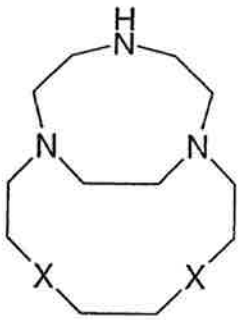
School of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Canberra ACT 2600, Australia.

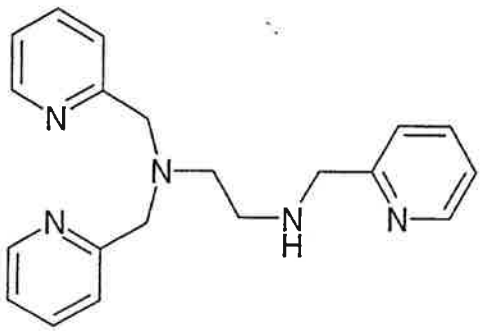
Part of a continuing study into the mechanism of hydrolysis of aminochloro cobalt (III) complexes, aminochlorocobalt (III) complexes with either 1' or 2' amines which have a trans configuration relative to chloride have been sought. The remaining cis bonded heteroatoms are fully substituted leaving no acidic protons. Complexation of several quinquidentate ligands of this kind will be dicussed.

The synthesis of quinquidentate ligands such as **1** and **2** were achieved using tosyl, and carbamyl aziridines generated *in situ* as key intermediates. Aziridines generated in this way provides an efficient method of alkylating amines, thiolates and alkoxides to give polyamines, aminothio ethers and amino ethers.



X = NCH_3 , S and O

1



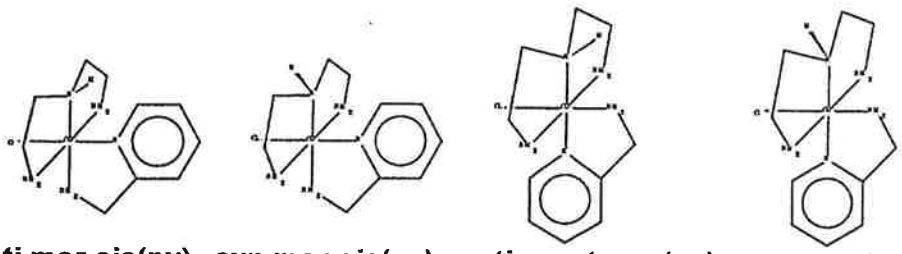
2

PT 38

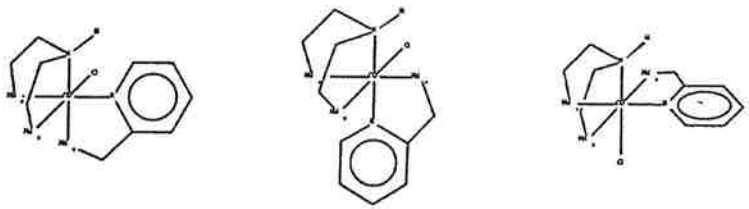
Complexes of the [Co(III)(triamine)(diamine)X] Kind: Synthesis, Structures and Properties of the Isomers of (diethelenetriamine)(2-aminomethylpyridine)chlorocobalt(III)

Tao Zhu and W.Gregory Jackson, School of Chemistry, University College (UNSW), Australian Defence Force Academy, Canberra, ACT, AUSTRALIA 2600

Abstract All seven possible geometric isomers (four mer- and three facial-) of (diethelenetriamine)(2-aminomethylpyridine)chlorocobalt(III) have been synthesised. The distribution of isomers depends upon the synthetic methods and conditions. The most elusive isomer was obtained by treating (diethelenetriamine)(2-aminomethylpyridine) phosphatocobalt(III) complex with hydrochloric acid. Their structures have been characterised by 2D-NMR spectroscopy (DQCOSY, NOESY and HETCOR).



anti-mer-cis(py) **syn-mer-cis(py)** **anti-mer-trans(py)** **syn-mer-trans(py)**



fac-cis(Cl)-cis(py) **fac-cis(Cl)-trans(py)** **fac-trans(Cl)-cis(py)**

The kinetics and stereochemical properties of these isomers were studied using VIS/UV and NMR spectroscopy. The kinetic results show that the mer-cis(py) isomers are more reactive than mer-trans(py) isomers. Stereochemical studies reveal mer-cis(py) isomers are kinetic products and mer-trans(py) the thermodynamic products. All four isomers yield a common distribution in base hydrolysis, indicative of deprotonation at the dien sec-NH and formation of a common pentacoordinate intermediate. The stereochemical inter-relationship observed for rearrangements of the various isomers in acid and basic solution confirm the structural assignments and the edge displacement principle.

PT 39

METAL COMPLEXES OF FUNCTIONALISED BENZIMIDAZOLE- AND IMIDAZOLE-BASED LIGANDS DESIGNED TO BIND TO DNA

Adel M. S. Garas[a], Robert S. Vagg[a] and Peter A. Williams[b]

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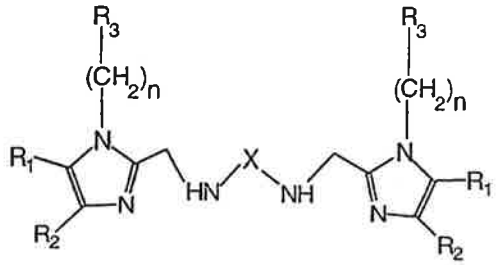
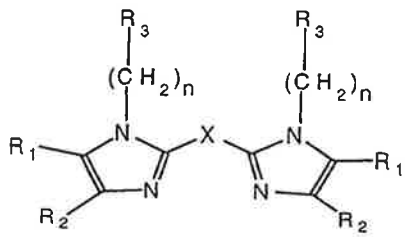
[b] *Department of Chemistry, University of Western Sydney, Nepean, NSW 2747, Australia*

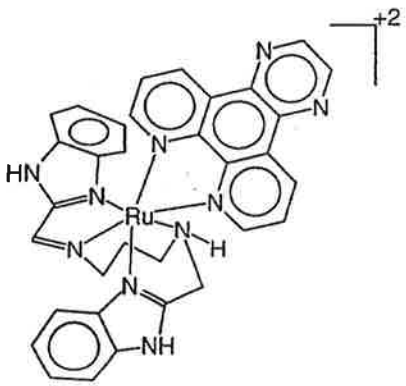
A series of new multidentate ligands which are derivatives of imidazole and benzimidazole have been prepared. These compounds, which are represented in general form below, have been characterized by their NMR and mass spectra. Complexes of these ligands with Co(III), Ru(II), Pd(II) and Pt(II) have been synthesised. Representative complexes also are illustrated below. The ligands have been functionalised so as to increase their potential to bind intercalatively to

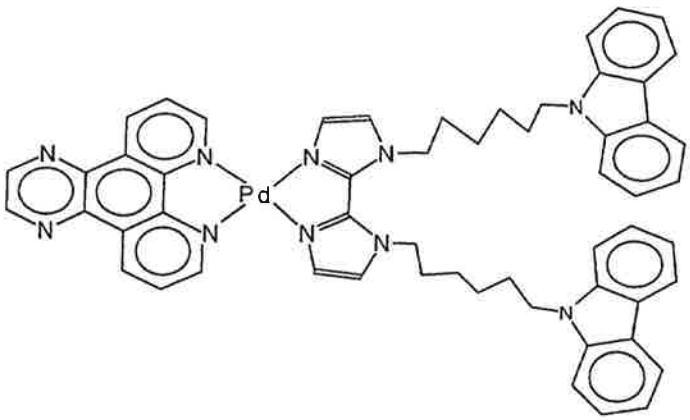


R_1	R_2	R_3	n	X
H	H	H	0	$(CH_2)_2$
H	CH_3	H	0	$(CH_2)_2$
H	CH_3	H	0	*R*-C_6H_{10}
H	H	H	0	*RR*-C_6H_{10}
$(CH)_4$		H	0	$(CH_2)_2$
$(CH)_4$		H	0	$(CH_2)_3$
$(CH)_4$		9-cbz	$(CH_2)_6$	$(CH_2)_3$
$(CH)_4$		H	0	C_6H_{10}
$(CH)_4$		9-cbz	$(CH_2)_6$	C_6H_{10}



R_1	R_2	R_3	n	X
H	H	9-cbz	4	0
H	H	9-cbz	6	0
$(CH)_4$		9-cbz	4	0
$(CH)_4$		9-cbz	6	$(CH_2)_2$
$(CH)_4$		9-cbz	6	$-C_6H_4-$
H	H	NH_2	4	0





DNA by incorporating tethered polycyclic groups such as carbazole or phenanthridine.

PT 40

MOLECULAR RECOGNITION BETWEEN CHIRAL METALLOINTERCALATORS AND DNA

Kymberley A. Vickery [1], Antonio M. Bonin [2], Robert S.Vagg [1*] and Peter A. Williams [3*]

[1] *School of Chemistry, Macquarie University, Sydney, N.S.W. 2109, Australia*

[2] *Toxicology Unit, N.I.O.H. & S., Sydney, N.S.W. 2050, Australia*

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The development and use of chiral metal complexes as molecular probes of nucleic acid structures have been the subject of intense research over the past two decades. To this end, novel substitutionally inert chiral ruthenium(II) complex cations of the form [Ru(*R*R**-picchxnMe$_2$)(bidentate)]$^{2+}$, where *R*R**-picchxnMe$_2$ is the linear N$_4$-tetradentate *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-*1R*,2R**-diaminocyclohexane, have been synthesised and a preliminary assessment made of their value as discriminatory metallointercalators of nucleic acids. Intermolecular interactions with DNA for the series of metalloprobes where the aromatic N$_2$-bidentate fragment is 1,10-phenanthroline *(phen),* dipyrido[3,2-d:2'3-f]quinoxaline *(dpq)* or 9,10-phenanthrenequinone diimine *(phdi)* have been studied. The chiral recognition properties of DNA towards the diastereomeric and enantiomeric forms of the cations were investigated using natural DNA, synthetic oligonucleotide fragments, polymers (poly[dG.dC])$_2$ poly[dA].poly[dT] and bacterial DNA systems. Equilibrium binding constants have been determined by intrinsic methods and these are used to rank the intercalating ability of the different bidentate systems as *phdi* > *dpq* > *phen*. Bacterial mutagenicity investigations correlate well with this ranking order, with the *cis*-α isomers demonstrating an implied higher intercalation affinity than for the *cis*-β forms in each of the bidentate systems. The findings are consistent with our design objectives and summaries of these results will be presented.

PT 41

NMR SOLUTION STRUCTURES OF Ru COMPLEXES AND THEIR OLIGONUCLEOTIDE ADDUCTS

Emma M. Proudfoot,[a] Peter H. Karuso,[a] Robert S. Vagg,[a] Kymberley A. Vickery[a] and Peter. A. Williams[b]

[a]*School of Chemistry, Macquarie University NSW 2109*
[b] *Department of Chemistry, University of Western Sydney Nepean, NSW 2747*

The design of metal complexes for sequence-specific DNA binding is an active area of current research,[1] and the elucidation of the structural aspects of such binding in solution is an important step in the design process as these are free from crystal packing forces. We have studied the solution structure of $[Ru(picchxnMe_2)(bidentate)]^{2+}$, alone and with oligonucleotides, by NMR spectroscopy. The results presented here are for the interaction between the α and β isomers of Δ-cis-$[Ru(RR\text{-}picchxnMe_2)(phen)]^{2+}$ with two oligonucleotide sequences. A NMR solution structure of Δ-cis-α-$[Ru(RR\text{-}picchxnMe_2)(phi)]^{2+}$ is also presented.

Results show that the α-*phen* complex binds to $[d(CGCGATCGCG)_2]$ at the single AT site from the minor groove.[2] Binding of α-*phen* to $[d(ATATCGATAT)_2]$ yields results which are consistent with binding occurring in the minor groove at the several AT sites available. Studies of β-*phen* with $[d(CGCGATCGCG)_2]$ show that the complex binds only to the ends of the DNA, indicating a change in binding site compared to α-*phen* and unfavourable steric clashes with the DNA.

1. C.M. Dupureur and J.K. Barton, *Inorg. Chem.*, **36**, 33 (1997).
2. E.M. Proudfoot, J.P. Mackay, R.S. Vagg, K.A. Vickery, P.A. Williams and P. Karuso, *Chem. Commun.*, 1623-1624 (1997).

PT 42

MOLECULAR RECOGNITION BETWEEN CHIRAL METALLOINTERCALATORS AND DNA

Kymberley A. Vickery [1], Antonio M. Bonin [2], Robert S.Vagg [1*] and Peter A. Williams [3*]

[1] *School of Chemistry, Macquarie University, Sydney, N.S.W. 2109, Australia*

[2] *Toxicology Unit, N.I.O.H. & S., Sydney, N.S.W. 2050, Australia*

[3] *Faculty of Science & Technology, University of Western Sydney, Nepean, N.S.W. 2747, Australia*

The development and use of chiral metal complexes as molecular probes of nucleic acid structures have been the subject of intense research over the past two decades. To this end, novel substitutionally inert chiral ruthenium(II) complex cations of the form [Ru(*R*R**-picchxnMe$_2$)(bidentate)]$^{2+}$, where *R*R**-picchxnMe$_2$ is the linear N_4-tetradentate *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-*1R*,2R**-diaminocyclohexane, have been synthesised and a preliminary assessment made of their value as discriminatory metallointercalators of nucleic acids. Intermolecular interactions with DNA for the series of metalloprobes where the aromatic N_2-bidentate fragment is 1,10-phenanthroline *(phen),* dipyrido[3,2-d:2'3-f]quinoxaline *(dpq)* or 9,10-phenanthrenequinone diimine *(phdi)* have been studied. The chiral recognition properties of DNA towards the diastereomeric and enantiomeric forms of the cations were investigated using natural DNA, synthetic oligonucleotide fragments, polymers (poly[dG.dC])$_2$ poly[dA].poly[dT] and bacterial DNA systems. Equilibrium binding constants have been determined by intrinsic methods and these are used to rank the intercalating ability of the different bidentate systems as *phdi* > *dpq* > *phen*. Bacterial mutagenicity investigations correlate well with this ranking order, with the Δ-*cis*-α isomers demonstrating an implied higher intercalation affinity than for the Λ and *cis*-β forms in each of the bidentate systems. The findings are consistent with our design objectives and summaries of these results will be presented.

TARGETING RHENIUM TO DNA

L.T. Ellis[a], **T.W. Hambley**[a], **R.B. Knott**[b] **and T.W. Jackson**[b]

[a]*School of Chemistry, University of Sydney, NSW, 2006*

[b]*Radiopharmaceutical Research and Developement, Menai, NSW, 2234*

Technetium is the most widely used radionuclide in nuclear medicine. Ligands incorporating technetium-99m are routinely used as imaging agents for many parts of the body such as brain, bone marrow, blood and lungs.[1] Technetium-99m emits a 142 keV γ photon which is readily detected using commercial γ cameras.[2]

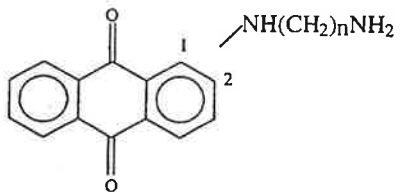
Rhenium has many chemical properties similar to those of technetium and nuclear properties that may provide additional therapeutic effects. ^{186}Re ($t_{1/2}$ 90 hrs) and ^{188}Re ($t_{1/2}$ 16.8 hrs) emit γ photons suitable for imaging (137 and 155 keV respectively), with additional high maximal and average β^- particles potentially suitable for therapeutic applications.[2]

β radiation can cause the destruction of cells[1] and hence a ^{186}Re or ^{188}Re complex may be beneficial in the treatment of some cancers. Our aim is to target the radionuclide to DNA using an attached intercalator and thus increase the radiation damage in the targeted region.

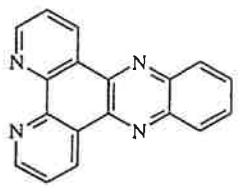
As a starting point, we have chosen amino anthraquinones (Fig.1) and the dipyrido[3,2-a:2',3'-c]phenazine hemihydrate (Fig.2) ligands. The anthraquinones contain different length amine chains at either the 1 or 2 position. We have compared these complexes to known platinum complexes.

Plasmid binding assays have been used to determine the binding to, and unwinding of, tightly coiled circular DNA and to determine how the different chain lengths, positions, ligand or type of metal present affects the binding.

Modelling has been used to determine if there are any steric barriers to binding caused by the amino chains in the different positions on the anthraquinones. This technique will help in the interpretation of the results from the plasmid binding assays.



amino anthraquinones
Figure 1



dipyrido[3,2-a:2',3'-c]phenazine hemihydrate
Figure 2

1. Kowalsky, R.J.and Perry, J.R. *Radiopharmaceuticals in nuclear medicine practice,* Appleton and Lange, Norwalk, CT, Los Altos, CA, 1987.

2. Blauenstein, P. *New J. Chem.* **1990**, *14*, 405-407.

*We gratefully acknowledge the support of AINSE in carrying out this work.

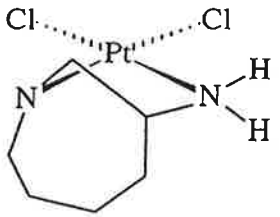
PT 44

STEREOSELECTIVE AND ENANTIOSELECTIVE INTERACTIONS BETWEEN CHIRAL PLATINUM COMPLEXES AND DNA

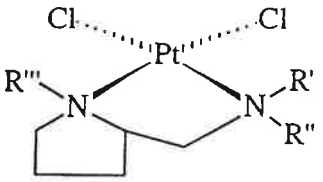
C.I. Diakos[a], H.M. Er[a], R.R. Fenton[a], T.W. Hambley[a], B.A. Messerle[a], M. McKeage[b], W.J. Esdale[b], P.J. Russell[b].

[a] School of Chemistry, University of Sydney, 2006.
[b] Oncology Research Centre, Prince of Wales Hospital, Randwick, 2031.

We have been using the chiral platinum complexes [Pt(ahaz)Cl_2] (ahaz = 3-aminohexahydroazepine) and [Pt(pyrr)Cl_2] (pyrr = 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.



[Pt(ahaz)Cl_2]



[Pt(pyrr)Cl_2]

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 directed toward the 3′ direction. We do indeed observe two isomers in digests of DNA treated with either *R*- or *S*-[Pt(ahaz)Cl_2]. 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 carried out 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. Temperature-variant 1D NMR spectra are being analysed and simulations performed to obtain guanine H8 exchange rates of the rotamers. The biological activity of the enantiomers is in apparent contrast with the formation of the GpG adducts in that the *R* enantiomer has greater or equal activity to the *S* in a number of cell lines.[1]

[1] Fenton, R.; Esdale, W.J.; Er, H.M.; O'Mara, S.M.; McKeage, M.; Russell, P.J.; Hambley, T.W. *J. Med. Chem.* **1997**, *40*, 1090-1098.

PT 45

ELECTROCHEMICAL STUDIES OF SEVERAL ANTI-TUMOUR PLATINUM COMPLEXES

Andrew R. Battle[1], Susan A. Turland[2], Helen R. Webb[2], Glen B. Deacon[2], Alan M. Bond[2] and Trevor W. Hambley[1]
[1]*School of Chemistry, University of Sydney, Sydney NSW 2006*
[2]*Department of Chemistry, Monash University, Clayton VIC 3168*

The majority of anti-tumour research using platinum has to date focussed on platinum(II) complexes. Platinum(IV) complexes are more kinetically inert, and exhibit fewer side effects than their platinum(II) analogues[1]. Platinum(IV) complexes are reduced *in vivo* to their corresponding platinum(II) complexes, but how completely and how rapidly this process occurs remains an open question.

Electrochemical studies of several platinum(IV) complexes were carried out (Figure 1). All of these complexes show reduction potentials in dichloromethane of -1.0V or lower versus Ferrocene$^+$/Ferrocene. Correlations between the reduction potentials and *in vitro* cytotoxicity have been investigated.

To assist in the oxidative synthesis of organoamido Pt(IV) complexes, the electrochemical oxidation of anti-cancer active [N,N'-bis-(2,3,5,6-tetrafluorophenyl)ethane-1,2-diaminato(2-)]-dipyridineplatinum(II) (Figure 2) was examined. Cyclic voltammetry showed two responses - one ligand based and the other metal based. The use of other techniques - rotating disk electrode voltammetry and bulk electrolysis has shown that both of these responses are two electron oxidations.

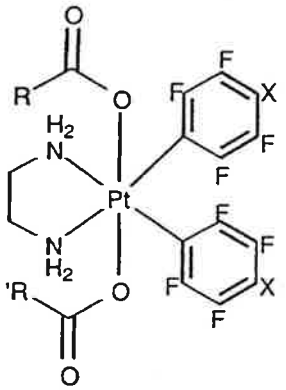


Figure 1 : General Structure of the Platinum(IV) complexes
X = F, H, OMe; R and R' = Me, Et, ^{i}Pr, ^{n}Pr, ^{n}Bu, CH_2Cl, OCH_3

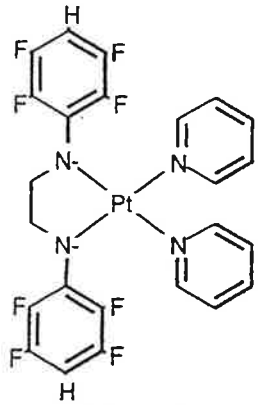


Figure 2

[1]Giandomenico, C.M., Abrams, M.J., Murrer, B.A., Vollano, J.F., and Matthey, J., *In proceedings of : The Sixth International Symposium on Platinum and other Metal Coordination Compounds in Cancer Chemotherapy;* Plenum Press; San Diego, C.A., P58 (1992).

