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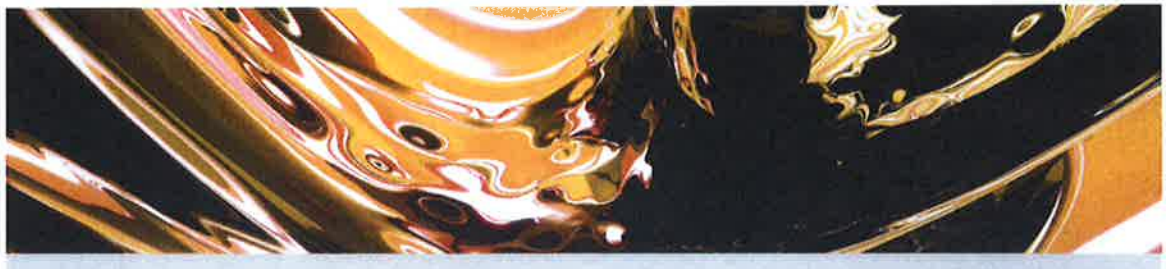
Program Book

ICCC39

PART 3



Poster Session 1
Abstracts 201 – 300

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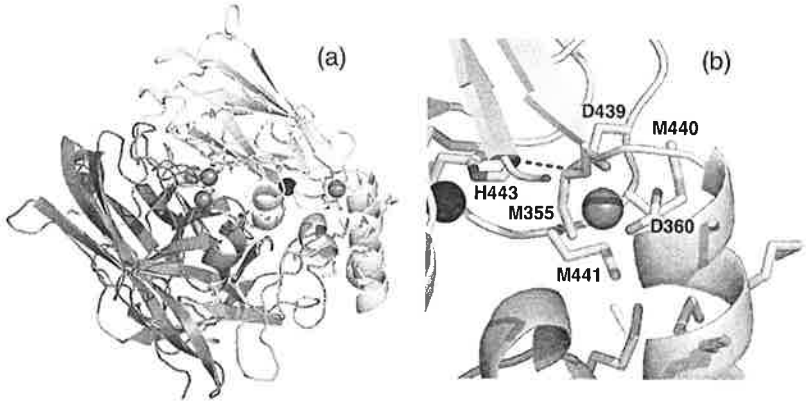
How does Biology Cope with Copper? It is Toxic but Essential.

Z. Xiao and A. G. Wedd
School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Parkville, Victoria 3010, Australia

Copper is an essential trace element required by all organisms. There are more than fifty known redox enzymes and hundreds more predicted from sequenced genomes. However, when uncontrolled, it is toxic as it can promote radical formation (Fenton chemistry) and replace native metals in proteins (Irving-Williams series). Specific pathways exist for its transport within cells. Disruption of these pathways is now linked to tuberculosis, certain cancers and neuro-degenerative diseases (Alzheimer, motor neurone, mad cow, etc).

Bacteria protect themselves from toxic copper in their environments by expressing resistance defenses, similar to antibiotic or drug resistance. The structure and reactivity of the molecules responsible for this resistance will be discussed. They comprise:-
(a) copper chaperone molecules (soluble ion transport);
(b) multi-copper oxidase enzymes (which couple oxidation of toxic cuprous copper to the safe four-electron reduction of dioxygen to water: see Figure);
(c) membrane-bound pumps (ion transport between compartments).

The molecular pathways responsible for uptake of nutrient copper and elimination of excess copper will be reviewed, including the diseases ensuing from faulty copper metabolism.



Acknowledgements: The Australian Research Council is thanked for support.

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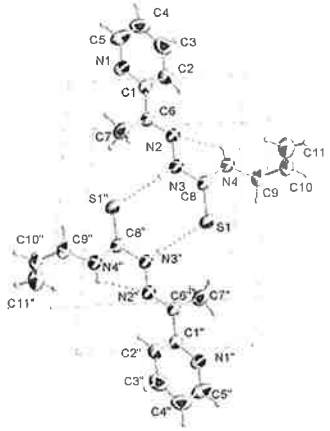
Novel and Biologically Relevant Complexes of Bismuth(III) with Aroylhydrazones and Thiosemicarbazones: Syntheses and Physicochemical Features

F. A. Al-Mjeni[1], M. A. Al-Azzani[1], M. S. Shongwe[1], E. Sinn[2], C. S. Schmiesing[2]
1. *Department of Chemistry, College of Science, Sultan Qaboos University, PO Box 36, Al-Khod 123, Muscat, Sultanate of Oman. E-mail: falmjeni@squ.edu.om*
2. *Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008-5413, USA*

Crystallographically elucidated bismuth(III) complexes of polydentate aroylhydrazones and thiosemicarbazones are few and far between.[1-3] Such main-group Schiff-base complexes invariably exhibit unusual and unpredictable geometries at the metal centres on account of the inert-pair effect coupled with the coordination versatility of the ligands due to their tendency to undergo tautomerisation. Aroylhydrazones and thiosemicarbazones are of considerable interest in iron-chelation therapy. However, they have also been demonstrated to exhibit pharmacological activity which is enhanced on complexation with bioactive metal ions. This work is driven primarily by the realisation that bismuth complexes of aroylhydrazones and thiosemicarbazones have a huge potential to display antimicrobial and antitumor activities.

This work presents selected aroylhydrazones and thiosemicarbazones along with their corresponding bismuth(III) complexes. Metal-assisted transformations of the ligands and formation of novel complexes are demonstrated crystallographically. The coordination behaviours of these Schiff-base ligands towards bismuth(III) are compared and contrasted with those towards iron. It is interesting to note that reaction conditions as well as stoichiometric ratios of the reactants are crucial factors in the formation of the complexes. Selected physicochemical properties of the ligands and the bismuth(III) complexes are discussed.



A pyridyl thiosemicarbazone

Acknowledgements: Sultan Qaboos University (Grant No. IG/SCI/CHEM/07/04) is gratefully acknowledged for financial support.