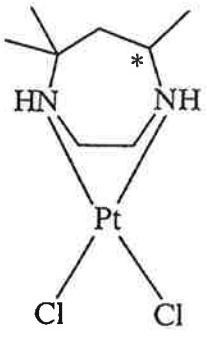
PT 46

BULKY PLATINUM COMPLEXES AS PROBES OF PLATINUM/DNA INTERACTIONS

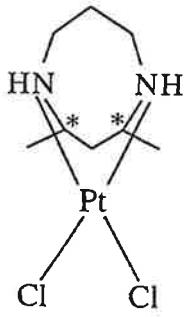
R.R Fenton, T.W. Hambley, M. Johnston, E.C.H. Ling, V.P. Munk, C.L. Teo.

School of Chemistry, University of Sydney, 2006.

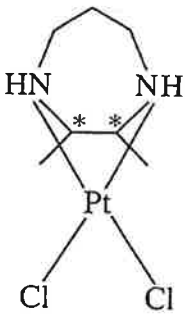
It is postulated that platinum-based anticancer drugs, such as *cis*-diamminedichloroplatinum(II) (*cisplatin*), act through binding to DNA. Such compounds form several intrastrand and interstrand DNA adducts however it is unclear as to which platinum-DNA adduct is primarily responsible for the anticancer activity. Through molecular modelling studies a compound was designed that should be able to form the interstrand adduct but be less suited to forming the intrastrand adduct.[1] This compound, $[Pt(hpip)Cl_2]$ (hpip = 1,4-diazacycloheptane), was found through DNA cross-linking studies to form only one-third as many intrastrand adducts as *cisplatin*.[1] *In vitro* cytotoxicity studies revealed that the $[Pt(hpip)Cl_2]$ complex was 50 times less toxic than *cisplatin*, indicating that interstrand adducts do not play a significant role in the anti-cancer activity of such compounds. $[Pt(hpip)Cl_2]$ also exhibited stereoselectivity in the formation of GpG adducts.



$[Pt(tmdz)Cl_2]$



$[Pt(dimedaco)Cl_2]$



$[Pt(dimehpip)Cl_2]$

A series of chiral diamine ligands (tmdz = 5,5,7-trimethyl-1,4-diazacycloheptane, dimedaco = 2,4-dimethyl-1,5-diazacyclooctane, dimehpip = 2,3-dimethyl-1,4-diazacycloheptane) that are structural analogues of hpip are being synthesised to determine whether the stereochemistry influences the type and distribution of platinum-DNA adducts formed, and therefore whether the platinum(II) complexes of these ligands exhibit any stereoselective cytotoxic activity.

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1. Ling, E.C.H.; Allen, G.W.; Hambley, T.W. *J. Am. Chem. Soc.* **1994**, *116*, 2673.

PT 47

MODELLING STUDIES OF BIS(PLATINUM) COMPLEXES DESIGNED TO PROBE DRUG – DNA INTERACTIONS

Andrew R. Jones[a], Trevor W. Hambley[a] and Nicholas P. Farrell[b]

[a]School of Chemistry, University of Sydney, NSW 2006, Australia.

[b]Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia.

Bis(platinum) complexes are an exciting new generation of platinum anti – cancer drugs, some of which are entering clinical trials. Their mechanism of action is different to that of *cisplatin* and thus they may be active against different tumours. Proposed mechanisms include a unique interstrand crosslink with the DNA[1] (Figure 1) or the bis(platinum) complex binding to both the DNA and a protein.

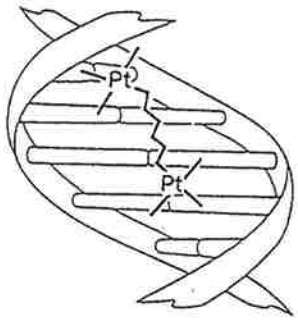


Figure 1 : Interstrand binding unique to bis(platinum) complexes.

Modelling studies were carried out on a number of bis(platinum) complexes bound to DNA via interstrand cross links. Different forms of DNA (B and Z) were also modelled to determine if the platinum ligands were more accessible for protein interaction in either form.

The bis(platinum) complex shown in Figure 2 was designed to be unable to form a cross link so as to test the role of these links. Modelling studies have been carried out to determine the possible interactions with the B and Z forms of DNA. A successful strategy has been devised for synthesising the complex. Anti-cancer activity tests and other DNA assays will be used to determine the role of the cross links.

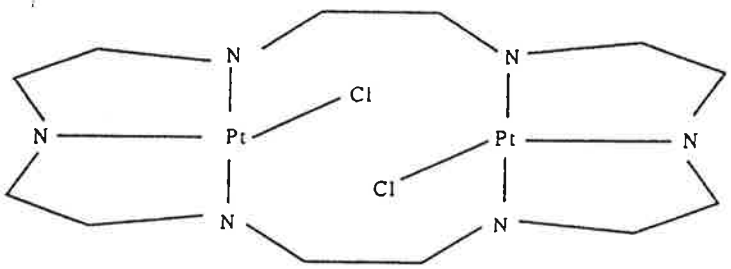


Figure 2 : $Pt_2[18]aneN6Cl_2$.

References:

1. Qu, Y. and Farrell, N.P. *J. Inorg. Biochem., 40, 255 (1990).*

PT 48

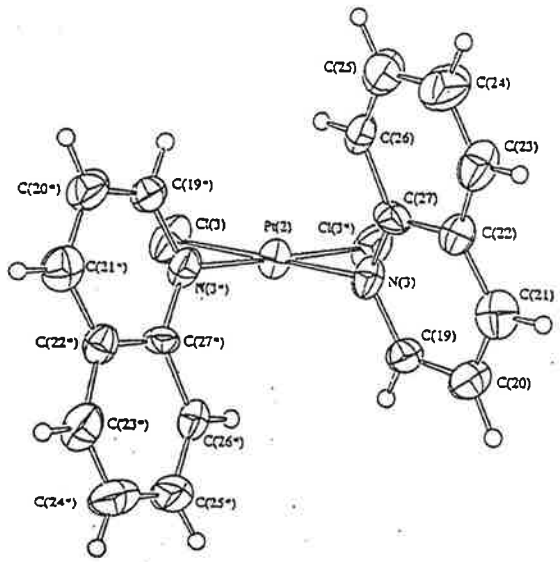
MOLECULAR CONFORMATION OF *cis*-[Pt(QUINOLINE)$_2$Cl$_2$] FROM X-RAY CRYSTALLOGRAPHIC, NMR SPECTROSCOPIC AND MOLECULAR MECHANICS EVIDENCE: RELEVANCE TO CISPLATIN-DNA INTERACTIONS.

Murray S. Davies, Barbara A. Messerle and Trevor W. Hambley

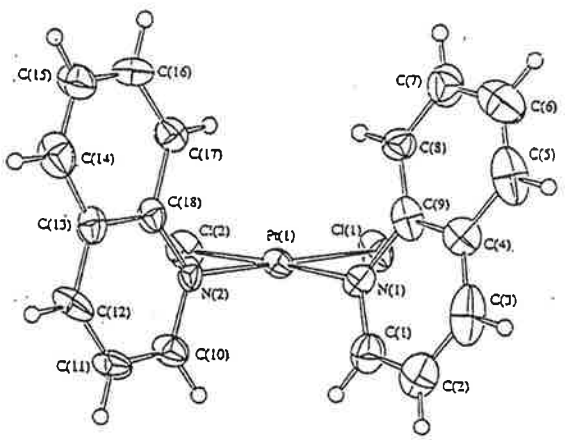
School of Chemistry, University of Sydney, Sydney NSW 2006, Australia

The preparation and characterisation of *cis*-[Pt^{II}(quinoline)$_2$Cl$_2$] by X-ray crystallography and NMR spectroscopy has been studied. In the solid state the complex exists as a mixture of both head-to-head (hth) and head-to-tail (htt) quinoline rotamers. In solution, the two rotamers interconvert at room temperature. Variable temperature ^{1}H NMR spectroscopy was used to investigate the barrier to interconversion of the two rotamers. NMR spectra were obtained in order to assign the quinoline ^{1}H resonances of both hth and htt species and NOESY spectra were used to determine the inter quinoline ^{1}H distances (H2-H2, H8-H8 for hth, H2-H8 for htt) for the two forms. These were compared with the values obtained from the crystal structure.

Molecular mechanics calculations were performed to determine the energy difference between the two rotamers. Internuclear distances were also compared against those determined by molecular modelling.



cis-[Pt(quinoline)$_2$Cl$_2$] in htt rotamer form



cis-[Pt(quinoline)$_2$Cl$_2$] in hth rotamer form

PT 49

[D,L-1,2-BIS(2-HYDROXYPHENYL)ETHYLENEDIAMINE]DICHLOROPLATINUM(II) – DNA ADDUCT PROFILE, DNA BINDING KINETICS AND MOLECULAR MODELLING STUDIES OF THE ENANTIOMERS

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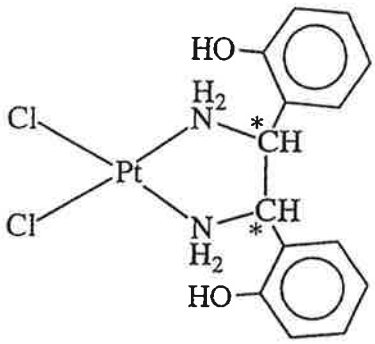
The complexes [D,L-1,2-Bis(2-hydroxyphenyl)ethylenediamine]dichloroplatinum(II) (D,L-2OH-$PtCl_2$) have shown high antitumor activity against human cancer cell lines and in animal experiments[1)]. The meso form, however, is less active. Resolution of the D,L-compound into its enantiomers led to different results in the cisplatin resistant human ovarian cancer cell line NIH:OVCAR-3, whereby the SS-enantiomer is markedly more active[2)]. In order to explain these differences in antitumour activity, the interactions between these enantiomeric platinum complexes and DNA have been studied.



2OH-$PtCl_2$

Thus, the DNA-adduct profile of each of the enantiomers and of the racemic mixture was determined. The platinum complexes were reacted for 2, 4, 8, 24 and 164 h with salmon sperm DNA (r_t = 0.05). The reaction mixture was analysed by HPLC and the peaks compared to those of the synthesised standard compounds. The platinum nucleotide adducts were assigned by NMR spectroscopy. The total extent of platinum-DNA binding was measured using graphite furnace AAS and UV spectroscopy. Molecular Modelling studies were also carried out to examine the interactions of both enantiomers with DNA and to establish a structure-activity relationship for these drugs.

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1) G. Bernhardt, R. Gust, H. Reile, H.-D. Orde, R. Müller, C. Keller, T. Spruß, H. Schönenberger, T. Burgemeister, A. Mannschreck, K.-J. Range, U. Klement; *J. Cancer Res. Clin. Oncol.*, **1992**, 118, 201

2) G. Bernhardt, R. Gust, H. Reile, H.-D. Orde, R. Müller, C. Keller, T. Spruß, H. Schönenberger, T. Burgemeister, A. Mannschreck, K.-J. Range, U. Klement; *J. Cancer Res. Clin. Oncol.*, **1992**, 118, 209

PT 50

PLATINATION KINETICS AND PRODUCT CHARACTERISATION OF DOUBLE STRANDED 14 BASE-PAIR 5'-AG-3' AND 5'-GA-3' OLIGONUCLEOTIDES

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The anti-cancer properties of the drug cisplatin are believed to arise from its binding to intracellular DNA, inducing a conformational change. The prime platination sites on DNA are intrastrand GpG (~70%) and ApG (~25%), the remainder of platinated sites being various GpXpG and interstrand sites. Bifunctional binding to GpA sites is not observed. To understand the selectivity of cisplatin for ApG over GpA sites, the kinetics of the reaction of cisplatin to defined AG and GA oligonucleotides have been studied.

The rates of the reaction between ^{15}N labelled cisplatin and *cis*-$[Pt(^{15}NH_3)_2(OH_2)_2]^{2+}$ with the self-complementary 14 base-pair oligonucleotides AATTAGTACTAATT (**AG**) and AATTGATATCAATT (**GA**) have been examined using [^1H, ^{15}N] HSQC 2D NMR spectroscopy. Cisplatin is seen to react via the hydrolysis product *cis*-$[Pt(^{15}NH_3)_2(OH_2)Cl]^+$ forming two monofunctional adducts on reaction with both **AG** and **GA**. These monofunctional adducts ring close affording the Pt-**AG** chelate, that exists in a pH and temperature dependent conformational equilibrium, and one Pt-**GA** chelate. Reaction of *cis*-$[Pt(^{15}NH_3)_2(OH_2)_2]^{2+}$ and the oligonucleotides is accelerated relative to cisplatin, all of the more reactive Pt diaqua species is consumed after 1 hour. The reaction between cisplatin and **AG** to form a monofunctional adduct is ~7 times as fast as with **GA**, but when the active diaqua form of cisplatin is used the rates of reaction are the same for both oligonucleotides. In both cases, ring closure is greatly slowed for **GA** relative to **AG.**

The reaction scheme and rate constants are reported for all 4 reactions. Comparisons are made between these parameters and those of a similar strand with a GG platination site. In addition, the equilibrium between the two forms of Pt-**AG** chelate is explored.

Δ,Λ-[Ru(phen)$_2$(dpq)]$^{2+}$ Interactions With the Hexanucleotide d(GTCGAC)$_2$ by Structural NMR Studies

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[B]Department of Chemistry, University College, (UNSW), Australian Defence Force Academy, Canberra 2600, Australia

The determination of the DNA binding geometry is a very important aspect in the study of the interactions of metallointercalators with nucleic acids. Recent studies have focused on the interactions of metallointercalators based on 9,10-diaminophenanthrene (*phi*) and dipyrido[3,2-a;2'3'-c]phenazine (*dppz*) ligands. Complexes based on *dppz* and *phi*, such as [Ru(phen)$_2$(dppz)]$^{2+}$ and [Rh(phen)$_2$(phi)]$^{3+}$, have unambiguously been shown to strongly bind (Ka>10^7 M^{-1}) DNA via intercalation in the major groove.

We report the NMR studies of the binding of Δ, Λ-[Ru(phen)$_2$(dpq)]$^{2+}$ an analogue of [Ru(phen)$_2$(dppz)]$^{2+}$ to the oligonucleotide d(GTCGAC)$_2$. The data from one and two-dimensional NMR binding experiments of the oligonucleotide-metal complex suggest that both Δ and Λ [Ru(phen)$_2$(dpq)]$^{2+}$ bind in the minor groove of DNA. In addition, evidence also indicates that both optical isomers of [Ru(phen)$_2$(dpq)]$^{2+}$ bind to the hexanucleotide d(GTCGAC)$_2$ by intercalation, of the *dpq* ligand, from the minor groove. A number of intermolecular NOE cross peaks between both Δ and Λ-[Ru(phen)$_2$(dpq)]$^{2+}$ and C$_3$, G$_4$ and A$_5$ minor groove resonances of the hexanucleotide were observed in NOESY spectra. This data, coupled with small chemical shift movements of 1,10-phenanthroline (*phen*) resonances in the 1D NMR titration's, indicate that the *dpq* ligand selectivity intercalates with the *phen* residing in the minor groove. To our knowledge, this is the first study that demonstrates that both enantiomers of an octahedral metallointercalators intercalate from the minor groove.

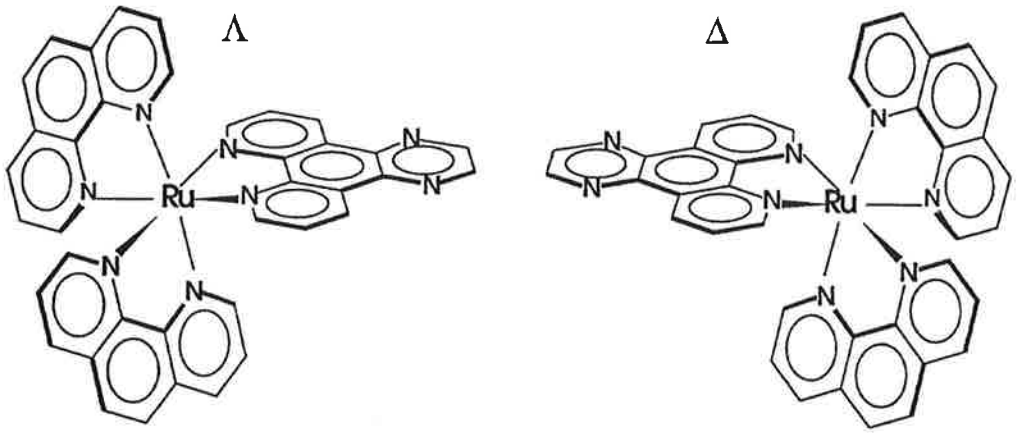

Figure 1: Structures of Δ and Λ -[Ru(phen)$_2$(dpq)]$^{2+}$.

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Molecular Recognition of DNA by Ruthenium(II) Polypyridyl Complexes

Ivan Greguric,[A] Janice Aldrich-Wright,[A] and Grant Collins,[B]

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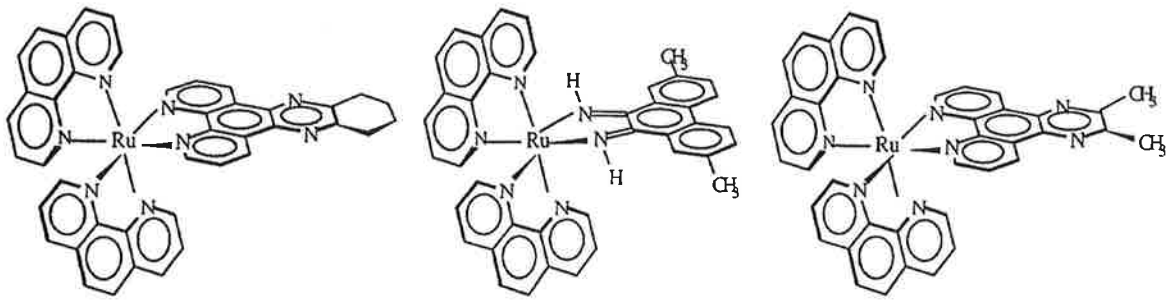
Even the simple metal complex, $[Ru(phen)_3]^{2+}$, has been reported to be sensitive to topographical changes in DNA, however there have been some uncertainties concerning the mode of binding and enantiomeric selectivity[1-3]. These uncertainties have been addressed by replacing one *phen* with a proven intercalating ligand such as dipyrido[3,2-a:2',3'-c]phenazine (*dppz*), which inserts, between the base pairs of DNA, eliminating any ambiguity concerning which bidentate intercalate[4-5], whilst increasing the binding affinity by two to three orders of magnitude[6]. This refinement, however, did not result in comprehensible structural details from the NMR binding studies. Unfavorable exchange kinetics coupled with a profusion of overlapping resonances were responsible for the lack of structural detail. Clearly, if the aromatic nature, the shape or the extent of interaction of *dppz* was refined perhaps the interaction would be less ardent and more favorable exchange kinetics could be achieved so that the binding geometry could be established. If, instead either dipyrido[3,2-d:2',3'-f]quinoxaline (*dpq*) or 9,10-diaminophenanthrene (*phi*) replaced one *phen*, only the finite area governed by the nucleotide bases would be overlapped. Further fine adjustments to the overall shape may be accomplished by the addition of functional groups to selected positions.

This paper reports the structural DNA studies by 2D NMR of a comprehensive matrix of metal complexes of the type Δ,Λ-$[Ru(ancillary\text{-}ligand)_2(intercalator)]^+$, formed from a combination of certain ancillary ligands, such as dimethylphen, *biq* and *dip*, with selected intercalators, such as dipyrido[3,2-a:2',3'-c]-6,7,8,9-tetrahydrophenazine (*dpqC*), dipyrido[3,2-a:2',3'-f]-2,3-dimethylquinoxaline ($dpqMe_2$) and 2,7-dimethyl-9,10-diaminophenanthrene ($Phime_2$). This approach has exposed binding information and has lead to refinements that have improved DNA affinity.



(1) **(2)** **(3)**

1. J. P. Rehmann and J. K. Barton, *Biochemistry*, **29**, (1990), 1701 & 1710
2. C. Hiort, B. Norden, and A. Rodger, *J. Am. Chem. Soc.*, **112**, (1990), 1971
3. M. Eriksson, M. Leijon, C. Hiort, B. Norden and A. Grasland, *J. Am. Chem. Soc.*, **114**, (1992), 4933 & *Biochemistry*, **33** (1994), 5031
4. C. Hiort, P. Lincoln and B. Norden, *J. Am. Chem. Soc.*, **115**, (1993), 3448
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6. I. Haq, P. Lincoln, D. Suh, B. Norden, Z. Chowdhry and J. B. Chaires, *J. Am. Chem. Soc.*, **117**, (1994), 14788

PT 53

The Synthesis of Platinum(II) Bipyridyls and Their Interactions With the Hexanucleotide d(GTCGAC)$_2$ by NMR Studies

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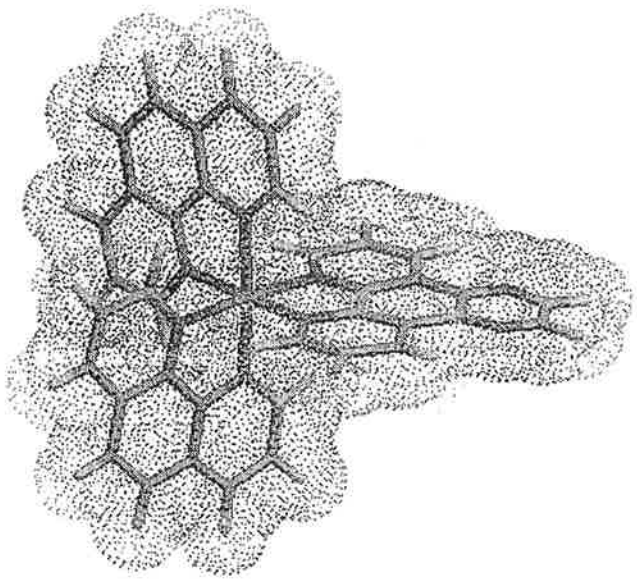
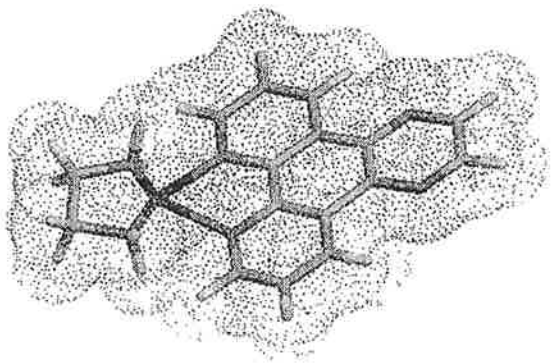
The determination of the binding geometry of metallointercalators that bind to DNA is a dynamic area of research, at the interface of biology and chemistry. Recent studies have revealed that octahedral metal complexes, such as [Ru(diimine)$_2$(dpq)]$^{2+}$ (**1**) (where diimine = 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline and *dpq* = dipyrido[3,2-*d*:2'3'-*f*]quinoxaline), bind selectively to DNA. The exchange kinetics, with the oligonucleotide d(GTCGAC)$_2$, was such that certain structural details, about the binding site, were evident and this data indicated that the *dpq* ligand selectively intercalated between **T$_2$**•**A$_5$** and **C$_3$**•**G$_4$** base pairs of the minor groove.

We were interested in examining the influence of the *dpq* ligand on the selectivity of binding by comparing octahedral intercalating complex with a square planar intercalating complex. This change in structure will affect the interactions within the intercalation cavity and may afford more explicit details about the binding geometry.

Here we report the synthesis and NMR binding study of square planar complexes, like [Pt(en)(X)]$^{2+}$, (**2**) (where en = ethylenediamine and X = *phen*, *dpq* and dipyrido[3,2-*d*:2'3'-*f*]2-methylquinoxaline *(dpqMe))* to the oligionucleoitide d(GTCGAC)$_2$. This range of complexes was chosen to highlight the π stacking, different aromatic areas, and symmetrical/asymmetrical characteristics of the ligands.



(1)
[Ru(diimine)$_2$(dpq)]$^{2+}$



(2)
[Pt(en)(dpq)]^2

THE BINDING OF OPTICALLY ACTIVE Ru(II) POLYPYRIDYL COMPLEXES WITH DNA

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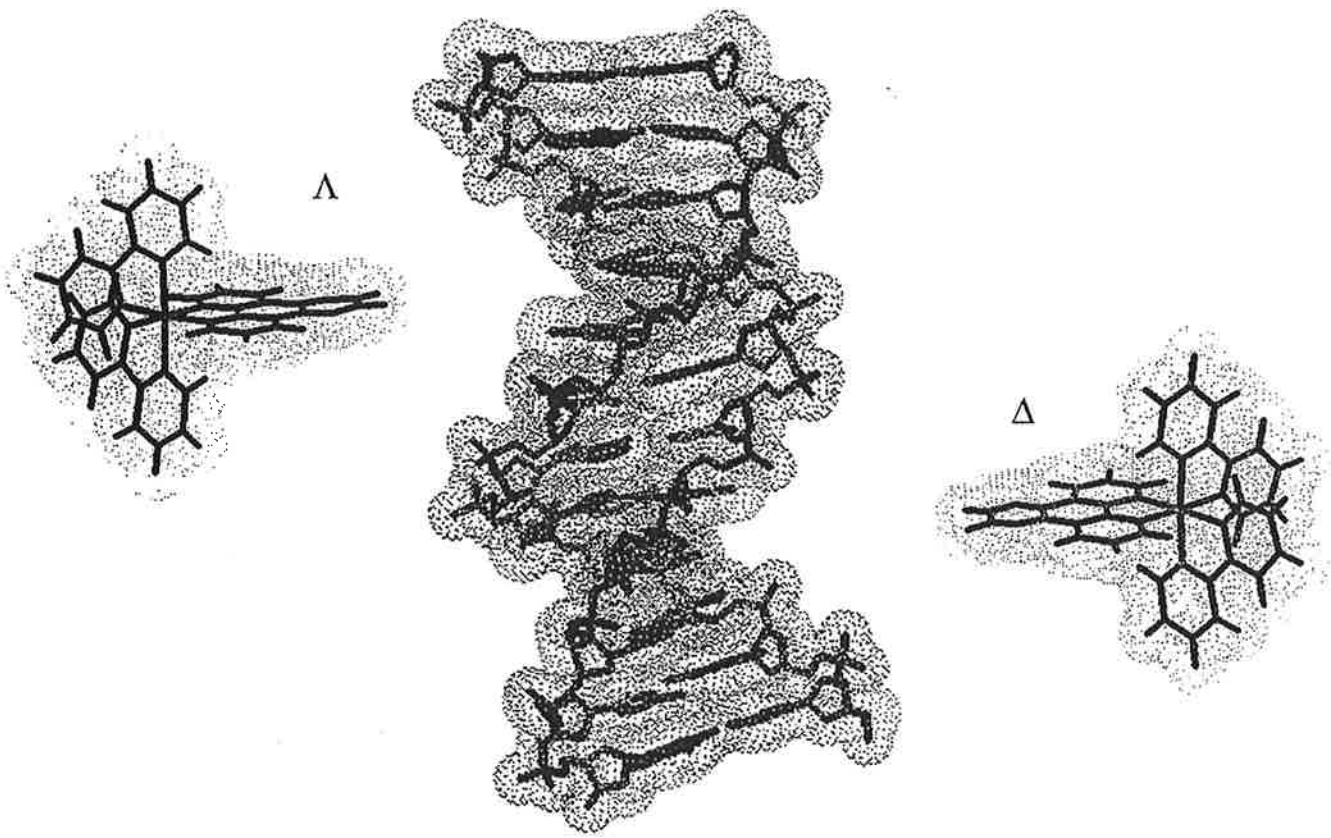
Campbelltown, NSW 2560

The topic of DNA intercalation has become quite popular in the last decade or so, and has received much attention by inorganic chemists. This work is primarily concerned with the way certain molecules associate with DNA. Intercalation describes the mode in which molecules with a flat planar shape or group stacks, wholly or partially, between the base pairs of the DNA. Because many of these compounds have been reported to exhibit preferences for certain sites along the double helix, they have the potential to be used as probes for DNA structure and possibly as anti-cancer drugs and antibiotics.

This study is concerned with the evaluation of a series of chiral Ruthenium(II) polypyridyl complexes of the type $[Ru(X)_2Y]^{2+}$ where X= 2,2'-bipyridyl *(bpy),* 4,4'-dimethyl-2,2'-dipyridyl *(DMB)* and 1,10-phenanthroline) *(phen)* and Y= *phen,* and selected aromatically extended derivatives like dipyrido[6,7-d:2',3'-f]quinoxaline *(dpq)* and dipyrido[6,7-d:2',3'-f](6,7,8,9-tetrahydro)phenazine *(dpqC).*

The investigation and comparison of the racemic, delta and lambda enantiomers of selected complexes is underway, using such techniques as DNA paper chromatography, UV-vis spectrometry and HPLC analysis.



PT 55

DNA NANOSHUTTLES

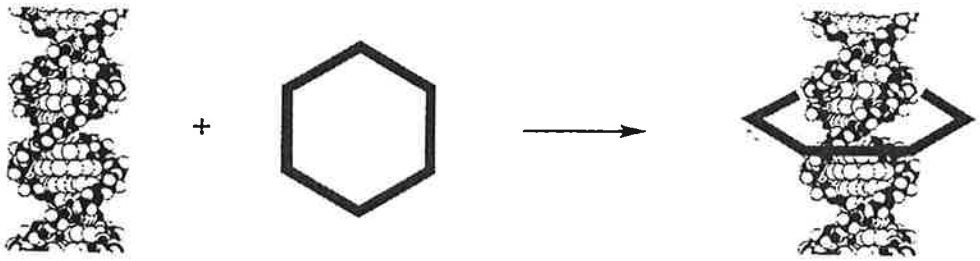
Louis M. Rendina

Department of Chemistry, The University of Adelaide

Adelaide, SA 5005.

Rotaxanes, including molecular shuttles, and their mechanically non-interlocked counterparts known as the pseudorotaxanes are well-known examples of synthetic supramolecular entities.[1,2] Nature has devised an exquisite type of pseudorotaxane involving a thread-like macromolecule (duplex DNA) encircled by a ring-like protein known as a DNA polymerase processivity factor or, more simply, a DNA sliding-clamp. Recently, the structures of the prokaryotic (β-subunit)[3] and eukaryotic (proliferating cell nuclear antigen, PCNA)[4] forms of the DNA sliding-clamp protein have been determined crystallographically. Both forms of the protein share a common structural motif, i.e. a closed-ring (toroidal) structure lined by α-helices that encircle duplex DNA. The charge distribution and orientation of the helices allow the protein to function by forming a tight clamp that can slide on DNA.

In principle, linear DNA could thread a nanoscale macrocycle in a similar manner to a DNA sliding-clamp protein. The resulting DNA-macrocycle entity may be considered to be an elaborate nanoscale version of a pseudorotaxane, where a thread-like macromolecule (DNA) is encircled by a ring-like molecule (the macrocycle) that is free to translocate along the duplex.



The use of rigid, nanoscale macrocycles as potential probes of DNA structure and function is unprecedented. This presentation will outline our efforts to target linear DNA with nanoscale molecular polygons of platinum that we have named "DNA nanoshuttles".

[1] Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 1154.
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[3] Kong, X.-P.; Onrust, R.; O'Donnell, M.; Kuriyan, J. *Cell*, **1992**, *69*, 425.
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PT 56

COMPARISON OF THE REACTIVITY OF *CIS*- AND *TRANS*-[RUCL$_2$(DMSO)$_4$] TOWARDS NUCLEOSIDES AND OLIGONUCLEOTIDES.

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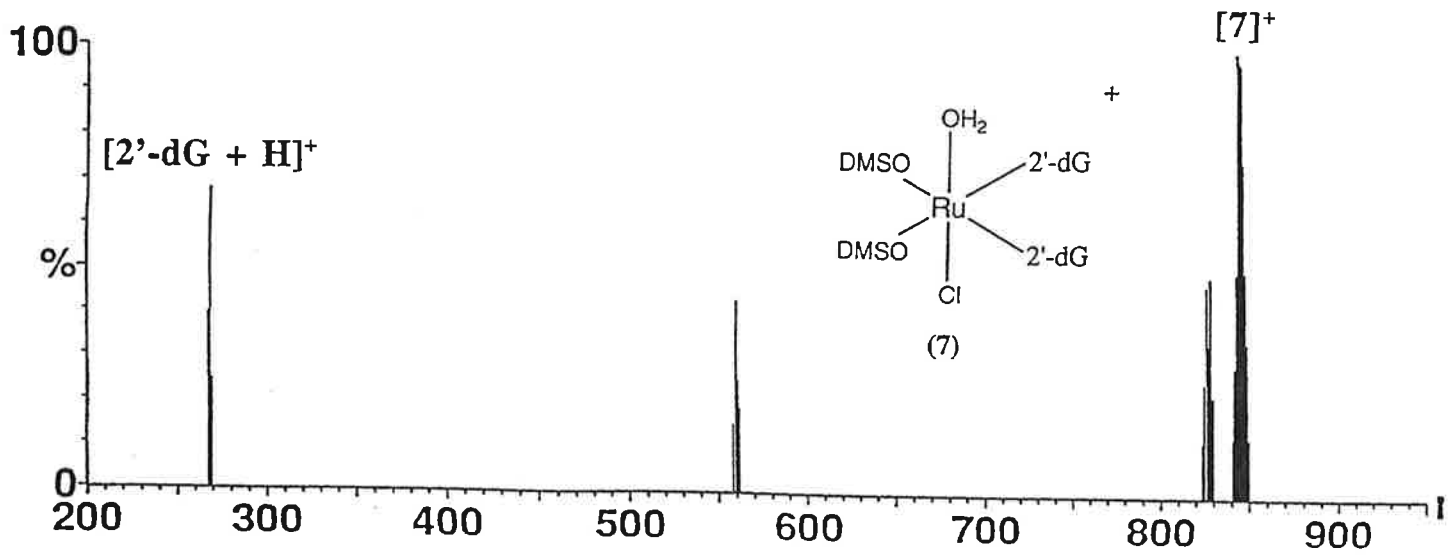
Department of Chemistry
University of Wollongong
Northfields Avenue, Wollongong, NSW, 2522

Electrospray ionisation mass spectrometry and ^{1}H NMR spectroscopy have been used to examine the reactions of *cis*-[RuCl$_2$(DMSO)$_4$] and *trans*-[RuCl$_2$(DMSO)$_4$] with deoxynucleosides. Both complexes react with 2´-deoxyguanosine to give identical products, two diastereoisomers containing a single nucleoside coordinated to ruthenium, and a *bis* adduct containing two coordinated nucleosides. Coordination of the nucleoside to ruthenium is via the N-7 atom in each complex. *Trans*-[RuCl$_2$(DMSO)$_4$] reacts with 2´-deoxyadenosine to give a pair of diastereoisomers in which the nucleosides are coordinated via their N-1 atoms. *Cis*-[RuCl$_2$(DMSO)$_4$] reacts less extensively with 2´-deoxyadenosine to give a mixture of products, each of which contains a single 2´-deoxyadenosine ligand coordinated to the metal through the N-1 atom. *Trans*-[RuCl$_2$(DMSO)$_4$] was found to react only to a small extent with 2´-deoxycytidine under conditions similar to those used for 2´-deoxyguanosine and 2´-deoxyadenosine, and not all with thymidine, even after prolonged periods. The implications of these results, and those of a preliminary investigation into the coordination of both complexes with oligonucleotides, for the mechanisms of antitumour activity of these two complexes are discussed.



Growth Inhibition Studies of Left- and Right-handed Disilver(I) and Digold(I)–Tetra(tertiary phosphine) Helicates

PT 57

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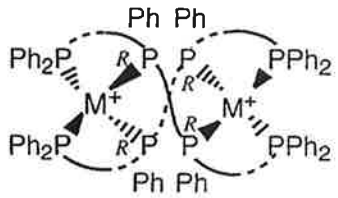
[c] *Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia*

Inorganic double-helices such as **1** may have either a left- (Λ-) or right- (Δ-) handed helical screw sense. The interaction of such helices with right-handed biological structures, such as B-DNA, in cells could theoretically be affected by their screw sense. The anti-tumour activity of the double- and side-by-side helices Λ-$[M_2\{(R,R)\text{-}\mathbf{2}\}_2](PF_6)_2$ and Δ-$[M_2\{(S,S)\text{-}\mathbf{2}\}_2](PF_6)_2$, as well as of $[M_2\{(R,S)\text{-}\mathbf{2}\}_2](PF_6)_2$ (where M = Ag(I) and Au(I))[1] have been assessed *in-vitro* and *in-vivo* against human cancer cell lines. The results indicate that the compounds are active with about the same dose potency as cisplatin. A definite, but relatively small enantiomeric selectivity was observed.



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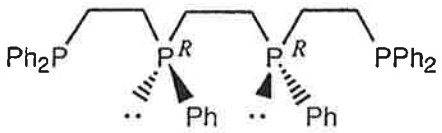


(*R*,*R*)-(–)-**2**

1. A. L. Airey, G. F. Swiegers, A. C. Willis, S. B. Wild *Inorg. Chem.* **1987**, *36*, 1588.

PT 58

MODEL COMPOUNDS OF GALACTOSE OXIDASE

Garry Mockler[a], Ray Butcher[b], Roger Kanitz[a], Owen McKern[a], Philip Morgan[a] and Margaret Sheil[a].

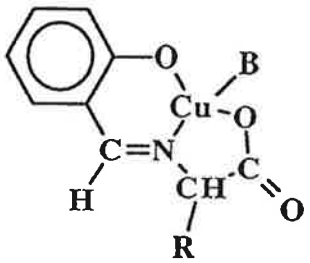
[a] Department of Chemistry, University of Wollongong, Wollongong NSW 2522.

[b] Department of Chemistry, Howard University, Washington DC 20059, USA.

Galactose oxidase is a fungal type 2 copper protein which catalyses the oxidation of alcohols to aldehydes.

$$RCH_2OH + O_2 \longrightarrow RCHO + H_2O_2$$

A series of copper(II) complexes of the type shown below have been synthesised and structurally characterised.



The reaction of these complexes with sugars has been investigated using mass spectrometry and UV-Vis and IR spectroscopy. Mass spectral data indicates that sugars bind to these copper complexes.

PT 59

INTERACTION OF IRON(II) MIXED-LIGAND COMPLEXES CONTAINING 1,10-PHENANTHROLINE AND 4,7-DIPHENYL-1,10-PHENANTHROLINE WITH CT-DNA

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[b]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Sekip Utara, Bulaksumur, Yogyakarta, Indonesia.

During the past decade a great deal of attention has been attracted to the interaction of octahedral complexes with DNA as an important issue of biochemistry and biophysics. It has been demonstrated experimentally that the size and shape of the ligand and ligand substituent affect the interaction of the complexes with DNA. For this reason, the mixed-ligand complexes containing 1,10-phenanthroline (phen) and its derivatives such as 4,7-diphenyl-1,10-phenanthroline (DIP) have been extensively exploited for DNA interaction studies. However the interaction of the mixed-ligand complexes with DNA has been limited to ruthenium(II) complexes and that of iron(II) complexes has been seldom reported. In this contribution we synthesized two types of iron(II) mixed-ligand complexes, *i.e.* $[Fe(phen)_2(DIP)]^{2+}$ and $[Fe(phen)(DIP)_2]^{2+}$ from $[Fe(phen)_3]^{2+}$ using ligand substitution reaction and semi-preparative HPLC method. The interaction of these two mixed-ligand complexes with CT (calf thymus)-DNA was investigated in comparison with that of $Fe(phen)_3^{2+}$. The UV/VIS spectroscopic results showed that the binding affinity of the metal complexes to DNA increases with the content of DIP ligand as indicated by their hypochromicity in the MLCT bands (Figure 1) and their binding constant (K_{app}). This trend is apparently consistent with the increase in the size and hydrophobicity of the complexes. Furthermore, a strong circular dichroism (CD) spectrum develops in the UV/VIS region upon addition of CT-DNA to the inversion-labile $[Fe(phen)_2DIP]^{2+}$ or $[Fe(phen)(DIP)_2]^{2+}$ (Figure 2), strongly indicating a shift in the enantiomer equilibrium (Pfeiffer effect). The shape of the induced CD spectra is indentical to that of Δ–enantiomer, directly suggesting that Δ–enantiomers of iron(II) mixed-ligand complexes are preferentially bound to CT-DNA.

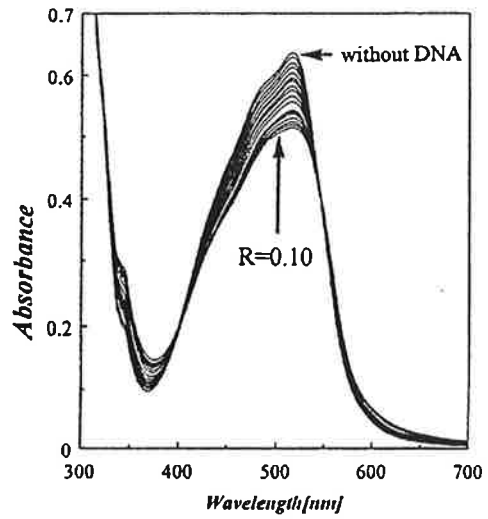

Figure 1 Visible Absorption spectra (Abs) of racemic $[Fe(phen)_2(DIP)]^{2+}$ at various [complex]/[CT-DNA] ratios (R) in Tris-HCl buffer pH=7.2 (μ=0.05 M NaCl, 25°C)

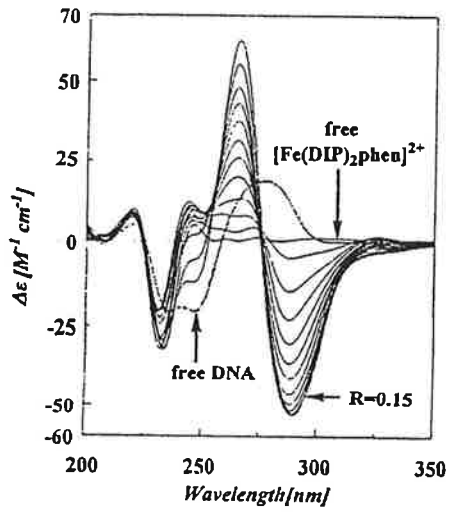

Figure 2 CD spectra of free DNA and of racemic $[Fe(phen)(DIP)_2]^{2+}$ in UV region at various [complex]/[CT-DNA] ratios (R). Conditions as in Figure 1.