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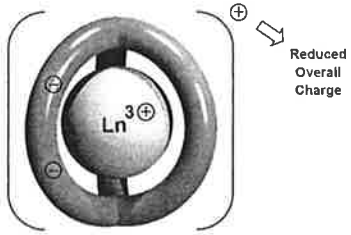
Synthesis of New Anionic Cryptands for Lanthanoid Complexation

N. Alzakhem[1], M. Seitz[1]
1. *Ruhr-University Bochum, NRW, Germany, email: nicola.alzakhem@rub.de*

Since Lehn's discovery[1] that cryptands based on bipyridines and related ligands are excellent candidates for the development of luminescent bioprobes with a number of rare earth elements, the corresponding lanthanoid cryptates have found widespread use in basic scientific research, as well as in commercial luminescent labels for various biomedical assays. Despite the many very attractive properties, especially the very high kinetic stability of the lanthanoid complexes, the unmitigated charge of +3 at the metal center is often problematic and facilitates the binding of water molecules, which are detrimental for the luminescence efficiency, or causes unspecific binding in biological systems.

We have developed new cryptands which have negativly charged chelating units within the backbone of the macrobicyclic framework. The synthesis and the luminescence properties of the cryptands and the lanthanoid cryptates will be presented.



Acknowledgements: We would like to acknowledge the German Research Foundation (DFG) and Fonds der Chemischen Industrie (FCI) for financial support.

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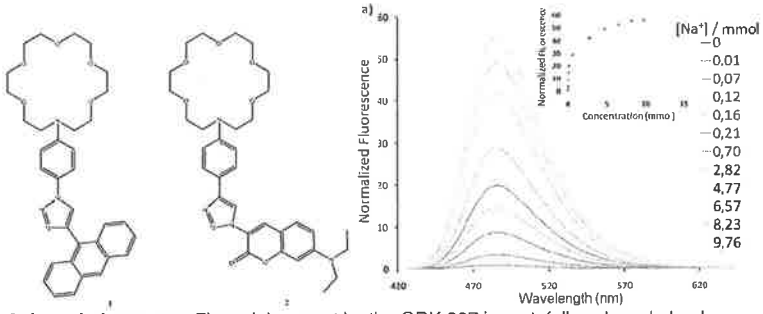
Unusually high cation-induced fluorescence enhancement of PCT-fluoroionophores with a 1,2,3-triazole as conjugative π-linker between fluorophore and ionophore[1]

S. Ast, H. Müller, H.-J. Holdt
University of Potsdam, Karl-Liebknecht Str. 24-25; Haus 26, 14476 Golm, Germany
sandra.ast@gmail.com

Recently fluoroionophores for Zn^{2+}[2], Ni^{2+}[3], Cu^{2+}[4], Hg^{2+}[5], and Ag^{+}[5] were generated by [3+2] cycloaddition of azido and alkinyl-functionalized fluorophores and ionophores. In these fluoroionophores the 1,2,3-triazolyls serve in addition to the conventional function as covalent linkers as both, chelating ligands to the metal ions and electronic transmitters of a coordination event to the fluorophore.[2a] The fluoroionophores feature either an electronic conjugation or deconjugation between the 1,2,3-triazole unit and the fluorophore. However and in all cases the 1,2,3-triazol and the receptor are connected by a deconjugated linker.
Recently Diederich et al. showed in a systematic investigation the role of the 1,2,3-triazoles as active π-linkers in Charge Transfer chromophores.[6] Such push-pull chromophores are only weakly or even non fluorescent.[7]
We found that simple click-generated fluoroionophores in which the fluorophore (electron acceptor) and the ionophore (electron donor) are conjugated by a 1,2,3-triazoldiyl unit work as PCT-fluoroionophores. Due to an efficient PCT these fluoroionophores are only weakly fluorescent in acetonitrile (Φ=0.005-0.007) and water (Φ=0.007-0.01). Upon coordination of a metal ion to the receptor the fluorescence quenching mechanism of the PCT is interrupted, thus increasing the fluorescence impressively.
The first examples of these new PCT-fluoroionophores are the dyes **1** and **2**. In acetonitrile the presence of sodium and potassium leads to a significant fluorescence enhancement of **1** (FE_{Na+}=36, FE_{K+}=14). An extraordinarily high fluorescence enhancement could be determined for **2** (FE_{Na+}=55, FE_{K+}=27) as it is illustrated in **Fig. a)**.
In water **1** and **2** showed a significant fluorescence enhancement solely for potassium.



Acknowledgements: Financial support by the GRK 387 is gratefully acknowledged.

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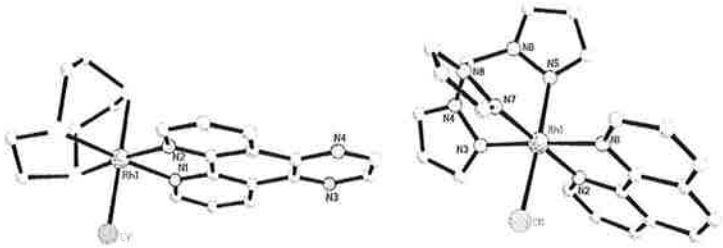
Biological interactions of cell-selective cytotoxic and apoptosis-inducing rhodium(III) compounds with facial tridentate coligands

R. Bieda, W. S. Sheldrick
Ruhr University of Bochum, Faculty of Chemistry and Biochemistry, Department of Analytical Chemistry, 44780 Bochum, Germany. E-mail: Ruth.Bieda@rub.de

Structure-activity relationships related to DNA interactions and cytotoxicity have been established for various rhodium compounds of the type of $[RhCl(pp)(L^3)]^{2+}$ (pp = bpy, bpm, phen, tap, dpq, dppz) containing tridentate ligands (L^3) = tpm or [9]aneS$_3$.[1,2] Transition metal complexes containing larger polypyridyl ligands (pp) are well known for their intercalation into DNA. We have now extended these studies to cover rhodium(III) complexes containing either bidentate amine or thioether ligands or monodentate ligands. Our investigations indicate that the presence of a polypyridyl ligand is not a prerequisite for high cytotoxicity but that bidentate chelate ligands may be necessary. Dichlorido complexes are much less active than monochlorido complexes.