PT 60

OROTIC ACID DERIVATIVES WITH POTENTIAL ANTITUMOR PROPERTIES: COMPARISON OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES

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b. Institut de Pharmacologie et de Biologie Structurale, 205 route de Narbonne, Toulouse, France
c. Laboratoire de Chimie Inorganique, Université Paul Sabatier, 118 Route de Narbonne, Toulouse, France.

Ethidium bromide was used to study the perturbations induced in salmon sperm DNA complexed by a series of platinum(II) and palladium(II) compounds with chloro and orotic acid derivatives as leaving groups. The antitumoral activity of these compounds against Sarcoma 180 cells grafted intraperitoneally into mice is correlated with their capacity to interact with DNA *in vitro* and to perturb its secondary structure.

Among these compounds [Pt(dach)(3-Me-orot)] and [Pt(dach)(5-F-orot)] do not interact with DNA *in vitro* and are inactive against Sarcoma 180 cells. This lack of activity originates from the strong chelating properties of the orotate ligand. The interaction with DNA is not the only prerequisite for a compound to be active towards tumor cells. [Pd(dach)Cl_2] is not antitumoral; this compound hydrolyses rapidly in solution and reacts with other biological molecules prior to reaching the pharmacological target, the DNA.

[Pd(dach)(3-Me-orot)] (T/C = 267%) and [Pd(dach)(3-F-orot)] (T/C = 270%) display significant antitumor activity.

PT 61

The Effect of Cr(VI/V) on the Zinc-Finger Transcription Protein GATA-1

Angela M. O'Connell,* Merlin Crossley,† Peter A. Lay* and Aviva Levina*

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

†Department of Biochemistry, University of Sydney, NSW, 2006.

Transcription of DNA to produce RNA is of vital importance in cell growth and differentiation and transcription factor proteins play a crucial role in this process. Any interference with such proteins can affect their binding to DNA and can promote cancer by changing transcription processes. The Zn^{2+} present in the DNA binding protein, GATA-1, plays a structural role in forming a loop of polypeptide, which binds specifically to a DNA sequence during transcription. In this zinc finger, the Zn^{2+} ion is bound to four thiol groups from cysteine residues. Since Cr(VI/V) complexes have a high reactivity with such groups, the chemistry and biochemistry of Cr with this protein were investigated to examine whether such reactions could influence transcription and hence, lead to promotion of genetic damage.

The interest in understanding the effects of Cr arises because of the need to understand potential mechanism(s) of Cr(VI)-induced cancers. Because of the industrial use of carcinogenic Cr(VI) has been a long-standing occupational health issue, the biochemical pathways that lead to such cancers have been of considerable interest over a number of years. We have investigated for the first time Cr(VI/V) interactions with the transcription factor protein, GATA-1, and model complexes (e.g., $[Zn(Cys)_2]$) and have observed reactions between Cr(V) and the bound thiolate groups. This changes the behaviour of the protein's natural capacity to bind to double-stranded DNA.

GATA-1 was produced by overexpression of its cloned gene in an inducible vector system. Gel shift techniques were employed to monitor the binding capabilities of GATA to ^{32}P-labelled DNA fragments upon treatment with chromium. It was observed that increasing concentrations of Cr decrease the amount of protein bound to DNA and also generate a new band in a dose-dependent manner. This implies an interaction between GATA and chromium, which interferes with the DNA binding ability of GATA. This has important implications for cell growth in which transcription is crucial, and hence, may be important in understanding Cr-induced cancers.

PT 62

EPR STUDIES OF THE OXIDATION OF CHROMIUM(III)GLYGLYGLY TO CHROMIUM(V) COMPLEXES: MUTAGENIC AND GENOTOXIC STUDIES OF CHROMIUM-PEPTIDE COMPLEXES.

Henrietta A. Headlam*, Peter A. Lay* and Antonio M. Bonin†

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

† National Occupation Health and Safety Commission, PO Box 58, Sydney, NSW, 2001.

The carcinogenic nature of Cr(VI) has been well established with numerous epidemiological studies. Cr(VI) alone does not damage DNA *in vitro*, however, in the presence of reductants it has been shown that various DNA lesions do occur. This suggests that the lower valent Cr species thus formed are the cancer causing agent/s. Cr(VI) has been shown to be reduced by various intracellular reductants to form relatively stable Cr(V) species. The small tripeptide, glutathione (GSH) and the amino acid, cysteine, which both contain a sulfur donor, have been the subject of a number of Cr(VI) reduction and biological studies. In more recent years our group has shown that macrocyclic tetraamide-*N* chromium(V) complexes are genotoxic and it is thought that chromium bound to biological ligands containing the amide group are also possible candidates for being involved in chromium carcinogenesis.

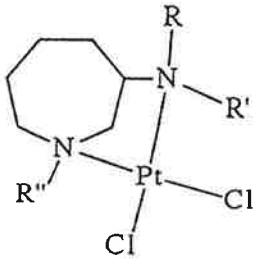
We have been investigating what role chromium(III) and -(V) - peptide complexes may play in Cr-induced carcinogenesis. The Cr(III) compound of triglycine, $Ba[Cr(glyglygly)(OH)_2]\cdot H_2O\cdot CH_3OH$, was oxidised using excess PbO_2 in various buffered solutions and the resultant Cr(V) species were studied using EPR and UV/Vis spectroscopy. The mutagenicity of the Cr(III)/glyglygly and Cr(V)/glyglygly complexes were studied using the Ames Test or bacterial mutagenicity assay employing the *S.* Typhimurium strains TA97a, TA100 and TA102. The genotoxicity of the Cr(III) and Cr(V) complexes were also studied using the micronucleous assay, which employed mammalian Chinese hamster V79 lung cells. These results showed that the Cr(III)/glyglygly complex was not mutagenic or genotoxic, however, the Cr(V) analogue produced dose-dependent results in both assays.

THE SYNTHESIS, CHARACTERISATION AND BIOLOGICAL TESTING OF CHIRAL PLATINUM(II) COMPLEXES.

E.M. Rezler, R.R. Fenton and T. W. Hambley

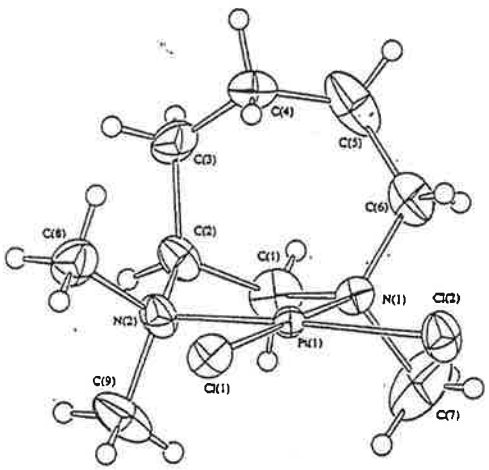
School of Chemistry, The University of Sydney, NSW Australia 2006.

A series of chiral platinum(II) complexes related to *cisplatin* have been synthesised in order to probe the effects of hydrogen bonding and steric interactions on platinum binding to DNA.



R, R', R'' = Et, Me or H

The platinum(II) complexes of *R*- and *S*-3-aminohexahydroazepine (ahaz) [1], [Pt(ahaz)Cl_2] have been shown to interact stereoselectively and enantioselectively with DNA [2] and therefore variants of these complexes have been synthesised. Novel synthetic pathways were used to prepare a series of derivatives of ahaz with alkyl substituents on both the exocyclic and endocyclic nitrogen atoms (shown above) and platinum(II) complexes of these ligands were synthesised. The crystal structures of [Pt(*S*-3-*N*-methylahaz)Cl_2], [Pt(*R*-3-*N*-ethylahaz)Cl_2], [Pt(*S*-3-*N*-dimethylahaz)Cl_2], [Pt(*S*-*N'N'*-dimethylahaz)Cl_2] and [Pt(*S*-trimethylahaz)Cl_2], have been determined and confirm the disposition of the amine groups. Preliminary *in vitro* assays of selected complexes exhibit a marked enantioselective trend whereby the *R*-enantiomers are more active than the *S*-enantiomers. Time dependent DNA binding studies and HPLC separation of the dG and d(GpG) adducts formed with both enantiomers of [Pt(3-*N*-methylahaz)Cl_2] will be discussed.



Ortep of [Pt(*S*-trimethylahaz)Cl_2].

[1] Saburi, M.;Kazuo, M.; Masatoshi, M.; Yasuo, M.; Sadao, Y.; Sei, T.; Tosio, S.; Kaoru, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 141-148.

[2] Fenton, R.R.; Easdale, W.J.; Er, H.M.; O'Mara, S.M.; McKeage, M.; Russell, P.J.; Hambley, T.W. *J. Med. Chem.* **1997**, *40*, 1090-1098.

PT 64

AN INVESTIGATION OF THE STRUCTURES OF METAL(II) AMINOACIDATO COMPLEXES

S.M. Moussa,[1] R.R. Fenton,[1] B.A. Hunter [2] and B.J. Kennedy.[1]

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[2] ANSTO, PMB 1 Menai, N.S.W., 2234, Australia

Powder X-ray and neutron diffraction techniques and the Rietveld method have been used to study the structures of the four bis(glycinato)copper(II) complexes. The two *cis*-modifications are orthorhombic, while the *trans*-modifications are monoclinic. The *cis*-monohydrate complex crystallises in the space group $P2_12_12_1$ with a = 10.8087(6) Å, b = 5.2116(3) Å, and c = 13.4972(9) Å. The anhydrous *cis*-complex crystallises in the space group $P2_12_12_1$ with a = 9.9906(8) Å, b = 5.2968(5) Å, and c = 13.250(2) Å. The structure of the *trans*-monohydrate complex, has been determined The modification crystallises in the space group I 2/a with a = 14.8385(5) Å, b = 5.2375(2) Å, c = 9.6507(3) Å and β = 87.238(2) ° (Figure 1).

The structures of *cis*- and *trans*-bis(alaninato)copper(II) have been re-determined using powder neutron and X-ray diffraction methods. Single crystal neutron diffraction methods were utilised to investigate the structure of the *cis*-[Cu(*l*-ala)$_2$] complex. The respective *d*-alanine complexes were also studied.

Methods for the solid-state preparation of the isomers of bis(glycinato)nickel(II) using thermal isomerisation and dehydration processes have been developed. The bis-*cis*- and *trans*-isomers have been isolated. Details of this and the other structures will be presented.

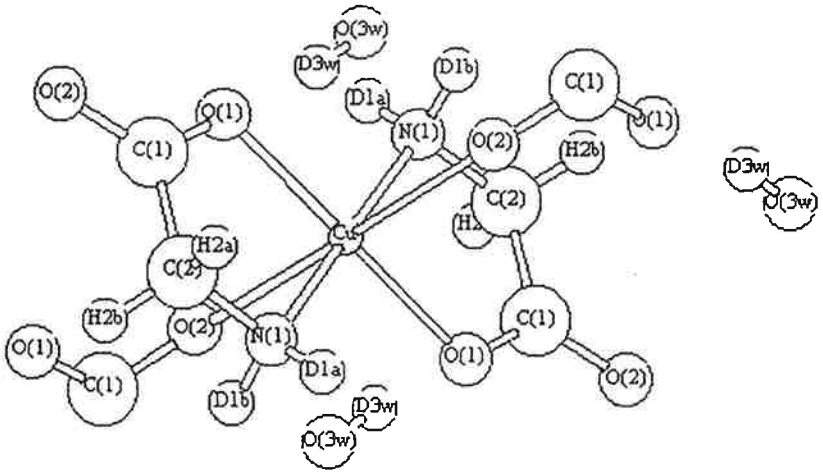

Figure 1 Representation of the *trans*-bis(glycinato)copper(II) monohydrate molecules showing the linkage of monomeric units *via* the carbonyl oxygen groups.

PT 65

CALCULATED MECHANISM FOR THE CONVERSION OF N_2 TO NH_3 BY NITROGENASE

Ian Dance

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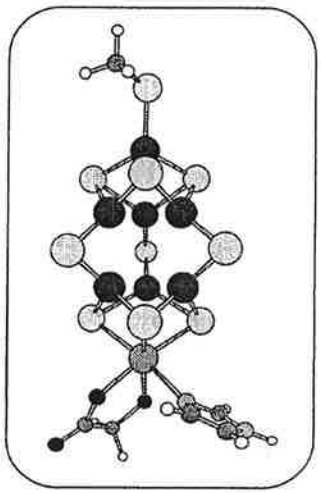
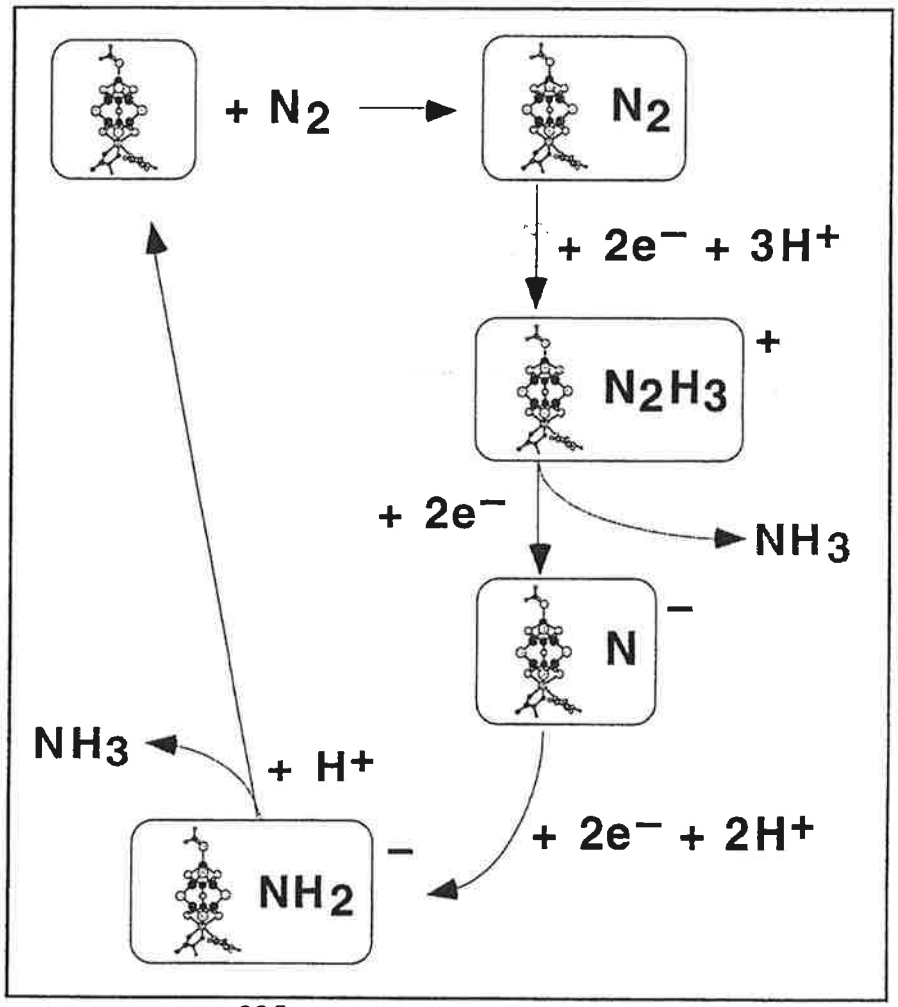


The enzyme nitrogenase achieves chemistry far beyond human capability in the laboratory, namely the reduction of N_2 to NH_3 under ambient conditions. How?

A calculated mechanism [Dance, *J. Chem. Soc., Chem. Commun.* **1997**, 165-166.] will be presented.



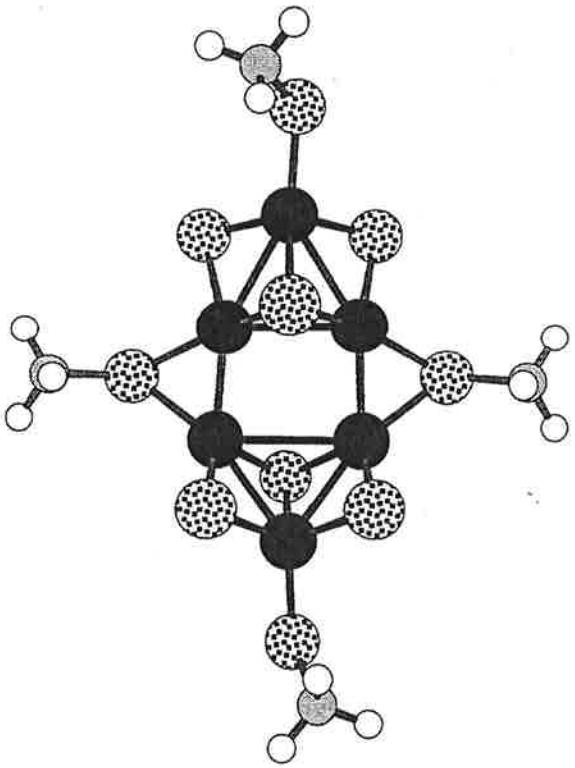
PT 66

CALCULATIONS ON THE POSSIBLE STRUCTURE AND MECHANISM OF THE FE/S/CYSTEINE CLUSTER OF HYDROGENASE

Ian Dance

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

The hydrogenases which catalyse the process $2e^- + 2H^+ \rightleftharpoons H_2$ use either an Fe/Ni active site or an Fe-only active site. The latter contains an Fe/S/cysteine cluster which is the "most conspicuously undefined cluster structure in iron–sulfur biochemistry".[1] It has been suggested that this site uses an $Fe_6S_6(S\text{-}cys)_4$ cluster which is related to the Fe_7MoS_9 cluster core at the active site of nitrogenase.[2]



The application of density functional calculations to the structural and mechanistic possibilities for the Fe-only hydrogenase will be presented.

(1) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem.Rev.* **1996**, *96*, 2239-2314.

(2) Kim, J.; Rees, D. C. *Biochemistry* **1994**, *33*, 389-97.

Strucural Effects at the Active Site of the Electron Transfer Protein Rubredoxin

Maddalena Lucarelli*, Megan Lavery*, Zhiguang Xiao*, Mitchell Guss# and Anthony G. Wedd*.

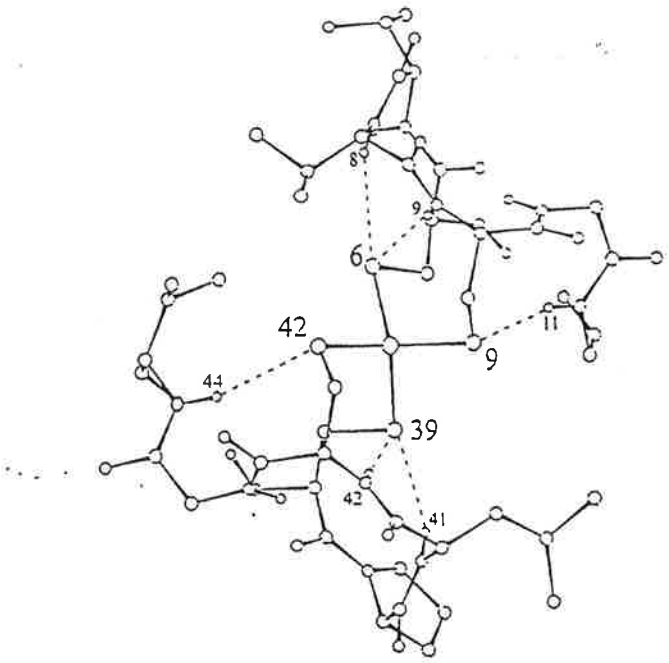
*School of Chemistry, University of Melbourne, Parkville, 3052

#School of Biochemistry, University of Sydney, Sydney, NSW, 2006

Rubredoxins (Rd) are small (ca. 6 kDa) iron-sulfur proteins whose function is electron transfer. The active site in the protein from *Clostridium pasteurianum (Cp)* features a single $Fe(S\text{-}Cys)_4$ centre of approximately D_{2d} local symmetry. Consequently, the four conserved cysteinyl ligands ($Fe\text{-}SCH_2\text{-}$) fall into two groups: residues 6 and 39 are buried inside the protein molecule and each sulphur atom participates in two peptide NH---S interactions; residues 9 and 42 are at the surface and each participates in one NH---S interaction (see Figure below) We have cloned and expressed a gene encoding *Cp*Rd in *E. coli.* and commenced generation of mutant forms.[1,2]

This poster will outline:-

1. the structural effects of substituting the native iron with Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Hg^{II} and Ga^{III} ;
2. the effect of converting the isopropyl sidechains of valine 8 and valine 44 to other alkyl groups. These two sidechains protect the active site sterically (see Figure below) and their controlled varation significantly modifies its reactivity.



References: **1** M. Ayhan, Z. Xiao, M.J. Lavery, A.M. Hamer, K. Nugent, S.D.B. Scrofani and A.G. Wedd, *Inorg. Chem.* 1996, *35*, 5902-5911. **2** 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, 1997 submitted for publication.

PT 68

THE CONTINUING SEARCH FOR MODELS OF THE MOLYBDENUM HYDROXYLASES

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School of Chemistry, University of Melbourne, Parkville, Victoria 3052

With the recent publication of the crystal structure of *D. gigas* aldehyde reductase, the search for mimics of the molybdenum active site is an ongoing and crucial component of the full understanding of the molybdenum enzymes. Models of di-oxo molybdenum centres are available but there has been little success in the modelling of molybdenum hydroxylases (e.g. xanthine oxidase), enzymes which incorporate oxo-thio donors (Fig. 1).

Figure 1. Active sites of the molybdenum enzymes possess di-oxo and oxo-thio Mo(VI) centres; (a) sulfite oxidase (X = anion), (b) xanthine oxidase

Recent work has proved useful in the understanding of dithiolene, oxo and thio ligands but the non-trivial task is now to incorporate these units into a faithful model of the active site. Research to date involves the synthesis of ligands containing the dithiolene unit and a steric bulk component. Work stimulated by Holm and co-workers utilises Diels Alder chemistry to build suitable ligands.

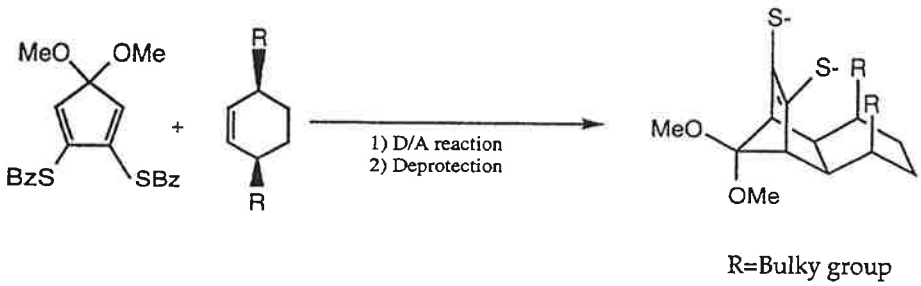

Figure 2. Examples of the synthesis of bulky dithiolene ligands.

An alternative to this approach is via calixarene chemistry. Employing the known thio calix[4]arene molecule will provide two dithiolate binding sites per molecule. The bulk of the calixarene will ensure a steric hindrance to dimerisation.

This poster will discuss the progress to date in utilising both these strategies in generating models of the molybdenum hydroxylases.

PT 69

AN INVESTIGATION INTO THE INTERACTION OF IRON(III) WITH L-DOPA

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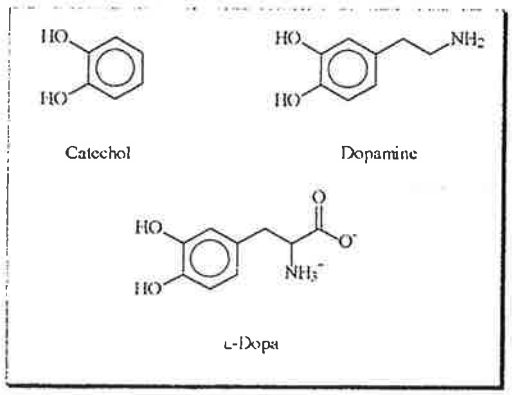
[a] *Department of Chemistry, The University of Queensland, Brisbane, 4072*
[b] *Department of Pharmacy, The University of Queensland, Brisbane, 4072*

L-Dopa is a Dopamine precursor which is used in the clinical treatment of Parkinson's Disease (PD). As many studies have shown that interaction with iron(III) greatly decreases the efficacy of L-Dopa, it is of great interest to gain a deeper understanding of this interaction. Thus, an investigation into the interaction between iron(III) and the ambidentate ligand L-Dopa was undertaken in order to gain an insight into the speciation of aqueous solutions of these components over a range of pH.



The interaction was followed by means of pH titrations monitored spectroscopically. The results of these pH titrations were analysed using the software package Specfit. Modelling of the data allowed the calculation of formation profiles, predicted electronic spectra, and overall formation constants for the system. Speciation data obtained indicated the existence of five different species for iron(III):L-Dopa over the pH range four to eleven. The data obtained for the iron(III):L-Dopa system exhibits a distinct similarity to the results obtained for both iron(III):catechol, and iron(III):dopamine systems under the same experimental conditions.

PT 70

STABILIZATION OF CHLORIDE CONTAINING MONO- AND BI-NUCLEAR COPPER(II) PATELLAMIDE D COMPLEXES BY ACETONITRILE

Joel D. A. Tyndall[a] Rodney M Cusack,[b] Anna L van den Brenk,[b] David P Fairlie,[a] Lawrence R Gahan,[b] and Graeme R. Hanson[c]

[a] 3D Centre, [b] Department of Chemistry and [c] Centre for Magnetic Resonance, The University of Queensland, Brisbane, Australia 4072

Patellamide D ($patH_4$), a cyclic octapeptide isolated from the ascidian *Lissoclinum patella* has a 24-azacrown-8 macrocyclic structure in which there are two oxazoline and two thiazole rings located alternately at each corner of a rectangular ring. In acetonitrile solution (MeCN) electronic absorption, circular dichroism, mass spectrometry and electron paramagnetic resonance spectroscopy reveal the formation of multiple mononuclear copper(II) complexes, such as $[Cu(patH_3)X]^+$ and $[Cu(pat'H_3)X]^+$ (X= Cl^- and MeCN) and the binuclear complex $[Cu_2(patH_2)Cl]^+$. The binuclear complex $[Cu_2(patH_2)Cl]^+$ is only partly converted to a species characterised as $[Cu_2(patH_2)(\mu\text{-}CO_3)]$ on standing. This is in marked contrast to the formation equilibria in methanol where $[Cu_2(patH_2)(\mu\text{-}CO_3)]$ forms immediately with excess base or upon the addition of carbonate.[1] Molecular modelling studies of $[Cu_2(patH_2)Cl]^+$ in which the solvent environment was simulated by varying the dielectric constants from 1 to 19 (MeCN:toluene (50:50)) to 36 (MeCN) suggest that chloride bridges the two Cu(II) ions in the dimer. Whilst there was very little change (within experimental error) to the calculated structures of the complex $[Cu_2(patH_2)Cl]^+$ upon varying the dielectric constant, there was a significant change to the bridging mode of the carbonate anion when the dielectric constant was increased from 1 to that corresponding to methanol (33) for $[Cu_2(patH_2)(\mu\text{-}CO_3)]$. Concomitant with this change in bridging mode was a decrease in the copper...copper distance from 4.43Å [2] to 3.8Å, in agreement with that obtained from the simulation of the EPR spectra of the complex.

1. van den Brenk, A. L., Fairlie, D. P., Gahan, L. R., Hanson, G. R., Hawkins, C. J. & Jones, A. *Inorg. Chem.*, 1994. **33,** 2280.

2. van den Brenk, A., Byriel, K. A., Fairlie, D. P., Gahan, L. R. Hanson, G. R., Hawkins, C. J., Jones, A., Kennard, C. H. L. & Murray, K. S., *Inorg. Chem.*, 1994. **33,** 3549.

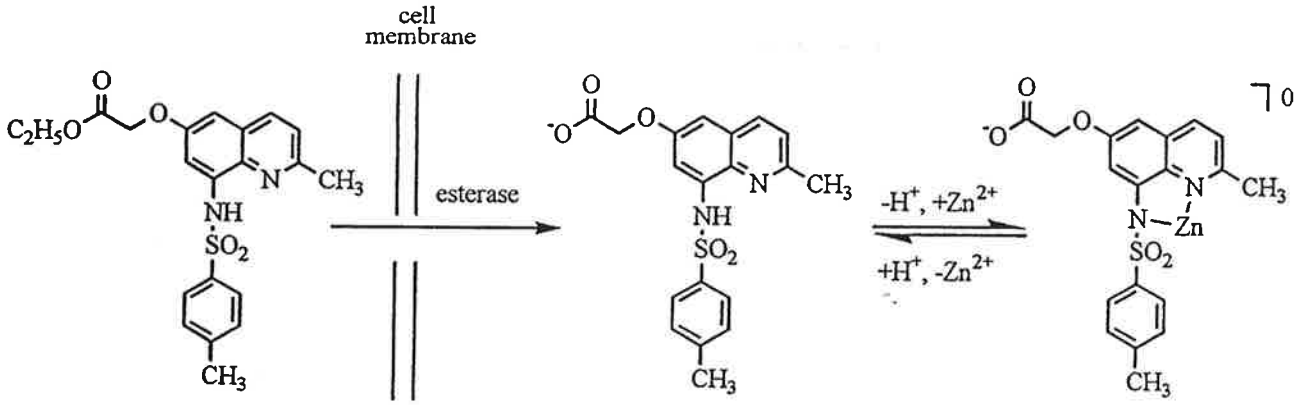
THE EFFECT OF COORDINATION ENVIRONMENT UPON THE FLUORESCENCE OF ZINQUIN

PT 71

K.M. Hendrickson, S.F. Lincoln and A.D. Ward

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

Zinc(II) has an important role in biochemical and nutritional processes, more than 300 enzymes contain Zn(II) as an essential component either for structural purposes or for catalytic activity. Much of this intracellular Zn(II) is strongly complexed, but there are readily exchangeable pools of less strongly bound Zn(II) which are important in a range of processes associated with cell growth. Intracellular Zn(II) which is amenable to ligand substitution (and herein is referred to as available Zn(II)) provides a route for detection through binding ligands which fluoresce upon coordination. The proposed mechanism of action of such a prototype fluorescent ligand, [2-methyl-8-(*p*-toluenesulfonamido-6-quinolyloxy]acetic ester/acid (Zinquin E and A), capable of detecting intracellular Zn(II) down to nanomolar concentration is shown below:[1]



Zinquin E non- fluorescent

Zinquin A anion non- fluorescent

Zn(II) complex strongly fluorescent

The nature of the Zn(II) that Zinquin binds to in the cell is uncertain, but it is probable that some of this available Zn(II) is partially bound by proteins. This has been modelled using various nitrogen and oxygen donor chelates to form ternary complexes of the type Zinquin A-Zn-L (where L = tacn, tacdo, cyclen, cyclam, tren, NTA, TEA). The complexation and spectroscopic properties of these ternary complexes are discussed along with the implications for the use of Zinquin E as an intracellular Zinc(II) probe.

1. K. M. Hendrickson, T. Rodopoulos, P.-A. Pittet, I. Mahadevan, S. F. Lincoln, A. D. Ward, T. Kurucsev, P. A. Duckworth, I. J. Forbes, P. D. Zalewski and W. H. Betts. *J. Chem. Soc., Dalton Trans.*, **1997**, 3879.

PT 72

PROBING THE NATURE OF POLYNUCLEAR THIOLATE COMPLEXES AND THEIR REDOX PRODUCTS

Sally Brooker,*[1] Paul D. Croucher,[1] Tony C. Davidson,[1] Geoffrey S. Dunbar,[1] S. Subramanian,[2] A. McAuley,[2] C.Y. Ralston[3] and S.P. Cramer[3]

[1]*Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand*

[2]*Department of Chemistry, Victoria University, Vancouver, Canada.*

[3]*Department of Applied Science, University of California at Davis, Davis, CA 95616 and Lawrence Berkeley National Laboratory, Energy and Environment Division, Berkeley, CA 94720, U.S.A.*

Research into the synthesis, structure and properties of first row transition metal complexes of thiolate-containing ligands is expected to shed light on the structure and mechanism of action of thiolate-containing metalloproteins such as Fe-S clusters, Ni-Fe hydrogenase and the Cu_A site of cytochrome c oxidase. In addition to acting as model compounds, the properties of the resulting complexes are expected to provide an interesting contrast to those of complexes of the widely used phenol and pyridine "head units" which provide much harder donors.

We have prepared a range of polynucleating ligands from the exciting "head unit" S-(2,6-diformyl-4-methylphenyl)dimethylthiocarbamate.[1] The structures and properties (in particular redox and L-edge studies) of a series of dizinc(II) and di- and tri-nickel complexes of both symmetrical and unsymmetrical Schiff-base ligands derived from this "head unit" will be presented. The thiolate-bridged dinickel complexes are first generation model complexes for the dinuclear Ni-Fe hydrogenase active site (until 1995 the active site was thought to be a mononickel centre so previous model complexes were largely mononuclear). These model complexes exhibit rich and exciting redox chemistry.

References

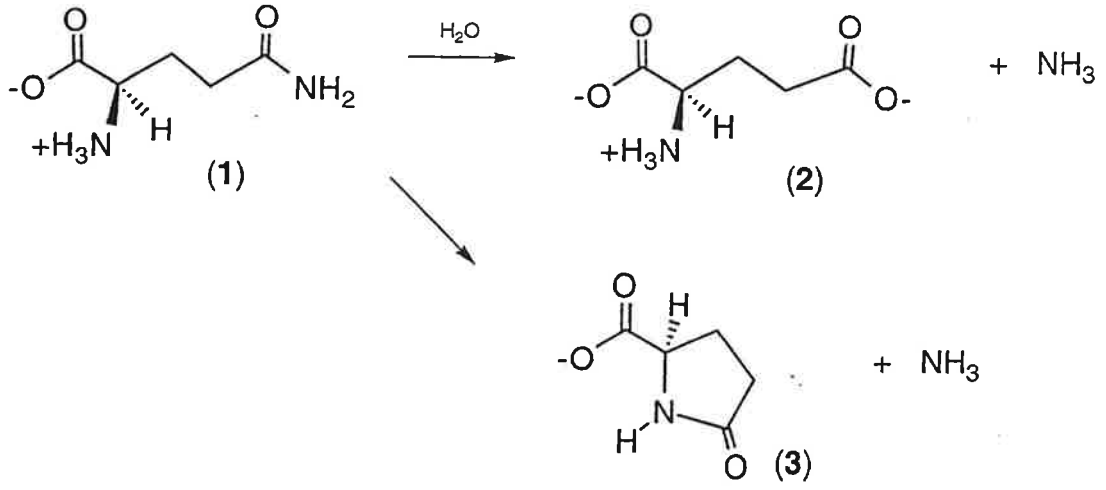
1. S. Brooker and P.D. Croucher, *J. Chem. Soc., Chem. Commun.*, 1993, 1278; *ibid.*., 1995, 1493; *ibid.*, 1995, 2075; *ibid.*, 1997, 459; S. Brooker, P.D. Croucher and F.M. Roxburgh, *J. Chem. Soc., Dalton Trans.*, 1996, 3031; S. Brooker and T.C. Davidson, *Chem. Commun.*, 1997, 2007.

REACTIONS OF GLUTAMINE AND PYROGLUTAMIC ACID COORDINATED TO COBALT(III)

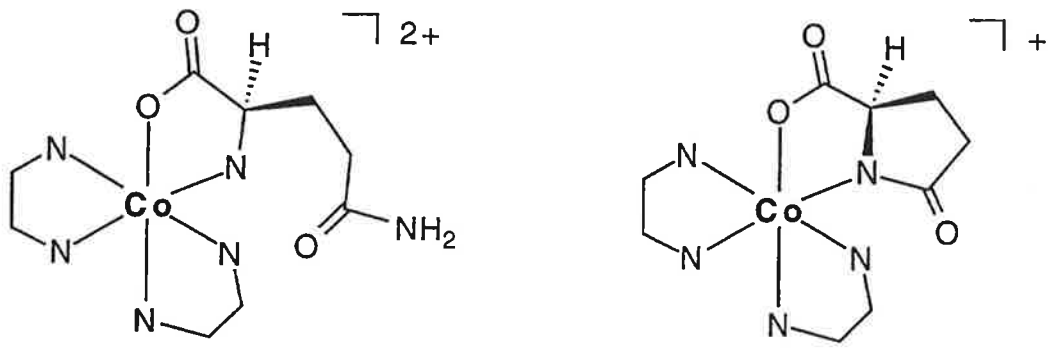
Patricia M. Angus

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

Glutamine (**1**) is a hydrophilic α-amino acid with three functional groups, each capable of bonding to a metal ion. It is abundant in mammalian systems in which it supplies nitrogen needed for purine and pyrimidine nucleotide synthesis and also transports excess ammonia to the liver for disposal. Deamination of free glutamine occurs at the amide group on the side chain and the reaction products may be either ammonia and glutamate ion (**2**) or ammonia and pyroglutamate (2-pyrrolidone-5-carboxylate, **3**):



This study has examined the effects of coordination to cobalt(III) on the reactions of glutamine and pyroglutamic acid. In particular the reactions of the following chelates have been investigated:



PT 74

EFFECT OF ORGANIC GROWTH MODIFIERS ON SYNTHETIC HYDROXYAPATITE (HAP) FORMATION

Rebeca Alvarez, Louise A. Evans and Ross Tassone

School of Chemistry, Materials and Forensic Science, University of Technology, Sydney. N.S.W. 2007, Australia.

In mammalian systems, bone mineralization occurs via deposition of hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) crystals onto an extracellular organic matrix comprising type I collagen and various non-collagenous proteins. Specifically, non-collagenous phosphoproteins containing polycarboxylate sequences are thought to control crystal nucleation and to subsequently modify crystal growth[1].

Apatite biominerals are much less common in invertebrate systems (eg. certain chiton teeth and brachiopod shells), invertebrate mineralized tissues being dominated by calcium carbonate tissues (eg. mollusc shells and coral). However, both apatite and calcium carbonate invertebrate systems may also contain significant amounts of phosphoserine and/or acidic amino acid residues[2,3] together with chitin (a polysaccharide). Chitin is analogous to collagen in vertebrate systems and has gained attention recently because of its biocompatibility and has found application as an artificial skin for burns victims, surgical sutures and as drug delivery carriers[4].

This study investigated the effect of both phosphorylated and acidic amino acid residues, as well as phosphorylated and reconstituted chitin on HAP formation. Poly Na-aspartate was found to have the greatest inhibitory effect. Granular aggregates of HAP could be induced to form directly on phosphorylated chitin surfaces.

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PT 75

CHARACTERIZATION OF THE APATITE BIOMINERAL IN THE RADULAR TEETH OF THE CHITON *Acanthopleura gaimardi*

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Biomineralization in chiton (Mollusca: Polyplacophora) teeth appears to be dominated by iron biominerals - magnetite (Fe_3O_4), lepidocrocite (γ-FeO.OH) and amorphous $FePO_4$[1,2]. However, in certain species, the latter mineral is replaced by an apatite material. In these species, the apatite mineralized anterior region of the tooth also contains parallel bundles of chitin fibres[3]. The resulting biocomposite has the necessary tensile strength and flexibility to withstand the stresses encountered during the feeding process as the animal scrapes crustose coralline algae from rocky substrates.

It is in the early stages of mineralization that the iron biominerals are deposited in the posterior region of the tooth, the anterior region being infilled with apatite only in later stages[4]. Thus, examination of the apatite mineral is difficult because of the presence of large amounts of organic material and the occurrence of the neighbouring iron biominerals.

In the current work, the apatite from an Australian east coast chiton species has been chemically isolated and then characterized and compared to biogenic counterparts using FT-IR spectroscopy, laser Raman spectroscopy and x-ray diffraction analysis.

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"Designing a Specific Host for Binding Nitrate"

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UNSW
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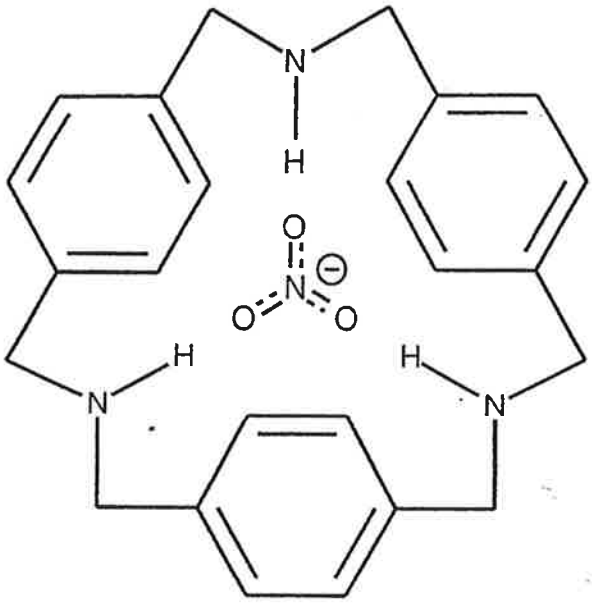
CANBERRA ACT 2600

The design of hosts to bind nitrate based on its charge density, shape and size was posed as an unsolved research problem to a group of second year Chemistry students.

Under guided supervision, a number of possible hosts, starting with simple cyclophanes, were designed by the students using semi-empirical and molecular mechanics modelling. Some triaza[3.3.3.] cyclophanes (including the para form as shown) were identified as possible hosts and were synthesised [1]. ^{15}N NMR showed all hosts had a binding interaction with $^{15}NO_3^-$ in D_2O.



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PT 77

Host-Guest Interactions of Cucurbituril a Molecular Cavity.