Figure 1: cancer cell

Interactions of the cytotoxic polypyridyl complexes with DNA were investigated by CD and UV/Vis spectroscopy and by gel electrophoresis. 2D NOESY experiments were performed for the larger polypyridyl [9]aneS$_3$ compounds with oligonucleotides and indicate sequence selective intercalation. Covalent peptide interactions were also established by ESI-MS. IC_{50} values toward the cancer cells MCF-7 and HT-29 as well as toward the human embryonic kidney cells HEK-293 were determined using the crystal violet assay. Apoptosis measurements were performed for BJAB lymphoma cells and healthy leukocyte cells which established a high degree of cell selectivity for specific complexes of the type $[RhCl(pp)([9]aneS_3)]^{2+}$.



a) b)

Figure 2: Crystal structure of a) $[RhCl(dpq)([9]aneS_3)]^{2+}$ and b) $[RhCl(phen)(tpm)]^{2+}$

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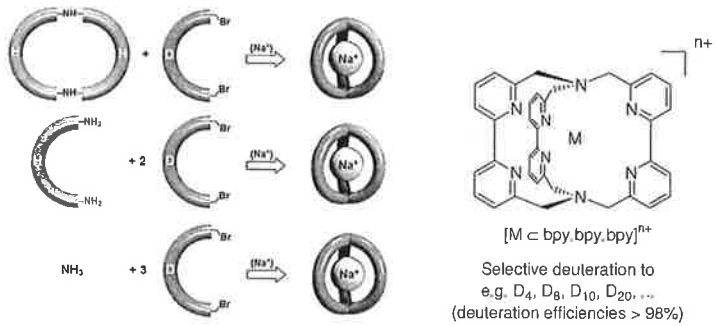
Selective Deuteration of Lanthanoid Bipyridine Cryptates

C. Bischof[1], J. Wahsner[1], J. Scholten[1], S. Trosien[1], M. Seitz[1]
1. *Ruhr-University Bochum, NRW, Germany, email: caroline.bischof@rub.de*

Lanthanoid cryptates based on bipyridines are efficient sensitizers for lanthanoid luminescence. The best-known example is Lehn's cryptate [bpy.bpy.bpy][1] that can act as antenna not only for the visible light emitters Sm, Eu, Tb and Dy, but also for the lanthanoids Nd and Yb which show luminescence in the near-infrared spectral region. The latter lanthanoids, due to the small energy gap between their emitting states and the corresponding ground state levels, are prone to quenching by C-H oscillators.[2] This problem can be ameliorated by the replacement of hydrogen by deuterium atoms, which show much less quenching ability. In our effort to develop more efficient near-IR emitting lanthanoid probes, we have developed practical deuteration protocols in order to selectively remove interfering C-H moieties. Our modular approach provides almost complete synthetic control over the location and the extent of deuteration and allows for the efficient incorporation of deuterium using relatively cheap deuterium sources with routinely >98% isotopic purity within the replaced group. With our procedure, it is also possible to completely perdeuterate Lehn's cryptand with only one additional step compared to the regular synthesis.



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Synthesis, Characterization and Antiproliferative Acitvity of $[Os^{IV}Cl_5(Hazole)]^-$ Complexes

G. E. Büchel[1], I. N. Stepanenko[1], M. Hejl[1], M. A. Jakupec[1], V. B. Arion[1], B. K. Keppler[1]

1. *University of Vienna, Institute of Inorganic Chemistry, Währinger Str. 42, A-1090 Vienna, Austria; e-mail: gabriel.buechel@univie.ac.at*

In the past several years the interest in exploring coordination and organometallic compounds of ruthenium's heavier congener osmium as potential antitumor agents has grown continuously [1]. Osmium generally tends to prefer higher oxidation states, stronger π-back donation in lower oxidation states, much stronger spin-orbital coupling as well as marked differences in metal-ligand exchange kinetics as compared to ruthenium. The antiproliferative activity of osmium compounds is varying from highly cytotoxic to non-cytotoxic. It can be very similar to that of structural ruthenium analogues, as is the case for $[Ru(\eta\text{-biphenyl})(en)Cl]BPh_4$ and $[Os(\eta\text{-biphenyl})(en)Cl]BF_4$ [2], similar only in certain cell lines or even quite contrasting, as in the case of $(H_2ind)[Os^{III}Cl_4(DMSO)(Hind)]$ and $(H_2im)[Ru^{III}Cl_4(DMSO)(Him)]$ (NAMI-A), an investigational antimetastatic drug currently in clinical phase II studies [3]. Therefore osmium appears to be interesting as it complements the growing family of tumor-inhibiting ruthenium compounds but also because of its different activity profile.

The osmium(III) complexes *trans*-$[Os^{III}Cl_2(Hazole)_4]Cl$, *cis*-$[Os^{III}Cl_2(Him)_4]Cl$ and *mer*-$[Os^{III}Cl_3(Hazole)_3]$ have already been reported [4]. In pursuing the long-term goal of establishing structure-activity relationships for osmium-chlorido-azole compounds, we prepared a novel osmium family of complexes with the general formula $[cation]^+[Os^{IV}Cl_5(Hazole)]^-$, exploring the Anderson rearrangement reaction. The mono-substituted product of this rearrangement was stabilized by the bulky tetrabutylammonium cation ($n\text{-}Bu_4N^+$). To enable the assessment of the antiproliferative activity of the osmium complexes, $n\text{-}Bu_4N^+$ was substituted by sodium (Na^+) and then azolium (H_2azole^+), which considerably improved the solubility in aqueous media. The compounds have been characterized by ^1H, ^{13}C and ^{15}N NMR as well as by two-dimensional NMR techniques, cyclic voltammetry, IR and UV–vis spectroscopy, ESI–MS, elemental analysis, magnetic susceptibility measurements and X-ray crystallography. The antiproliferative activity of the sodium and azolium salts was assessed *in vitro* in three human cancer cell lines, namely CH1 (ovarian carcinoma), A549 (non-small cell lung cancer) and SW480 (colon adenocarcinoma). The tested compounds were found to possess modest antiproliferative activities with IC_{50} values about one order of magnitude higher than those for the corresponding ruthenium(III) analogue with indazole, $(H_2ind)_2[Ru^{III}Cl_5(Hind)]$ (IC_{50} = 35 μM and 37 μM in CH1 and SW480 cells, respectively) [5].