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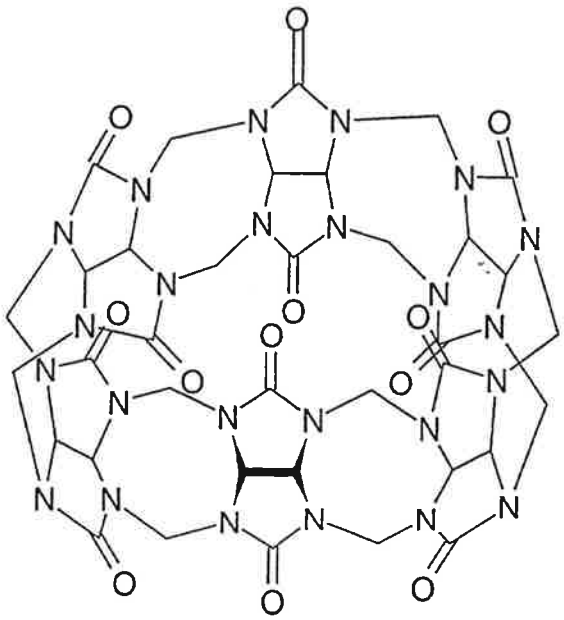
Cucurbituril **1** is a suitable guest for some small molecules and ions[1,2]. The range of guests is limited by the size of the cavity and the solubility of the molecule is limited to a few acidic solvents. Synthetic approaches to new cucurbiturils have been examined and the importance of cesium and ammonium cations as templates in attaining cavities of differing sizes has been studied.

The binding of cesium and some small organic molecules has been examined. Complexes between cesium and synthetic precursors to cucurbiturils will be dicussed and the significances highlighted.



1

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PT 78

INTRAMOLECULAR HYDROPHOBIC BONDING IN CHIRAL COMPLEXES

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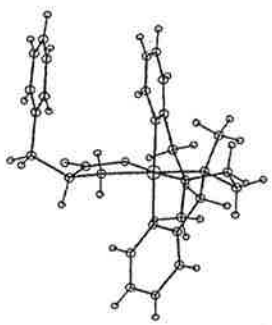
We have been exploring intramolecular hydrophobic bonds between phenyl and pyridyl groups in complexes based on $[Co(picenMe_2)(R^*\text{-phe})]^{2+}$ ($picenMe_2$ = *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-ethylenediamine, phe = phenylalaninato), because of their relationship to a class of molecules capable of binding to DNA. Previously, such interactions were reported for Λ-α-$[Co(S,S\text{-picchxnMe}_2)(S\text{-phe})]^{2+}$ [1] ($picchxnMe_2$ = *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-1*R**,2*R**-diaminocyclohexane), and have been found in the Δ-α-*RRS*-phe analogue, $picpnMe_2$ complexes (picpnMe2 = *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-1,2*R**-diaminopropane) and *R**-trpytophanato congeners [2]. The hydrophobic bond manifested in the solid state as shown in the single-crystal X-ray structure, persists in solution and is disrupted only by solvents such as pyridine, which interacts with the molecule in a different way to other solvents.

Reaction of Δ,Λ-$[Co(picenMe_2)Cl_2]^+$ with *S*-pheH, followed by treatment of the orange solution mixture with $NaClO_4$ yields crystals of Δ-α-$[Co(picenMe_2)(S\text{-phe})](ClO_4)_2$ as the least soluble diastereoisomer, thus affording *inter alia*, a resolution of the cobalt centre. A perspective drawing of the complex cation is shown below. In the solid state the phenyl group is bonded to one of the pyridyl residues, as is found in similar species. Energetics of the systems have been investigated and are reported along with an assessment of the likely mode of binding of the various complexes to DNA.



Δ-α-$[Co(picenMe_2)(S\text{-phe})]^{2+}$

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PT 79

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

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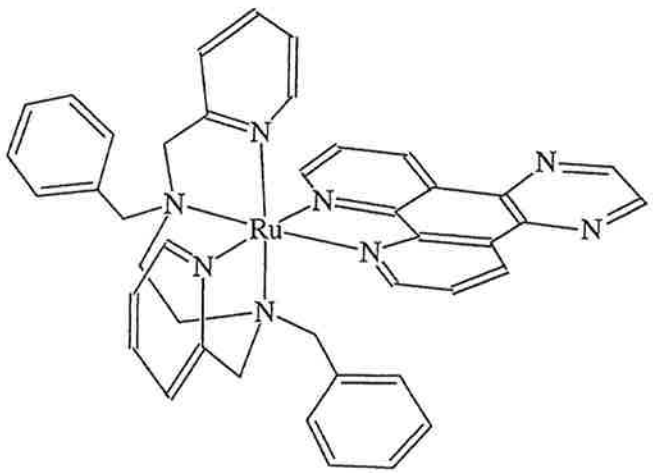
Strong intermolecular interactions between π systems have been known for over half a century, and play a fundamental role in diverse molecular recognition phenomena of importance to the fields of biology and molecular engineering.

The main aim of this research project is to study the propensity for π-stacking of ternary metal complexes which contain a flat aromatic chromophore as a molecular fragment. As an example the concentration-dependence of the NMR spectra for one of these complexes, β-[Ru(picenBz$_2$)(dpq)]Cl$_2$ (illustrated) where *picenBz*$_2$ is the tetradentate ligand 1,6-di(2'-pyridyl)-2,5-dibenzyl-2,5-diazahexane and *dpq* is the bidentate ligand dipyrido[3,2-d:2'3'-f]quinoxaline, has been studied in D_2O solutions. Marked changes in the positions of the aromatic proton chemical shifts are observed as the concentration of the species is varied. These changes are thought to be caused by intermolecular association between the metal complexes due to a π-stacking interaction between the bidentate portion of each complex ion, which leads to the formation of dimers and molecular aggregates in solution. The results of this study will be reported. An investigation, using visible hypochromism, of the ability of this complex to intercalate into calf thymus DNA will also be reported.



β-[Ru(picenBz$_2$)(dpq)]Cl$_2$

PT 80

CONTROLLING THE STEREOCHEMISTRY OF OLIGONUCLEAR COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II) WITH A TRIS-CHELATING BRIDGING LIGAND

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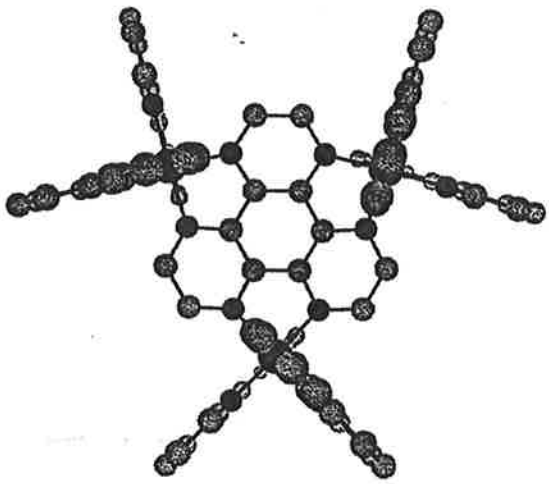
Considerable research has focused on polypyridyl complexes of ruthenium and osmium, and their application to photochemical molecular devices (PMD's)[1] and as biochemical probes by virtue of DNA intercalation.[2] In many of these studies, the implications of stereochemistry in the complexes - both mononuclear and polynuclear - has received limited attention.

This study examines the isolation and characterisation of the stereoisomers of the homo- and hetero-nuclear complexes $[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$ and $[\{Ru(pp)_2\}_2\{Os(pp)_2\}(\mu\text{-HAT})]^{6+}$ respectively {where pp = 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy)} and the homonuclear heteroleptic complex $[\{Ru(Me_2bpy)_2\}\{Ru(phen)_2\}\{Ru(bpy)_2\}(\mu\text{-HAT})]^{6+}$ (where Me_2bpy = 4,4'-dimethyl-2,2'-bipyridine, and HAT is the tris-chelating bridging ligand 1,4,5,8,9,12-hexaazatriphenylene).

The stereoisomers of the above complexes {*eg. homo-chiral* (Δ^3/Λ^3)- and *hetero-chiral* ($\Delta^2\Lambda/\Lambda^2\Delta$)-$\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$} were obtained by a combination of stereoselective syntheses utilising chirally predetermined building blocks and a cation-exchange chromatographic technique. The diastereoisomeric forms of each species were characterised by electrochemistry and NMR spectroscopy, and the enantiomers characterised by circular dichroism studies.

$\Lambda^2\Delta/\underline{\Delta}^2\underline{\Lambda}$-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$



$\underline{\Delta}^3/\Lambda^3$-$[\{Ru(bpy)_2\}_3\{\mu\text{-HAT})]^{6+}$

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PT 81

SEPARATION OF THE GEOMETRIC ISOMERS OF A DINUCLEAR POLYPYRIDYL COMPLEX OF RUTHENIUM

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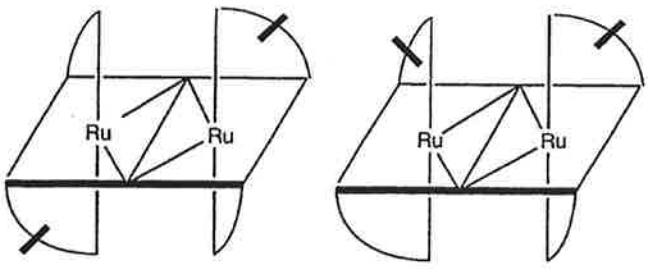
Tris(bidentate) complexes of octahedral metal centres have an inherent chirality or "handedness", denoted as Δ or Λ. If one of these ligands is used as part of a bridging ligand, then the resulting dinuclear species may have three distinct stereoisomers (e.g. ΔΔ , ΛΛ and the ΔΛ/ΛΔ forms) - if the terminal ligands are identical.

Previous studies within our group have led to the separation and characterisation of the diastereoisomers (i.e. ΔΔ/ΛΛ and ΔΛ/ΛΔ) of such dinuclear ruthenium complexes.[1]

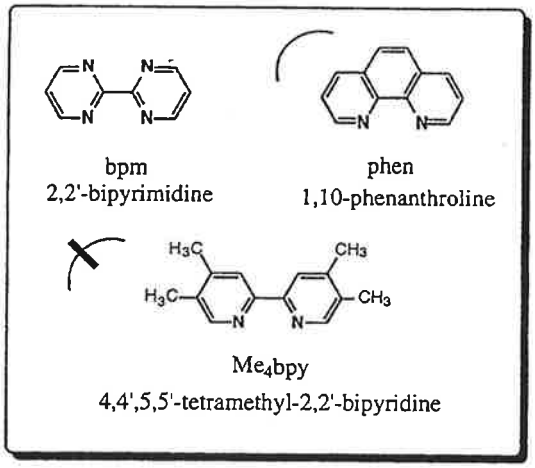
In cases where the terminal ligands are not identical, there will be additional stereoisomers, in the form of geometric isomers. This aspect of ligand-bridged dinuclear complexes has been overlooked until this point.

We have successfully separated and characterised the diastereoisomers and the geometric isomers of the complex, $[Ru(phen)(Me_4bpy)]_2(\mu\text{-bpm})]^{4+}$ (as shown below in one of its *meso* diastereoisomeric form)



trans *cis*

meso {ΛΔ (≡ ΔΛ)}



This paper will address the synthesis, stereochemistry and characterisation of the stereoisomers of this system.

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PT 82

SYNTHESIS OF d^6 METAL COMPLEXES VIA THE CYCLOADDITION OF PRE-FORMED MONONUCLEAR BUILDING BLOCKS

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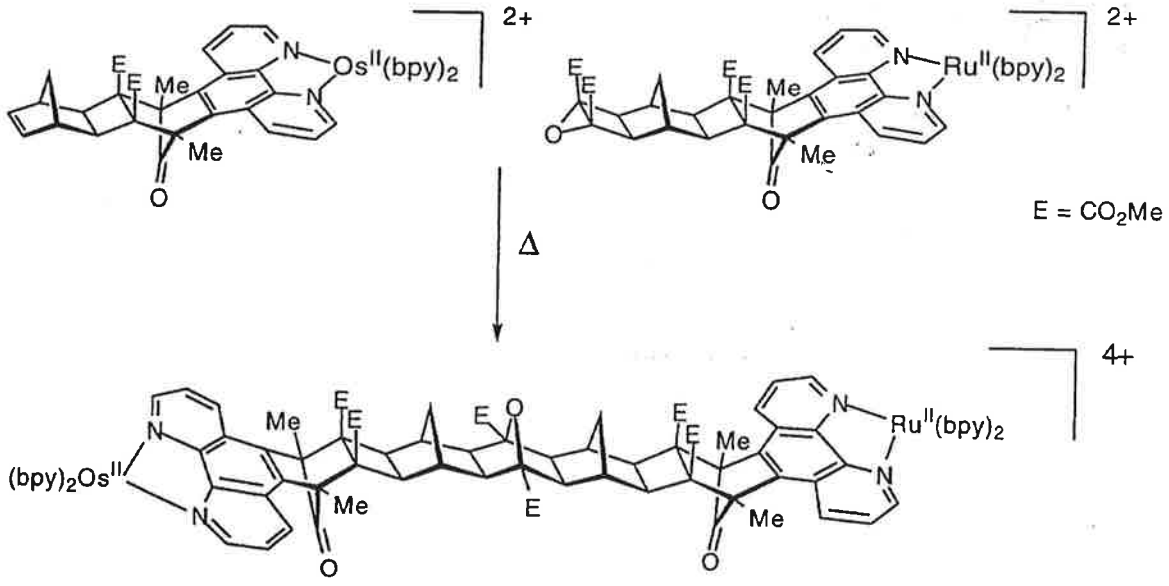
Austin C. Schultz and Ronald N. Warrener

Centre for Molecular Architecture
Central Queensland University,
Rockhampton, Queensland 4702

We have previously utilised norbornane-linked bis(1,10-phenanthroline)-type ligands in the synthesis of homodinuclear complexes containing ruthenium(II), osmium(II) and platinum(II) centres. Similar scaffold-like structures have also been used in the design of chromophore-quencher type complexes.

Initial attempts to synthesize heterodinuclear species using "molrac" ligands were unsuccessful because it was not practicable to prepare the required mononuclear precursor complexes . We now report a convergent method of complex design, whereby pre-formed mononuclear building blocks are stereospecifically linked to give the desired dinuclear mixed-metal product.



By using this cycloaddition protocol, an electron donor/acceptor functionality may also be attached to a metal complex.

PT 83

THE IMPORTANCE OF SECOND-SPHERE ANION INTERACTIONS IN THE SEPARATION OF STEREOISOMERS OF LIGAND-BRIDGED DIRUTHENIUM(II) COMPLEXES

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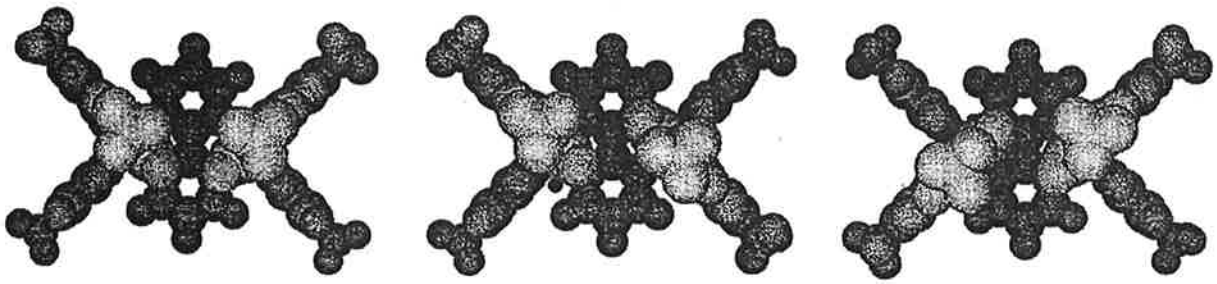
The study of polymetallic molecular assemblies is a rapidly expanding field of chemistry[1] in such divergent areas as artificial photosynthesis and DNA intercalation. However, the possible stereoisomeric complexities of such species have surprisingly been overlooked. To address this problem we have been investigating the isolation of individual diastereoisomers and enantiomeric pairs of oligonuclear polypyridyl complexes of ruthenium(II) using cation exchange chromatography.[2] We have became aware that there is a significant interaction between the complex and the counter anion, as well as with the ion-exchange support itself. From a classical coordination chemistry perspective, anions have usually been regarded as being isolated from the complex unless they are occupying a formal coordination site upon the metal. This generally is the case with the typical counter anions such as hexafluorophosphate or halide; however using simple organic anions we have observed a high degree of second-sphere association.



Meso Λ–Δ (≡ Δ–Λ) **Λ–Λ** **Racemic pair** **Δ–Δ**

Diastereoisomers of $[(Me_2bpy)_2Ru\text{-}bpm\text{-}Ru(Me_2bpy)_2]^{4+}$

NMR experiments reveal a surprisingly high binding affinity for both aromatic and aliphatic carboxylates with polypyridyl complexes of ruthenium(II) in aqueous solution. These results correlate with the behaviour of these species on the cation exchange support, demonstrated by the isolation of all the possible stereoisomers of $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-bpm})]^{4+}$ (Me_2bpy = 4,4'-dimethyl-2,2'-bipyridine, bpm: 2,2'-bipyrimidine). A mechanism will be postulated to predict the best anion, and eluent concentration, to facilitate efficient stereochemical (including chiral) separation of these polymetallic species.

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PT 84

PROTONATION STUDIES OF REDUCED AND EXCITED STATES IN RUTHENIUM(II) COMPLEXES

Peter A. Anderson,[a] Robert F. Anderson,[b] Masaoki Furue,[c] Morton Z. Hoffman,[d] F. Richard Keene[a] and Brett D. Yeomans[a]

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[b] *Department of Chemistry, University of Auckland University, Auckland, New Zealand.*

[c] *Department of Environmental Systems Engineering, Kochi University of Technology, Tosayamada-cho, Kochi 782, Japan.*

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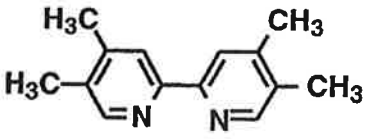
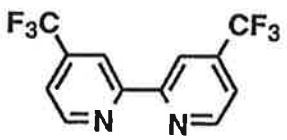
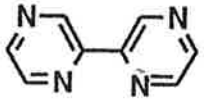
Ruthenium(II) complexes containing polypyridyl ligands have been widely studied as potential photosensitisers in solar energy conversion. Ligands having non-coordinating nitrogen atoms in the ring system (e.g. bpz or dpp) are capable of protonation, and the acid/base behaviour will differ between the ground state, excited state or one-electron ligand-reduced species: such characteristics will provide information relevant to understanding physical properties of complexes.[1-3] Tuning of these properties can be achieved through the incorporation of non-participating ligands with substantially different substituents, such as Me_4bpy and $(CF_3)_2$bpy. In particular, $(CF_3)_2$bpy is considered to be a strongly electron-withdrawing ligand possessing a low ligand π^* energy level.



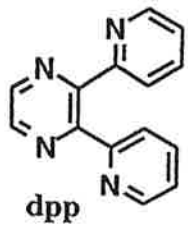
Me_4bpy
4,4',5,5'-tetramethyl-2,2'-bipyridine



$(CF_3)_2$bpy
4,4'-bis(trifluoromethyl) -2,2'bipyridine



bpz
2,2'-bipyrazine



dpp
2,3-bis(2-pyridyl)pyrazine

Using pulse radiolysis techniques, the one-electron reduced forms of several polypyridyl complexes of ruthenium(II) have been generated in aqueous solution. The visible absorption spectra of the fully protonated, $[RuL_2(L'H)]^{\bullet 2+}$, and non-protonated, $[RuL_2L']^{\bullet +}$, forms can be calculated from changes in absorbance associated with their reduction. By using a range of solutions at different pH, pK_a values for the reduced $[RuL_2(L'H)]^{\bullet 2+}$ species have been determined by monitoring absorbance changes at specific wavelengths.

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PT 85

DETERMINATION OF REVERSIBLE REDOX POTENTIALS OF HIGHLY SURFACE ACTIVE POLYPYRIDINE RUTHENIUM THIOCYANATO COMPLEXES

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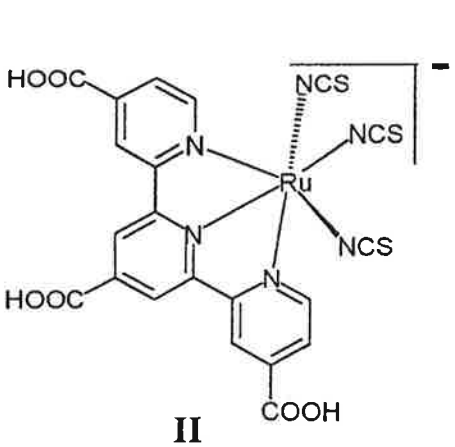
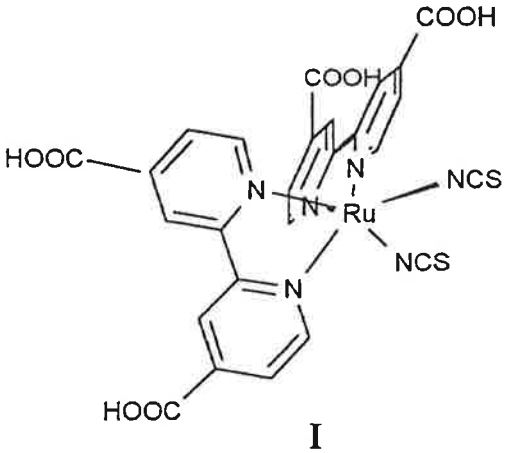
In recent years polypyridine ruthenium compounds have gained much attention as very powerful sensitizers in photo electrochemical cells of the Grätzel type. We investigated the solution electrochemistry of cis-diisothiocyanato-bis-(2,2'-bipyridine-4,4'-dicarboxylate)-ruthenium(II)[1] **(I)**, the most successful sensitizer for these types of cells known so far, and the new triisothiocyanato-2,2':6',2"-terpyridine-4,4',4"-tricarboxylate-ruthenium(II)[2] **(II)**.