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Water-soluble *Bis*(thiosemicarbazone) as a Sensitive Probe and Metal Buffer for Zinc

G. Buncic[1], P. S. Donnelly[1], B. M. Paterson[1], J. M. White[1], M. Zimmermann[1], Z. Xiao[1], and A. G. Wedd[1]

1. *School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Parkville, Victoria 3010, Australia. Email: g.buncic@pgrad.unimelb.edu.au, pauld@unimelb.edu.au, z.xiao@unimelb.edu.au*

Zinc is an essential nutrient for living organisms. In plants for example, specific proteins are involved in its root-to-shoot translocation. One major challenge in quantitatively characterising Zn^{2+} samples arises from its d^{10} electronic configuration, which makes it spectroscopically silent. Molecular probes with known binding affinities for Zn^{2+} and well defined spectroscopic properties in its presence are very useful for such studies. A new water soluble, phenyl sulfonate substituted *bis*(thiosemicarbazone) ligand $[H_2L]^-$ was prepared and its potential as a molecular probe for zinc was investigated.[1] The probe was applied to the determination of binding affinities of HMA4n and HMA7n (N-terminal domains of plant proteins HMA4 and HMA7) for Zn^{2+}, whose binding affinities for this metal ion were studied previously.[2] The ligand shows an intense absorbance increase in visible region (λ_{max} 414 nm; ε, 1.8(4) x 10^4 M^{-1} cm^{-1}), a tight isosbestic point at 361 nm and a 1 : 1 binding upon titration with Zn^{2+} in buffer (pH 7.2), (Figure 1). Its binding affinity for Zn^{2+} was determined by competition to be (K_D) 5.9(3) x 10^{-9} M at pH 7.3. This enabled for the binding affinities of HMA4n and HMA7n to be determined by competition with $[H_2L]^-$ (Figure 2), giving values of 1.6(1) x 10^{-10} M and 5.7(1) x 10^{-9} M respectively for these two metal ion binding domains.

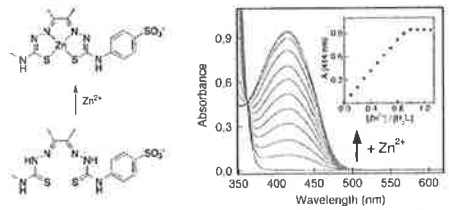

Figure 1. Ligand $[H_2L]^-$ forming a complex with Zn^{2+} (**left**). $[H_2L]^-$ (60 μM) in buffer (pH 7.2) titrated with Zn^{2+} (1.0 mM). Inset: plot of A (414 nm) versus $[Zn^{2+}]$ / $[H_2L]^-$ (**right**).

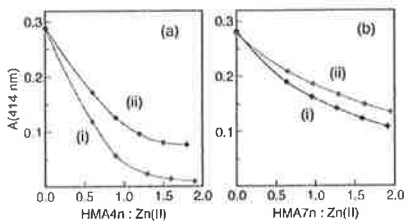

Figure 2. Determination of dissociation constants (K_D) of HMA4n and HMA7n proteins for Zn^{2+} in buffer (50 mM; pH 7.3; 100 mM NaCl) by competition with $[H_2L]^-$. (a) Decrease in A_{414} of solutions containing $[Zn^{2+}]_{total}$ = ~16 μM and $[H_2L^-]_{total}$ = 30 μM in (i) or 180 μM in (ii) with increasing amount of HMA4n. (b) Decrease in A_{414} of solutions containing $[Zn^{2+}]_{total}$ = ~15.5 μM and $[H_2L^-]_{total}$ = 20 μM in (i) or 30 μM in (ii) with increasing amount of HMA7n.

Acknowledgements: We acknowledge the Australian Research Council for funding this project.

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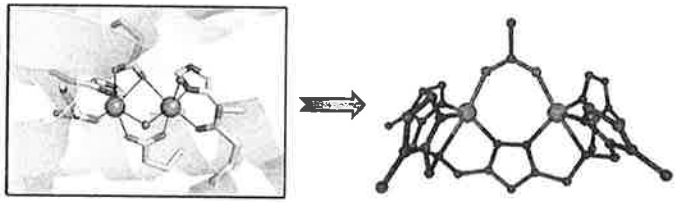
A new Approach towards Functional Biomimetic Model Systems for Binuclear Nonheme-Iron-Oxo Enzymes

B. Burger, S. Wöckel, S. Dechert, S. Demeshko, F. Meyer*
1. *Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4, D-37077 Göttingen, Germany*
Email: boris.burger@chemie.uni-goettingen.de

Diiron-oxo enzymes are widespread in nature and possess a variety of biochemical functions. Despite the structural similarities of their active sites, the spectrum of reactivity is quite diverse.[1] However, most of these systems are capable of reacting with and directly activating dioxygen in a first step, to utilize it for further transformations such as the impressive hydroxylation of methane to methanol by sMMO.[2]
Model systems have already revealed some insight into the processes that are involved in dioxygen activation as well as in the subsequent oxygenation chemistry.[3,4] However, there is still need and interest to develop and investigate new synthetic models and catalysts not only to advance understanding of the biological processes but also to establish a substantial application for such systems in synthetic oxidation or oxygenation chemistry.[4]
On the basis of a highly preorganized chelating pyrazole ligand system[5, 6] we recently developed a new bioinspired approach for mimicking the binuclear active centers of nonheme, μ-carboxylate-bridged diiron enzymes.



Structure of the active center of sMMO found in *methylococcus capsulatus* in its ferrous form[7] and molecular structure of a selected pyrazolate-based diferrous model complex.[8]

We report here on the synthesis and characterization of these newly designed, highly reactive pyrazolate-based diferrous nonheme model complexes. The reactivity of the systems towards dioxygen was studied using spectroscopic methods and their activity in oxygenation reactions of relevant subtrates was tested.[8] Some of our recent results regarding this new type of bioinspired pyrazolate-diiron complexes, their usage in dioxygen activation and oxygenation chemistry are presented.

Acknowledgements: The authors gratefully acknowledge financial support by the Evonik Foundation (travel grant and PhD fellowship for B.B.) and the Deutsche Forschungsgemeinschaft (DFG, IRTG 1422 Metal Sites in Biomolecules: Structures, Regulation and Mechanisms).