Cyclic voltammograms of **I** and **II** showed no fully reversible oxidation or reduction processes. They were masked and governed by adsorption and precipitation processes on all electrode materials (Pt, Au, GC) and in all solvents (acetone, DMF, acetonitrile) investigated. The oxidations for **I** and **II**, each one electron processes, were governed by reactant and product adsorption. Rotating disk electrode (RDE) and ultramicrodisk electrode (UMDE) measurements proved to be the most valuable methods to measure the true redox potentials of the oxidations. Reduction of ruthenium bipyridine compounds are generally bipyridine based. Upon reduction of **I** in acetone and acetonitrile, a polymer that could be mechanically separated, was formed. Consecutive cyclic voltammetric scans to sufficiently negative potentials with high scan rates stripped off the polymer and made two (one for **II**) one electron reduction processes accessible. Due to precipitation of the polymer onto the electrode, RDE and UMDE could not be used for measuring the reduction processes.



II



I

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PT 86

CAGE COMPLEXES AS SOLAR ENERGY CONVERSION SYSTEMS.

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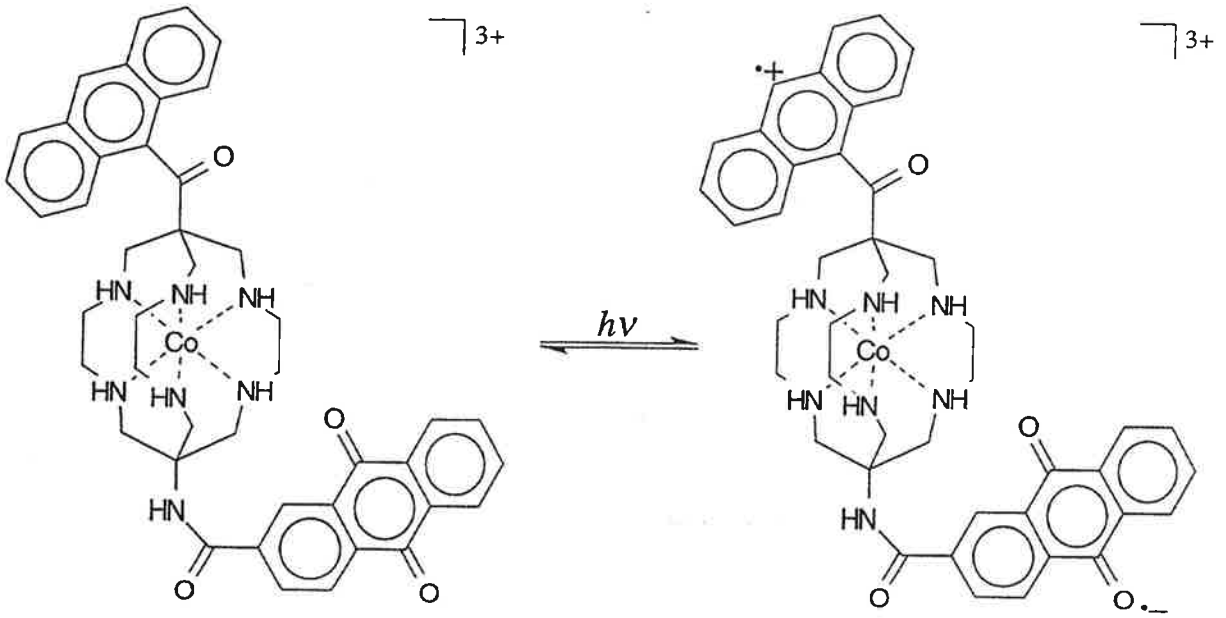
A. H. W. Mau
CSIRO Division of Molecular Science, Clayton Victoria.

Systems that capture solar energy and use it in chemical processes are of obvious importance. We are currently exploring a compound which may eventually help catalyse the reaction:

$$H_2O + h\nu \rightarrow H_2 + {}^1/_2\, O_2$$

The compound consists of a photoactive electron donor, separated from an electron acceptor by a spacer group. Metal cages are ideally suited for use as the spacer group as they undergo reversible electron transfer reactions, are extraordinarily stable and are useful in solubilising the aromatic components in water. Initially, we have used anthracene as the photoactive electron donor and anthraquinone as the electron acceptor to generate the following system:



The synthesis of this compound and related analogues will be presented along with some preliminary photo-electrochemical results, such as the lifetime of the diradical species.

PT 87

TERNARY COMPLEXES OF 6^A-(3-AMINOETHYLAMINO)-6^A-DEOXY-β-CYCLODEXTRIN

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Natural and modified cyclodextrins exist in single enantiomeric forms and, when acting as host molecules, may preferentially complex one enantiomer of a chiral guest to produce two diastereomeric host-guest complexes of differing thermodynamic stability.[1] The degree of enantioselectivity varies with the nature of the cyclodextrin and the guests. When aromatic molecules are the guest, the aromatic moiety enters the cavity of the cyclodextrin and interacts with the hydroxyl or polar groups of the cyclodextrin with differing intensities. Thus, (R)- & (S)-guests experience different geometric and electrostatic interactions, which may lead to differing stabilities in the two diastereomeric host-guest complexes.

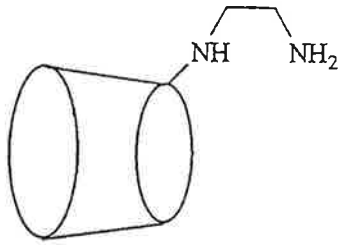

Fig 1. 6^A-(3-aminoethylamino)-6-deoxy-β-cyclodextrin (βCDen)

In this study the enantioselectivity of a modified cyclodextrin and the corresponding ternary metallocyclodextrins using (R)- & (S)- tryptophan was determined. To do this, a pH titration study was carried out using 6^A-(3-aminoethylamino)-6^A-deoxy-β-cyclodextrin (βCDen)(Fig 1) to form the metallocyclodextrins, $[M(\beta CDen)]^{2+}$, where M = Zn^{2+}, Co^{2+}, Cu^{2+} & Ni^{2+}. The ternary complexes were formed using the above metallocyclodextrins and the (R)- & (S)- tryptophan anion to form $[M(\beta CDen)(R)\text{-}Trp]^+$ & $[M(\beta CDen)(S)\text{-}Trp]^+$. The stability constants of these metallocyclodextrins and ternary complexes will be discussed in the poster presentation.

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PT 88

ALKYNYLRUTHENIUM DENDRIMERS

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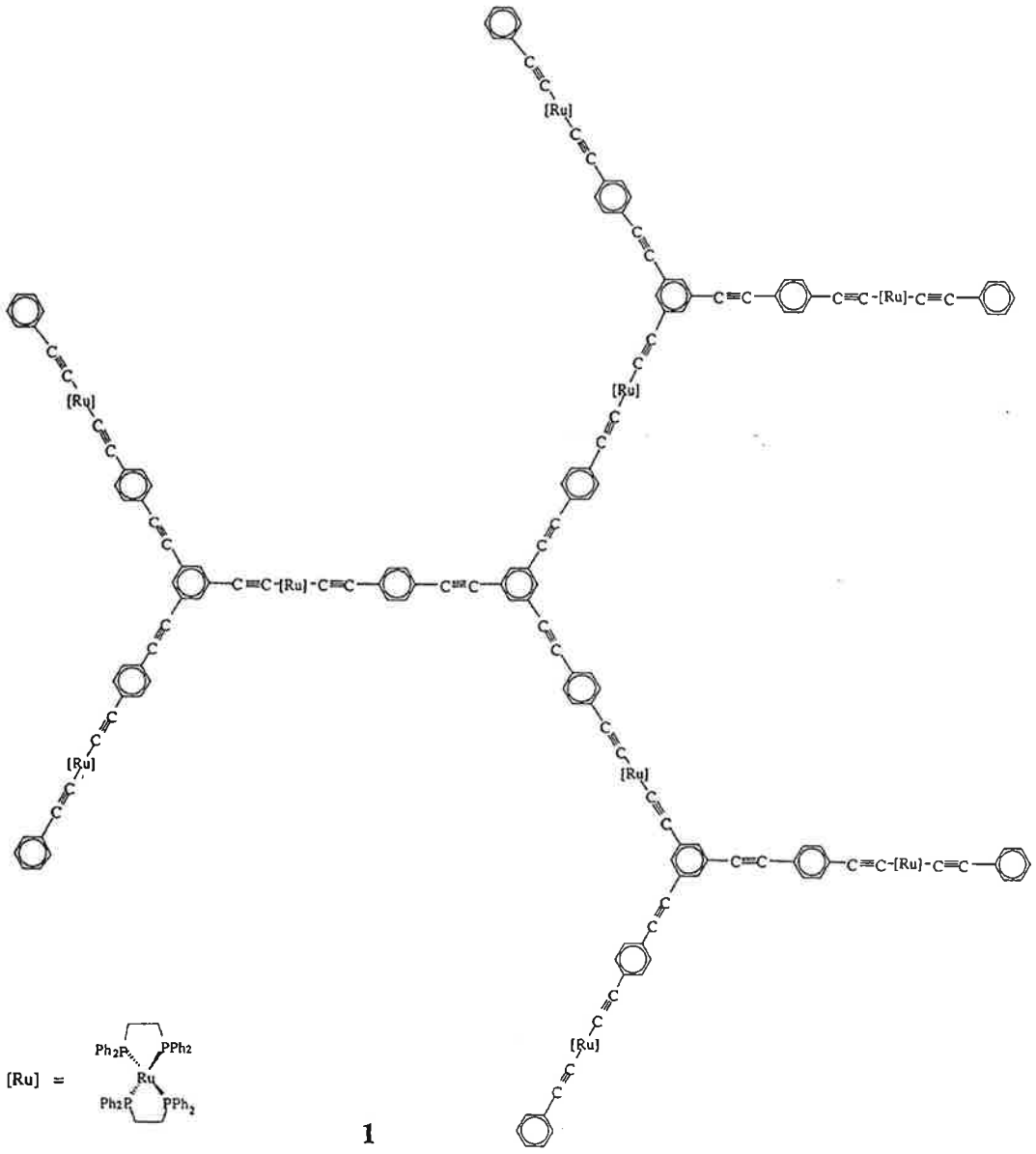
Dendrimers have attracted a great deal of interest recently.[1] Organometallic dendrimers may contain multiple coordination sites or multi-electron transfer redox centres and have potential for a range of applications (e.g. as novel catalysts in molecular electronic and photochemical devices for information storage and switching, and as energy transfer and conversion devices). However, few examples of organometallic dendrimers with the metal centres in each layer (rather than just at the periphery) have been reported. We have recently established a program to construct alkynylmetal dendrimers based on bis(diphosphine)ruthenium and 1,3,5-triethynylbenzene building blocks, and incorporating ethynylarene "spacers". Results from studies thus far, including the synthesis and characterization of **1**, will be presented.



1

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PT 89

THE SYNTHESIS AND APPLICATION OF METALLOPORPHYRINS AS ANION SENSORS

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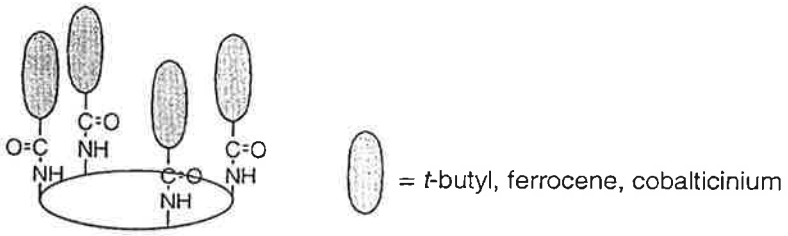
The development of compounds which act as anion sensors have attracted considerable research interest. This interest is mainly attributed to the significant biological role played by various anions. Anions maybe recognised by either a metal centre directly binding the anion[1], or amide protons hydrogen bond the anionic guest species[2]. The strategy employed in this work combines these two mechanisms of action, utilising a porphyrin with both a metal binding site and amide groups in a geometrically favourable position.

This paper discusses synthesis, characterisation and testing of a number of elaborated free-base and metalloporphyrins as potential anion sensors. Lead compounds in this series are based on the Collman picket fence porphyrin[3], with picket groups including ferrocene, cobalticinium and pyridine.



These free-base porphyrins have been metallated with a range of first row transition metals, M= Mn^{III}, Co^{III}, Cu^{II}, Zn^{II}, Fe^{III}, fig. 1. The testing of PVC membranes containing these metalloporphyrins for a potentiometric response to anions showed only positive responses for the manganese (III) complexes.

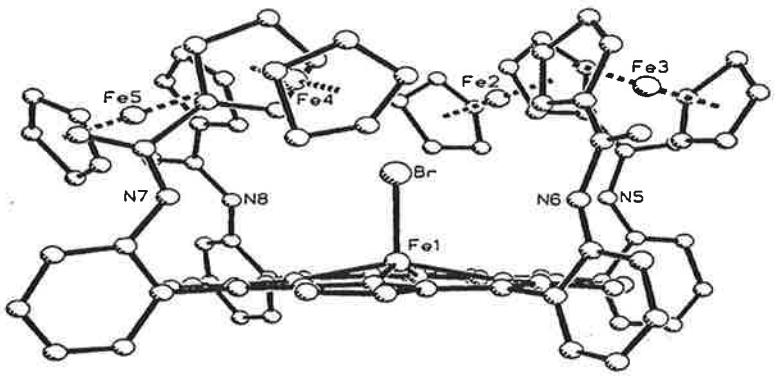


Figure 1. ORTEP of meso-tetra (α^4-*o*-ferrocenylamidophenyl) porphyrinato Iron (III) bromide

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PT 90

DENSITY FUNCTIONAL STUDIES OF IRON PORPHYRIN HYDROCARBON INTERACTIONS.

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It has been observed that iron porphyrins unencumbered by axial ligands can interact with aliphatic and aromatic hydrocarbons[1,2]. The iron(III) complex of 5,10,15,20 tetraphenyl porphyrin when crystallised with a weakly coordinating anion in aromatic solvents gives structures with a molecule of the aromatic solvent in close proximity to the mean plane of the porphyrin (2.9Å) and the central iron atom (2.94Å)[1].
In contrast we have recently isolated an iron(II) porphyrin heptane complex in iron(II) double A-frame porphyrin[2]. The weak complex is stabilised by inclusion of the heptane molecule within a molecular cavity formed by the elaborated porphyrin. The terminal methyl group of the heptane binds to the iron(II) atom (Fe-C 2.5-2.8Å).

We report here density functional calculations[3] of the structure and energetics of these two systems. In the first case fully optimised molecular structures have been calculated for the isolated Fe(porphine) cation (intermediate spin S=3/2) and complexes with benzene, toluene and p-xylene. The aromatic ring is aligned with the most electron rich part of the molecule centred over the iron(III) atom.
In the second case density functional calculations of the molecular structures of the methane, ethane, propane and butane complexes of iron(II) porphine have been performed. The position of the H atom in the Fe..H-C bond (undetected in the x-ray structure) is calculated to be 2.0-2.13Å) from the Fe atom with a further H atom at (2.62-2.65Å). This leads to an asymmetric bidentate structure for the Fe-alkane complex.

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PT 91

CONTROLLING THE STRUCTURE OF SUPRAMOLECULAR PORPHYRIN ARRAYS.

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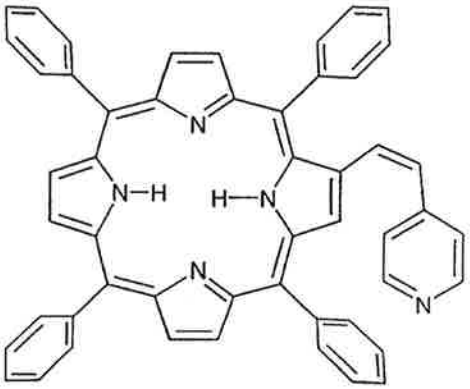
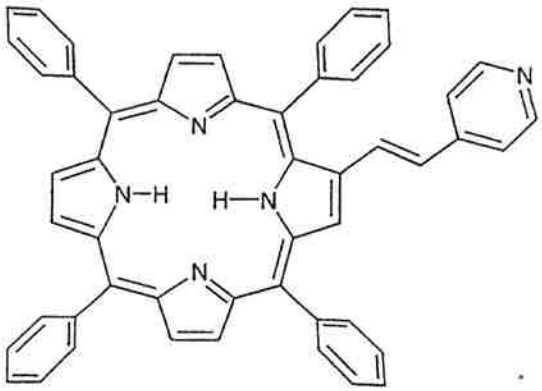
The alkene linkage in compounds **1a** and **1b** allows us to exert a control over the supramolecular structure of their derivatives. This is achieved by either beginning with the appropriate *cis* or *trans* alkene as in traditional supramolecular chemistry or more significantly by converting the alkene, in the supramolecular complex, from *trans* to *cis* (or vice versa) and effectively switching from one supramolecular array to another. The synthesis of porphyrin arrays based upon these ligands will be presented.



1b



1a

PT 92

PORPHYRINS LINKED TO PLATINUM(II) COMPLEXES - THE BUILDING BLOCKS

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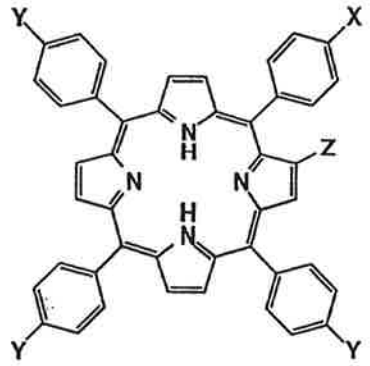
Cancer is a disease which is now Australia's leading cause of death. Development of new ways of treating cancer centres on the manipulation of components that deliver a drug specifically to cancer cells. The majority of these complexes use classic intercalators tethered to a chemically reactive platinum functionality. There have been many reports on the use of porphyrins in cancer therapy as reagents in photodynamic therapy. The demonstrated localisation property of porphyrins was an incentive for using porphyrins as carrier ligands. Our efforts have focussed on linking porphyrins to various platinum derivatives.

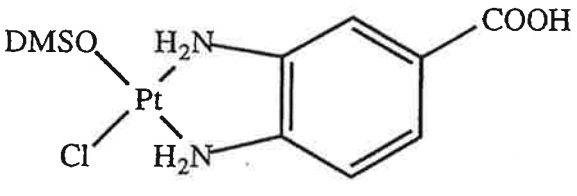
A series of amino porphyrins have been investigated with the amine group attached to either a phenyl ring ($X=NH_2$, $Y=H,SO_3^-$, $Z=H$) or the porphyrin backbone ($X,Y=H,Z=NH_2$) of tetraphenylporphyrin (TPP).

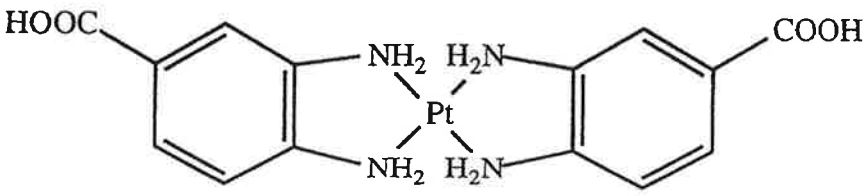


$X=H,NH_2$, $Y=H,SO_3^-$, $Z=H,NH_2$

A number of these have also been used in preliminary tests of their cytotoxicity with the human tumour cell lines HL-60 and U-937.

The platinum complexes contain a variety of ligands including aspartic acid, serine, lysine and diaminobenzoic acid. These have generally been coordinated through the diamine functionalities, leaving the carboxylic acid moiety for linking to the porphyrins. For example, the adjacent complexes have been formed in the reaction with diaminobenzoic acid:





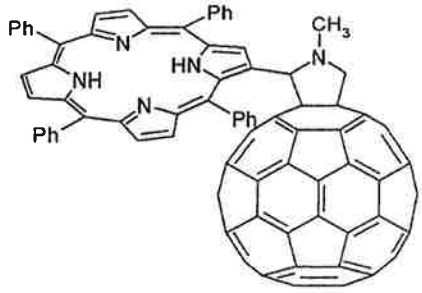
PT 93

SYNTHESIS AND STRUCTURES OF FULLERENE-PORPHYRIN CONJUGATES AND COCRYSTALLATES

Peter D. W. Boyd, Penelope J. Brothers, Anthony K. Burrell*, Leila Chaker, Michael C. Hodgson, David Officer* and Clifton E. F. Rickard

Department of Chemistry, The University of Auckland, Auckland, New Zealand and
* *Department of Chemistry, Massey University, Palmerston North, New Zealand.*

We have recently reported the synthesis, the ground state perturbation of the porphyrin electronic spectrum by C_{60} substituent, redox potentials and photoinduced electron transfer for a porphyrin C_{60} dyad, **1**.[1,2,3]



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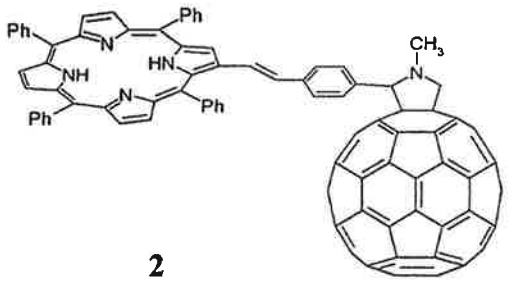
The X-ray crystal structure of **1** shows an interesting intermolecular packing relationship between the C_{60} and the porphyrin. There are close intermolecular contacts (2.78Å) between the inner 16-atom core of the porphyrin and the fullerene. These are short in comparison to contacts in structures such as graphite (3.35Å), porphyrin-porphyrin (>3.2Å), to the separations of C_{60} from arene rings(3.0-3.5Å) and ball to ball separations (>3.2Å).

In this work we report:
(a) X-ray structures of materials obtained by cocrystallisation of C_{60} with the porphyrin molecules 5,10,15,20 tetraphenylporphyrin or 5,10,15,20 tetra(0-pivalamidophenyl)porphyrin. These show similar close contacts between the porphyrin core and the "electron rich" carbon atoms involved in the 6-6 ring junction of the fullerene. This mode of interaction is in contrast to reported arene-C_{60} interactions.
(b) The synthesis, structures, electrochemical and electronic spectral properties of new fullerene-porphyrin dyads such as **2** and **3**.



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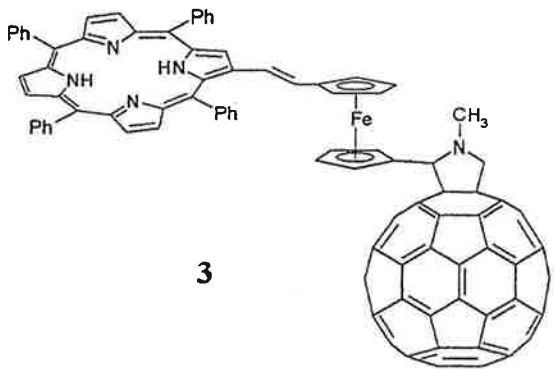

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PT 24

SUPRAMOLECULAR COMPLEXATION OF FULLERENES

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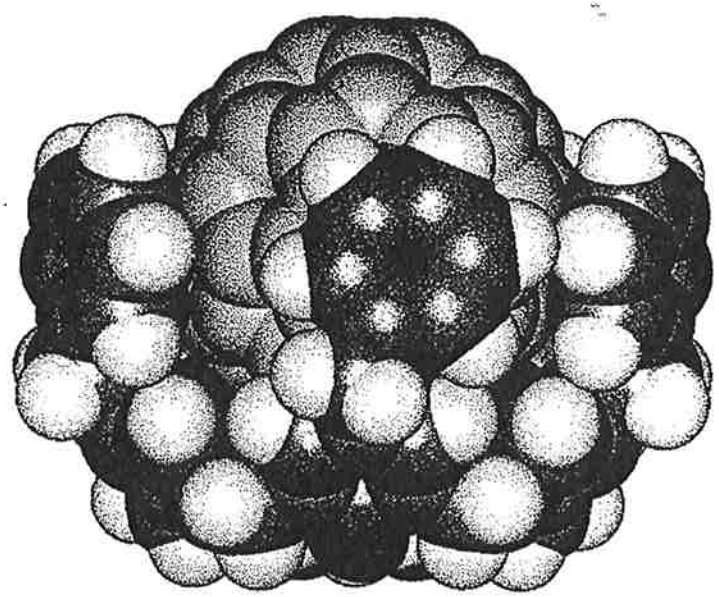
An ongoing part of our research has been the supramolecular complexation of globular molecules. Recent work in our group with functionalised calix[n]arenes and other host molecules has led to the formation of supramolecular complexes of C_{60} and C_{70}. In the solid state, p-benzylcalix[5]arene forms a 2:1 complex with C_{60} however, solution studies indicate that a 1:1 species predominates. p-Benzylcalix[7]arene, although planar, forms guest-host complexes with C_{60} and has a particularly high affinity for C_{70} which has been exploited to isolate pure C_{70} from fullerite, a crude mixture of fullerenes. A summary of recent results will be presented.



PT 95

COORDINATION CHEMISTRY AT THE METAL / POLYMER INTERFACE

Aeron Coombes, Jeffrey K. Crass and Anthony T. Baker
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The enhancement of the adhesion of platinum metal to polyethylene terephthalate (PET) film and fibre surfaces has been achieved through chemical modification of the substrate surface. Reaction of PET with multifunctional amines (eg trien) has been carried out with varying conditions of reaction (temperature, time, etc). The presence of the free amine groups at the polymer surface has been demonstrated by attenuated total reflectance FTIR spectroscopy. Assays have also been developed to determine the extent of functionalisation.

The degree of functionalisation of the polymer surface can be increased by longer reaction times. There is a trade-off between increasing the density of free amine sites at the surface and degradation of the bulk polymer. In general aminolysis is found to cause less polymer degradation than ester hydrolysis using sodium hydroxide solutions. It has been found that the integrity of the polymer substrate can be further improved by annealing prior to treatment with amines.

The aminated samples have been coated with platinum by electroless plating. Enhanced adhesion was observed, with the samples treated with tetraethylenepentamine giving the best results.

INTELLIGENT POLYMERS FOR METAL ION SEPARATION

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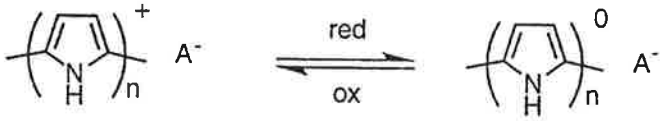
Conducting electroactive polymers (CEPs) are a group of compounds whose physical and chemical properties can be modified by altering the identity of anionic dopant molecules that are incorporated into the polymer during growth. One of the most important properties of CEPs is their ability to reversibly undergo reduction and then oxidation in response to an applied electrical signal, as illustrated below for polypyrrole.



Immediately after preparation the CEP is electrically neutral. After reduction of the polymer backbone the CEP becomes negatively charged overall if the dopant anion is retained in its structure. In this state cations present in solution can be incorporated into the polymer. Subsequent oxidation of the CEP will return it to its original neutral charged state and result in expulsion of any incorporated cations. In this way it is possible for CEPs to function as electrochemically controllable cation exchange resins or membranes which selectively transport cations.

This paper presents results of investigations into the synthesis, characterisation and metal ion transport properties of two CEPs. The first of these is polypyrrole, containing polyvinylphosphate as the dopant anion. The second is polyaniline, synthesised with a hexasulfonated calixarene as the dopant.

PT 97

A Debye-Hückel Theory for Metal Ion Binding to Biomolecules

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The site-site Ornstein-Zernike equation is used together with a simple Debye-Huckel type closure for ion correlations to derive a theory for metal ion binding to large biomolecules immersed in electrolyte solutions. Shifts in the binding constant as a function of electrolyte concentration and site mutation are calculated for the protein calbindin and shown to compare extremely well with experiment. As well, the theory is able to reasonably accurately predict shifts in pKa values for various acidic sites. The theory can be easily applied to large biomolecules as well as to smaller complexes.

PT 98

Triorganostannyl Cations — NMR, ESMS and *ab initio* Computational Studies

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The speciation of triorganostannyl trifluoromethanesulfonates, $R_3Sn(trif)$, in solution was probed using electrospray mass spectrometry (ESMS) and ^{119}Sn NMR spectroscopy. NMR experiments imply the existance of extensive ion pairing in solution. Positive ion ESMS indicates that triorganostannyl cations are transferred from solution into the gas phase, both as simple R_3Sn^+ cations and as solvated species $R_3Sn(solv)_n^+$.

Lewis base adduction studies indicate that $R_3Sn(trif)$ are only slightly more Lewis acidic than the corresponding chlorides R_3SnCl whereas *ab initio* calculations (for the gas phase) demonstrate that the three coordinate trigonal planar R_3Sn cation is substantially more Lewis acidic than four-coordinate R_3SnCl. This apparent discrepancy arises from the incomplete dissociation of $R_3Sn(trif)$ in solution.

ESMS shows intramolecular H atom transfer to tin occurs from some R groups at moderate to high cone voltages. Hydrogen atom transfer is accompanied by alkene elimination. Study of a number of R groups indicates that H atom transfer has steric requirements, and this process has also been studied by *ab initio* calculations.

PT 99

Generation of Optically Active Polyanilines Using the Novel Chiral Reagent Iron (III) (+)-camphorsulphonate

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University of Wollongong, Wollongong, NSW 2525

We have recently described[1] the first preparation of optically active polyanilines. The emeraldine salts PAn.(+)-HCSA and PAn.(-)-HCSA (HCSA = camphorsulphonic acid) were obtained via either (i) the electrochemical polymerisation of aniline in the presence of (+)- or (-)-HCSA, or (ii) the doping of EB with (+)- or (-)-HCSA.

We now wish to report an alternate route to optically active polyanilines using the novel reagent iron (III)-(+)-camphorsulphonate. This salt was synthesised using a method similar to that used previously[2] to synthesise iron (III)-p-toluenesulphonate, namely refluxing iron (III) hydroxide with a 25% deficiency of (+)-camphorsulphonic acid in methanol for 24 hours, filtering and evaporating the methanol filtrate.

The chemical oxisation of aniline (0.75 mol dm^{-3}) with an aqueous solution of Fe{(+)-CSA}3 (2.75 mol dm^{-3}) at room temperature for 24 hr gave a dark green precipitate of PAn.(+)-HCSA. It was readily soluble in a range of organic solvents (NMP, DMSO, $CHCl_3$), exhibiting a two strong circular dichroism bands in the visible region at 405 and 460 nm in DMSO. The iron (III)-(+)-camphorsulphonate therefore carries out two roles in the above synthesis, namely oxidative polymerisation of aniline and the induction of optical activity into the polyaniline chain.

Metal salts such as $FeCl_3$, $Zn(ClO_4)_2$ and LiCl have been shown[3] to behave in a similar fashion to acids by "psuedo-doping" EB to give a metal-doped polyaniline. We have found that EB is also readily "doped" by the chiral Fe{(+)-CSA}3 salt in a range of organic solvents, as evidenced by the appearence of an intense localised polaron band at ca. 870 nm. The metal-doped polyaniline emeraldine salt was found to be optically active, with similar chiroptical properties to the previously reported[1] PAn.(+)-HCSA.

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STRUCTURES OF PALLADIUM ACETATE

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The 'structure' of palladium(II) acetate is well-known to be trimeric, with bridging acetate ligands around a triangle of square-planar palladium atoms. Several crystal structures have been reported, with different lattice solvent molecules of crystallisation.

Yet solution nmr spectra are not consistent with the maintenance of this structure. Instead of the single peak expected for the symmetric trimeric structure, multiple peaks are observed in both the ^{1}H and ^{13}C spectra. Furthermore, different commercial batches of palladium acetate have very different infrared spectra and reportedly have different catalytic activities.

We have prepared yet another crystal modification of palladium acetate $[Pd_3(OAc)_6]\cdot CH_2Cl_2$, which again contains the expected trimeric structure as determined by single crystal X-ray diffraction. The infrared spectrum of this solid showed two strong acetate C-O bands at 1432 and 1608 $cm^{(1}$. Some commercial samples which had additional adsorption bands in this region could be purified to yield the same simple spectrum.

The solution nmr spectra of this pure material in chloroform, dichloromethane, acetone and benzene all gave multiple peaks, inconsistent with the maintenance of the trimeric structure in solution. Only in deuteroacetic acid is a single peak observed.

The temperature dependence of the ^{1}H nmr spectrum in benzene gave no evidence of the trimer-monomer equilibrium reported by Wilkinson based on ebulloscopic measurements. An estimate of the magnitude of the effect expected in boiling benzene suggests that it would be within the experimental error and that this often-quoted equilibrium probably does not exist.

STUDIES ON COBALT CARBOXYLATES

J.K. Beattie, C.U. Beck, J.A. Klepetko, A.F. Masters and P. Turner
School of Chemistry, F11, The University of Sydney, NSW, 2006

Cobalt carboxylates are amongst the most widely used homogeneous catalysts in industry, however, the constitution of the deceptively simply named "cobalt acetate" is still not definitively established. We report here synthetic and physiochemical studies on a range of dimeric, trimeric, tetrameric and octameric derivates produced from preparations and reactions of cobalt acetate.

COMPLEXES OF THE PENTAPHENYLCYCLOPENTADIENYL AND RELATED LIGANDS

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Bulky cyclopentadienyl ligands have the potential to confer unusual steric, electronic and reactivity properties on their metal complexes. The pentaarylcyclopentadientyl ligands are particularly sterically demanding. We report here the synthesis and physiochemical studies on a range of transition metal derivatives of these ligands.

PT 103

THE SYNTHESIS OF CARBOXYMETHYLATED CAGE AMINES.

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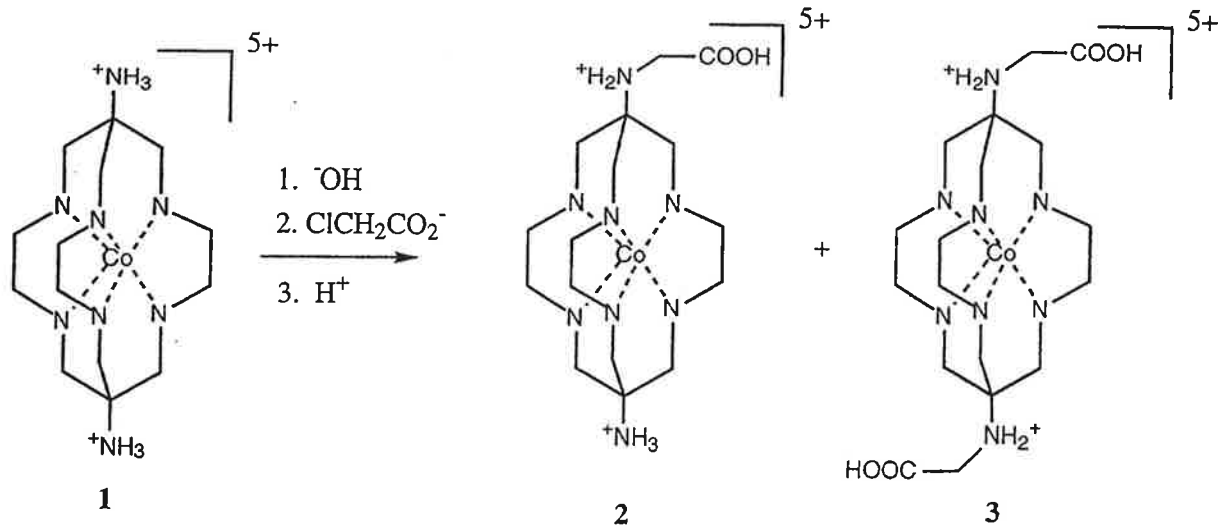
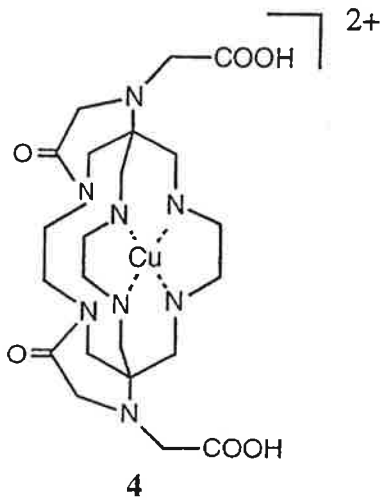
The metal complexes of functionalised polyamine cages are of interest due to their many potential applications as in radiopharmaceuticals and relaxivity agents. Alkylation reactions involving chloroacetic acid as the alkylating reagent have led to the synthesis and characterisation of several carboxymethylated derivatives of the bicyclic octamine ligand, "diaminosarcophagine (1)". Metal ion coordination has been used to protect the secondary nitrogen centres of the ligand and allow selective alkylation of the primary amines. The cobalt complex of the ligand has been used to synthesise the mono (2) and dicarboxymethylated (3) ligands.



1 2 3

Alkylation of copper diaminosarcophagine allows the synthesis of the tetracarboxymethylated ligand which following treatment in acid forms the lactamised derivative of the ligand (4).



4

The reaction of the free diaminosarcophagine ligand with alkylating agents will also be discussed.

Inorganic Chemistry Division
IC'98 Conference

Wollongong, New South Wales, Australia
1-5 February 1998

Oral Contributions:

SYMPOSIUM ON CHEMICAL SAFETY & EDUCATION

THE INDUSTRIAL PERSPECTIVE ON OCCUPATIONAL HEALTH, SAFETY AND THE ENVIRONMENT

Graeme A.L. Paul
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The principles of Occupational health, Safety and the Environment, OHS & E, are well understood by Industry and are promoted using the principles of Responsible Care and other supportive means.

This valuable and ethical promotion has the benefits of creating cost savings for Industry in many ways, some direct and other more subtle indirect ways.

In this modern age we also are faced with the communications and technology revolution, this means that the previously uniformed community is now receiving a plethora of information and misinformation with the result that minor issues can be blown up out of all proportion. The net result is that in the 1990's, in response to community influence we are being swamped with "improvements" in safety and environmental legislation, legislation at all levels of government.

We stand knee-deep in acts, regulations, codes of practice, regulatory guidelines, fines and penalties some of which are draconian in their nature. As a conservative estimate business is staggering under a dead weight of paper work from some 60,000 regulations that have come into force over the past three decades. Small Business and Consumer Affairs Minister Geoff Prosser spoke on this subject at a conference on June 12, 1996 which was convened to cut the burden of unnecessary regulations faced by small business.

Of all these regulations, the SH & E Acts and Regulations are broad and key Regulations in our society which have the reverse of the normal presumption of innocence, that is in the event of an incident the onus is not on the prosecution to prove guilt but it is a requirement of our defence to prove innocence. The defence against a prosecution usually reduces to being able to prove a due diligence was exercised to prevent the incident occurring.

Until June this year the most critical Acts in force in OHS & E have been the Clean Air Act, the Clean Waters Act, the Noise Abatement Act, the Occupational Health and Safety Act and Regulations and the Environmental Offences and Penalties Act.

Detailed discussion on changes to the legislative framework and penalties that have been brought into operation since June 1997 will be presented.

SY 2

E H & S ISSUES FOR UNIVERSITIES: EDUCATION AND COMPLIANCE

David Lloyd-Jones
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Legislative changes in O H & S have had a major impact on Australian universities, particularly chemistry departments because of their handling of dangerous goods. Compliance with Acts and Regulations has become an imperative and is a major force in shaping the O H & S policies for universities. The means by which UTS is dealing with the issue of compliance will be discussed.

Universities also have a responsibility to educate. UTS has long had a formal 'chemical safety' subject and this has been upgraded recently. Some of the features of this course include discussion of laboratory safety, hazardous goods legislation and on-line access to ChemWatch for MSDSs. Staff at UTS have been involved in surveying chemical safety education in Australia and these findings will be reported.

LEARNING CHEMISTRY THROUGH VISUALISATION OF THE MOLECULAR LEVEL SY 3

Roy Tasker
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A deep understanding of chemistry involves being able to link what one *sees* substances doing in the laboratory, to what one *imagines* is happening within these substances at the invisible molecular/ionic level. Only then can these ideas be *communicated* meaningfully using abstract symbolism (eg. chemical formulas), terminology and mathematics.

Due to a shortage of high quality resources that portray the molecular level most chemistry teaching occurs at the laboratory and symbolic levels, in the hope that mental models of the molecular world will 'develop naturally'. Students are therefore left to develop these models from the static, often oversimplified two-dimensional diagrams in textbooks, or static, often confusing ball and stick models, or from their own imagination. However, there is convincing evidence[1] that most student difficulties and misconceptions in chemistry stem from inadequate or inaccurate molecular models.

In the VisChem project a team of chemical educators is producing multimedia resources to explicitly link these three levels - the *molecular*, *laboratory*, and *symbolic* - and conducting action research in how and what students can learn from such resources. The most novel resources have been a series of 3D animations which portray substances in the solid, liquid, and gaseous states; during phase changes (eg. melting); and when they react together, at the level of molecules, atoms and ions. The animations are designed to correct specific misconceptions in chemistry identified from educational research.

Visualising the invisible molecular world to generate mental models requires imagination. For example, the speed of atomic and molecular movements, and the uncertain (non-Newtonian) nature of electrons in atoms, require substantial 'artistic license' to enable the structure and collisions at this level to be represented. For this reason students need to be constantly reminded that these animations are only 'models' of reality. Great care has been taken in the representation of molecular structures and processes because research by Ben-Zvi[2] and others has indicated that misconceptions can be generated easily, and perpetuated, with poorly drawn images.

In this presentation I will show:

- a number of multi-particle *VisChem* animations portraying solvation of ions, successive complexation, and oxidation/reduction
- a few examples of seriously flawed animations, available on CD supplements to leading textbooks, to illustrate aspects of the abuse of the medium
- some examples of multi-representation *VisChem* QTVR animations that link symbolic textbook representations of molecular structures to their 3D configurations

[1] Lijnse PL, Licht P, Waarlo AJ and de Vos W (Eds.) (1990) *Relating Macroscopic Phenomena to Microscopic Particles*. Proceedings of Conference at Utrecht Centre for Science and Mathematics Education, University of Utrecht, and references therein.

[2] Ben-Zvi, R, Eylon, B and Silberstein, J. (1988). Theories, Principles and Laws. *Education in Chemistry* May, 89-92; Ben-Zvi, R, Eylon, B and Silberstein, J. (1987). Students Visualisation of a Chemical Reaction. *Education in Chemistry* July, 117-120.

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