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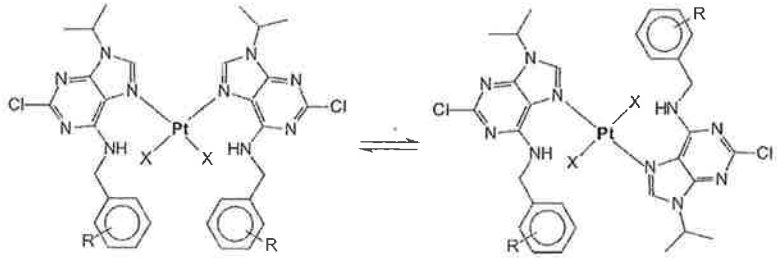
Isomerisation of Pt(II) and Pd(II) square-planar complexes with 6-benzylaminopurine derivatives: A Quantum Chemical Study

M. Cajan[1] and A. Kalup[1]
1. *Department of Inorganic Chemistry, Faculty of Science, Palacky University Olomouc, Tr. 17. listopadu 12, 771 46 Olomouc, Czech Republic)*

N6-Substituted adenine derivatives belong to a group of both natural and artificial compounds named *cytokinins*, which have a large scale of physiological effects regulating the cell cycle. Besides that, these compounds also show a strong cytotoxic effect against some human carcinoma cell lines *via* inhibition of cell cycle regulation enzymes, like cyclin-dependent kinases.[1] As we have found, this cytotoxicity may be strongly increased by the coordination of cytokinin-derived compounds to a suitable transition metal, such as Pt(II), Pd(II), Co(II), Fe(III), etc.[2] On the other hand, such properties are quite often influenced by a number of effects like reaction with a solvent, kinetic stability, *cis-trans* isomerisation, etc. Moreover, the molecular structure, its stability as well as related properties of the complexes in the solid state can be different from those in the solution just due to the above mentioned effects.
Coordination compounds of platinum and palladium have a large scale of various applications as is evident from the big number of works published every year. Especially in this case, the biological, catalytic and other activities strongly depend on the coordination sphere arrangement, and hence on the stability of every particular isomer in the equilibrium mixture. Thus, in the presented work, the equilibrium structures and relative stabilities of the previously prepared Pt(II) or Pd(II) complexes involving cytokinins and cyclin-dependent kinase inhibitors derived from 6-benzylaminopurine of the general composition $[Pt(L)_2X_2]$ and $[Pd(L)_2X_2]$ (L = 6-benzylaminopurine derivatives) have been investigated at the density functional theory (DFT) and RI-MP2 levels. The special attention has been devoted to the analysis of potential energy hypersurface of the *cis-trans* isomerisation reaction, and the structural and energy characterization of the transition states found.



cis-$[Pt(L)_2X_2]$ *trans*-$[Pt(L)_2X_2]$

Figure 1: Schematic representation of the *cis*- and *trans*- forms of studied complexes.

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Ligands for Fluorescence Imaging of Cellular Iron

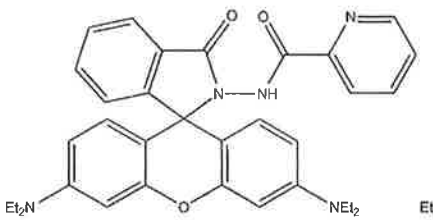
J. D. Chartres[1], P. V. Bernhardt[1], P. C. Sharpe[1]

1. *School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia. j.chartres@uq.edu.au*

Iron-containing proteins participate in many and varied biological processes such as energy production, respiration, cell replication and electron transfer.[1] As such, a method of imaging Iron (Fe) in living cells is extremely desirable. Cellular imaging of metal ions is a rapidly growing field[2] and careful design of ligands has enabled the mapping of cellular concentrations of many different metal ions.

A number of reported fluorescent probes (e.g. calcein,[3] phen green SKA,[4] hydroxypyridinones[5]) have been utilised to quantify chelatable iron pool concentrations in cells.[6] However these approaches are fraught with difficulties, all being based on quenching of the fluorescence when bound to Fe. More recently, examples of 'turn-on' fluorescent probes for Fe(III) have been reported.[7-10]

We have synthesised 'turn-on' fluorescent probes **1** and **2** based on a rhodamine B fluorescent reporter moiety coupled to either an isonicotinoylhydrazide or 2-acetylpyridine hydrazone chelation site. Upon binding a metal ion, the rhodamine B hydrazine undergoes ring-opening to give its fluorescent form. By selecting the appropriate metal-chelating group we have been able to demonstrate selective fluorescence signal enhancement in the presence of Fe(III) when compared to other metal ions.



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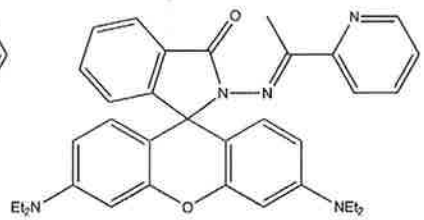

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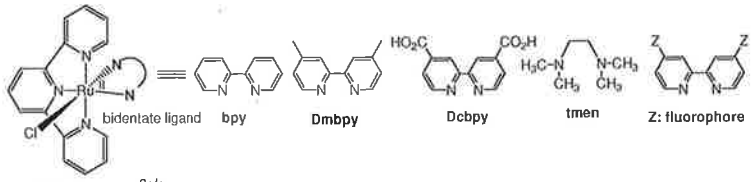
Modified Bipyridine Ligand of Ruthenium Complexes Related to the Anti-proliferations in Zebrafish

C.-C. Cheng[1], Y.-H. Chen[2], M.-L. Chiou[1], C.-H. Chiou[1]

1. *Department of Applied Chemistry, National Chia-Yi University, Chia-Yi City, Taiwan 60004, ROC. E-mail: cccheng@mail.ncyu.edu.tw*
2. *Department of Chemistry, Tamkang University, Tamsui, Taiwan, ROC.*

Ruthenium complexes are known to possess less toxicity and higher water-solubility than cisplatin, giving them great potential as anti-tumour metallodrugs. Recently, many small molecules adopted by zebrafish show the important behaviors to be as a new kind phenotype for clinic purpose. In this report, zebrafish acts as a whole-organism model to screen new Ru complexes for anti-proliferation activity.[1] After soaking the embryos in Ru(terpy)(NN)Cl$^+$ (NN, bidentate nitrogen ligand) derivatives, only [Ru(terpy)(bpy)Cl]Cl-treated embryos displayed obvious phenotypes such as fin reduction. The electronic effect of bipyridine derivatives in ruthenium complexes shows the significant influence in the bacterial and zebrafish growth. TUNEL assay combined with immunostainings revealed that treatment with cisplatin, [Ru(terpy)(bpy)Cl]Cl and [Ru(terpy)(dmbpy)Cl]Cl led to proliferating fin mesenchymal cells undergoing apoptosis, and consequently causing fin-reduction phenotypes. Furthermore, [Ru(terpy)(bpy)Cl]Cl was able to activate the P53-dependent and independent pathways, and induce human hepatoma cell undergo apoptosis. Furthermore, a red fluorophore linked with ruthenium complex was designed and synthesized to examine its uptake pathway in zebrafish for developing a clinical diagnostic reagent.



[Ru(terpy)(NN)X]$^{2+/+}$

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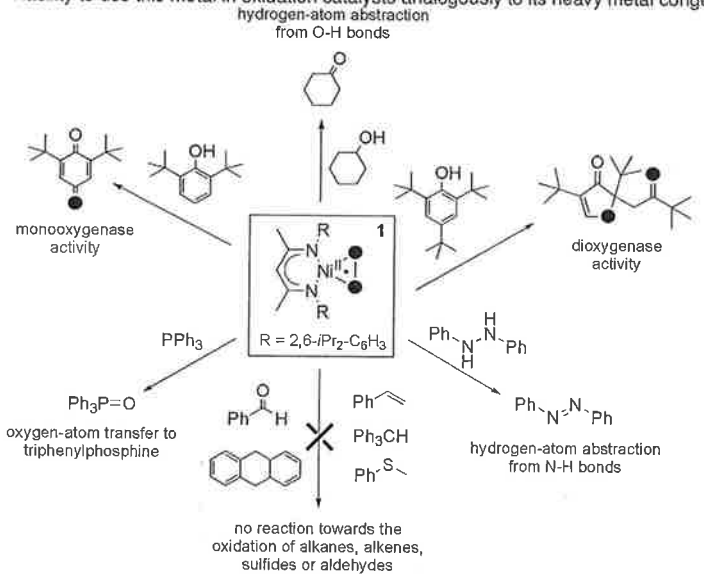
Dioxygenase-like activity of an isolable nickel(II)-superoxo compound

A. Company[1], S. Yao[1], K. Ray[2], M. Driess*[,1]

1. *Institute of Chemistry: Metalorganics and Inorganic Materials. Technische Universität Berlin, Strasse des 17. Juni 135, Sekr. C2, D-10623 Berlin (Germany). E-mail: anna.company@gmail.com*
2. *Synthetic Bioinorganic Chemistry. Humboldt-University Berlin. Brook-Taylor Strasse 2, D-12489 Berlin (Germany).*

Although O_2 activation by metals such as iron and copper has been a matter of intensive research in the last decades,[1] this type of chemistry for nickel centres is still in its infancy. Moreover, studies regarding the oxidizing ability of the resulting "Ni_n-O_2" species towards exogenous substrates are very scarce.[2] In this work, we report on the reactivity of an isolable and thermally stable nickel-superoxo compound [Ni^{II}(β-diketiminato)($O_2^{\cdot-}$)] (**1**)[3] towards different types of organic substrates. Interestingly, compound **1** performs hydrogen-atom abstraction from O-H and N-H bonds and most importantly it shows an unprecedented dioxygenase-like activity in the oxidation of 2,4,6-tri-*tert*-butylphenol. This reaction most probably occurs through the mediation of a putative [Ni^{III}-oxo] intermediate. Results presented here evidence the potential oxidizing power of Ni-dioxygen species and further support the viability to use this metal in oxidation catalysts analogously to its heavy metal congener, palladium.



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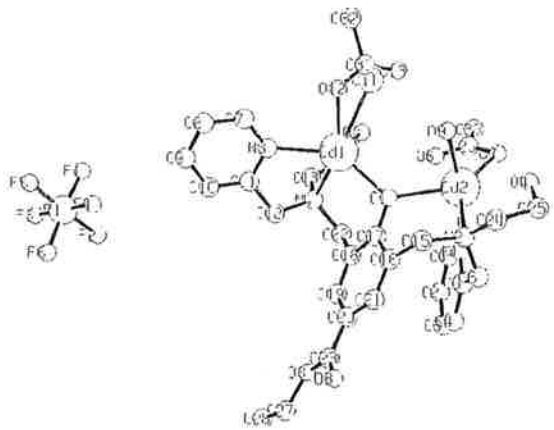
A New GpdQ-Biomimetic Cadmium(II) Complex and its Potential Application in Bioremediation

L.J. Daumann[1], L.R. Gahan[1] and G. Schenk[1]

1. *School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Queensland, AUSTRALIA 4072, gahan@uq.edu.au*

The synthesis of the new polydentate ligand ethyl 4-hydroxy-3,5-bis(((2-hydroxyethyl)(pyridin-2-ylmethyl)amino)methyl)benzoate mimicking the active site of the glycerophosphodiester degrading enzyme GpdQ is reported. The ligand features an ester-moiety for binding on surfaces/resins for a potential application in bioremediation. The ligand was complexed to divalent cadmium and the phosphoesterase-like activity of the complex was studied using the substrate bis(2,4-dinitrophenol) phosphate (bdNPP). X-ray analysis of the complex revealed that it crystallised as a dimer of two dinuclear cadmium complex units, bridged by the oxygen of the ethyl ester group. The charge is balanced by two hexafluorophosphate anions. The ORTEP plot of one monomeric unit of this complex is shown below.



Macrocyclic Receptor Showing Extremely High Sr(II)/Ca(II) and Pb(II)/Ca(II) Selectivities: Potential Application in Chelation Treatment of Metal Intoxication.

A. de Blas[1], R. Ferreirós-Martínez[1], D. Esteban-Gómez[1], C. Platas-Iglesias[1], and T. Rodríguez-Blas[1]
1. *Departamento de Química Fundamental, Universidade da Coruña, Campus da Zapateira, Alejandro de la Sota 1, 15008 A Coruña, Spain. E-mail: andres.blas@udc.es*

An important field of application of chelate-forming compounds is the removal of toxic metal ions or radioactive isotopes from living organisms. Indeed, extensive clinical experience demonstrated that the prognosis in acute and chronic intoxications with a range of metal ions can be improved considerably by administration of a suitable chelating agent. The cyclic framework of crown ethers provides an interesting platform for the complexation of different metal ions. Moreover, the relative facility with which crown ethers can be functionalized with pendant arm(s) containing additional donor atom(s) allows to enhance the cation binding ability and the selectivity of the parent crown ether. Particularly, the 18-membered ring of 4,13-diaza-18-crown-6 is known to be an useful platform for the design of selective ligands for large metal ions such as Pb(II) and Sr(II). Herein we report the complexation properties of the macrocyclic ligand *N,N'*-Bis[(6-carboxy-2-pyridil)methyl]-4,13-diaza-18-crown-6 (H_2**bp18c6**) towards different divalent metal ions [Zn(II), Cd(II), Pb(II), Sr(II) and Ca(II)] in aqueous solution.

Potentiometric measurements indicate that **bp18c6** is well suited for the complexation of large metal ions such as Pb(II) and Sr(II). The **bp18c6** complex of Pb(II) shows the highest $\log K_{ML}$ value among the different divalent metal ions studied in this work. The $\log K_{PbL}$ value obtained for **bp18c6** is considerably higher than those reported for bpy18c6, odda and oddm, and *ca.* 1.8 $\log K$ units lower than that reported for edta. The $\log K_{ML}$ values reported in Table 1 evidence an unprecedented selectivity of **bp18c6** for Pb(II) over Ca(II), Cd(II) and Zn(II), with $\Delta\log K_{ML} = \log K_{PbL} - \log K_{XL}$ values of 11.0 (X = Ca), 7.3 (X = Cd) and 7.0 (X = Zn). The speciation diagrams highlight the selectivity of **bp18c6** for Pb over Cd and Zn and Ca. For instance Pb(II) is almost totally complexed at pH 3 (99.1%), while only 70.5% of the total Zn(II), 24.6% of the total Cd(II) and $8\cdot10^{-4}$% of the total Ca(II) are complexed under the same conditions. Concerning the Sr(II)/Ca(II) selectivity at pH 6.5 Sr(II) is almost totally complexed (99.6%), while only 60.1% of the total Ca(II) is complexed under the same conditions. It must be noticed that **bp18c6** shows the highest Sr(II)/Ca(II) selectivity reported so far.

Table 1. Thermodynamic stability constants of **bp18c6** and its metal complexes as determined by pH-potentiometry [I = 0.1 M KNO_3]. Data reported previously for related systems are provided for comparison.

	bp18c6	bp12c4	bp15c5	odda	oddm	edta	bpy18c6
$\log K_{ZnL}$	9.23(2)	15.48	11.14	8.42	6.25	16.5	6.96
$\log K_{CdL}$	8.95(1)	16.84	15.84	11.07	10.3	16.5	10.96
$\log K_{PbL}$	16.23(7)	15.44	17.17	13.55	13.0	18.0	11.67
$\log K_{CaL}$	5.25(6)	10.70	9.12	8.39	7.55	10.6	3.63
$\log K_{SrL}$	9.57(4)			8.29	9.79	8.68	

In order to rationalize this behavior, the structure of the complexes in solution has been investigated by ^{1}H and ^{13}C NMR spectroscopy, as well as by theoretical calculations performed at the DFT (B3LYP) level. The selectivity that **bp18c6** shows for Sr(II) over Ca(II) can be attributed to a better fit between the large Sr(II) ions and the relatively large crown fragment of the ligand. The X-ray crystal structure of the Pb(II) complex shows that the $\Delta(\delta\lambda\delta)(\delta\lambda\delta)$ conformation observed in solution is also maintained in the solid state in which the Pb(II) lone pair is stereochemically active. The X-ray structures of the Zn(II) and Cd(II) complexes show that these metal ions are exocyclicly coordinated by the ligand, which explains the high Pb(II)/Cd(II) and Pb(II)/Zn(II) selectivities.

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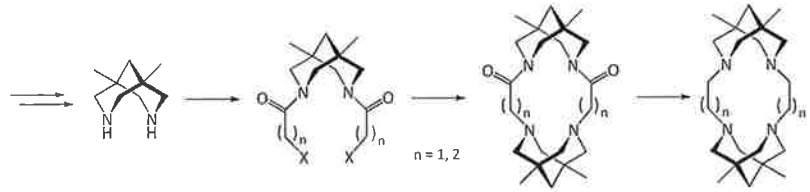
Very rigid and highly preorganized tetraazamacrocyclic ligands and their copper(II) complexes.

M. Kerscher
1. *Universität Heidelberg, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. E-mail: marion.kerscher@aci.uni-heidelberg.de*

The synthesis of novel tetraazamacrocycle derivatives and their copper(II) coordination chemistry will be presented.



The very rigid diazaadamantane-derived caps of the macrocyclic ligands lead to restricted configurational and conformational flexibility as well as a high degree of preorganization and complementary. These specific features result in high in-plane ligand field strength, which leads to uncommon properties of the corresponding transition metal complexes. The main focus will point at X-ray crystallographic and spectroscopic investigations of the corresponding copper(II) compounds.

Spectral investigation of the inclusion compound Al-quercetin/βCD and a comparative study of its electrochemical behaviour and antioxidant ability.

K. Dias[1], S. Nikolaou[1], W. F. De Giovani[2].

1. *Departamento de Física e Química, Faculdade de Ciências Farmacêuticas de Ribeirão Preto, Universidade de São Paulo, Av. do Café s/n, 14040-903, Ribeirão Preto, SP, Brasil.*
2. *Departamento de Química, Faculdade de Filosofia Ciências e letras de RibeirãoPreto, Universidade de São Paulo, Av. Bandeirantes 3900, 14040-901, Ribeirão Preto, SP, Brasil.*

Recently we have reported in literature [1] the synthesis and spectral investigation of Al-quercetin/βCD ($[Al_2(quercetin)(H_2O)_8]Cl_4$/βCD) and Al-catechin/βCD ($[Al(catechin)(H_2O)_5]Cl_2$/ βCD) by different analyses: IR, UV-vis, ^1H and ^{13}C NMR, TG and DTA. The present studies focus Circular Dichroism, ^1H NMR and UV-visible spectroscopies study for the inclusion compound Al-quercetin/βCD. Then, we investigate the effect of the βCD in the relationship between antioxidant ability and electrochemical oxidation [2-3].

Al-quercetin in water exhibited two absorption peaks characteristics of complex formed at 270nm (Band II) and 450nm (Band I) respectively. The increase in βCD concentration from 50-200 μmol L^{-1} resulted in an increase in the absorption of Al-quercetin. The molecular extinction coefficient ε of the Al-quercetin in water and Al-quercetin/βCD were 8992 L mol^{-1} cm^{-1}, 9236 L mol^{-1} cm^{-1} and 10160 L mol^{-1} cm^{-1}, 11073 L mol^{-1} cm^{-1} for (Band I) and (Band II) respectively The linear behavior for βCD (r^2 = 0.99999; 0.99992) is consistent with 1:1 molecular compound formation [1] for Al-quercetin and βCD. Inclusion of Al-quercetin into βCD cavity was detectable by ^1H NMR, from comparison of the free βCD and after of the βCD inclusion process. The protons signals of Al-quercetin were hardly detectable, due to their very poor water solubilities and the presence of βCD, which is much more soluble. However, the difference in proton chemical shift values between βCD in free and included state suggested the formation of Al-quercetin/βCD compound. The 5-H inner proton of βCD presented larger chemical shift than 3-H and 6-H, due to the anisotropic current of complex, which represented that the Al-quercetin molecule entered into the cavity of βCD.

In the Circular Dichroism spectrum, the Al-quercetin complex displayed a band with positive signal between 330-430 nm (Band I), meaning that the coordination of quercetin with the Al (III) ion promotes modification on the flavonoid opticall activity. The spectrum of Al-quercetin/βCD inclusion compound showed the maximum positive induced Cotton effect in the range from 300 to 500 nm, suggesting that the cynamoil chromophore (B ring and part of the C ring) is located inside the βCD cavity and the positive bands observed for the inclusion compound show that the dipole moment of the included chromophores are aligned along the Z-axis of the βCD cavity [4]. The antioxidant activity of the investigated compounds was probed by the scavenge of $DPPH^{\cdot}$ method. The values of antioxidant activities expressed by EC_{50} parameter for the flavonoids complexes were slightly lower than their inclusion compounds. This suggests that the βCD presence maintains their antioxidant properties. The EC_{50} values found to Al-quercetin and Al-quercetin/βCD were 15.3 ± 0.75 and 18.4 ± 0.99 respectively. This means that under the conditions employed, to reach 50% of $DPPH^{\cdot}$ at steady state it was necessary almost the same concentration of Al-quercetin and Al-quercetin/βCD, in other words, about 150 μmol L^{-1}.

Chronoamperometric measurements showed that the current–time ratio was largely dependent on the concentration of βCD. The diffusion coefficients determined in this work for both compounds actually show that the included specie takes a longer time to act than the free quercetin complex, what is propably responsible for the higher EC_{50} value observed for the inclusion compound.

Acknowledgements

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Evaluation of *In Vitro* Cytotoxic Activity of $[Pt(ox)(L_n)_2]$ Complexes Involving Adenine-based N-donor Ligands

Z. Dvořák[1], R. Vrzal[1], P. Štarha[2], I. Popa[2], Z. Trávníček[2]

1. *Department of Cell Biology and Genetics, Faculty of Science, Palacký University, Šlechtitelů 11, CZ-783 71 Olomouc, Czech Republic, moulin@email.cz*
2. *Department of Inorganic Chemistry, Faculty of Science, Palacký University, Tř. 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic, zdenek.travnicek@upol.cz*

A series of mononuclear square-planar platinum(II) oxalato (ox) complexes involving N6-benzyl-9-isopropyladenine derivatives was prepared using the synthetic strategy with $K_2[Pt(ox)_2]\cdot 2H_2O$ employed as a starting platinum(II) compound. The obtained products were fully characterized by various physical methods including a single crystal X-ray analysis (see Fig. 1). Based on a degree of substitution of the N6-benzyl-9-isopropyladenine moiety, the prepared platinum(II) complexes can be divided into two groups. The first group involves 2-chloro-N6-benzyl-9-isopropyladenine and its benzyl-substituted derivatives,[1] while the second one contains potent cyclin-dependent kinase inhibitors derived from *roscovitine*, i.e. 2-(1-ethyl-2-hydroxyethyl)-N6-benzyl-9-isopropyladenine, and its benzyl-substituted analogues.[2]

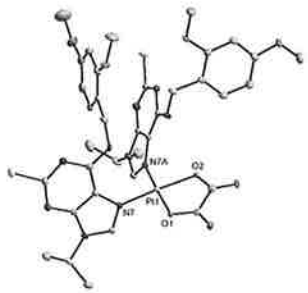

Fig. 1

The presented platinum(II) oxalato complexes were prepared with the aim to strive to develop a new group of highly cytotoxic platinum-based compounds, potentially used in clinical cancer therapy. Their *in vitro* cytotoxic activity was evaluated by an MTT assay against human cancer cell lines, including ovarian carcinoma (A2780), cisplatin resistant ovarian carcinoma (A2780cis), malignant melanoma (G361), breast adenocarcinoma (MCF7), lung carcinoma (A549), osteosarcoma (HOS) and cervix epitheloid carcinoma (HeLa).[3] The significant *in vitro* cytotoxicity was determined for several representatives of the tested platinum(II) oxalato complexes against some of the named cancer cells (up to ten times higher compared to commercially used platinum-based anticancer drug *cisplatin*), which will be discussed in more detail within the framework of the contribution. Selected complexes were also tested for their *in vitro* cytotoxic effect in primary cultures of human hepatocytes. No hepatotoxic effect of these substances was observed up to 50.0 μM concentration, and thus, the discussed platinum(II) oxalato complexes can be considered to be safe for liver from the toxicological point of view.

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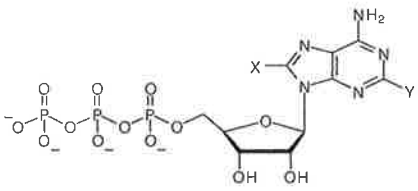
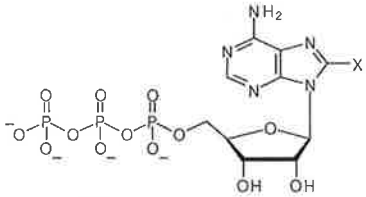
How do adenine modifications in ATP affect the properties of the corresponding Cu(II) complexes?

B. Fischer[1], Y. Itzhakov[1]
1. *Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel. bfischer@mail.biu.ac.il*

Nucleobase-modified nucleotides are extensively used as biological probes or drug candidates. Yet, their acid-base equilibria and coordination with metal ions have been hardly studied. Therefore, here, we studied by potentiometric titrations a series of base-modified adenosine 5′-triphosphate analogues, **1-10**, and evaluated the effect of electron-withdrawing (EW) or donating (ED) groups at the adenine C2 or C8 position, on acid-base equilibria and stability constants of the corresponding complexes with Cu(II) ions. pK_{a1} (N1H) is considerably influenced by base substitutions, whereas the influence on the pK_{a2} (terminal phosphate) is minor, e.g., pK_{a1} 4.80, pK_{a2} 6.58 in 8-NHBu-ATP, **5**, vs. 4.00 and 6.54, respectively, in ATP, **1**. Additional deprotonation reaction was observed upon introducing 8-oxo or 8-thioxo group, namely N7H ionization: pK_{a3} 8.89 in 8-oxo-ATP and 7.29 in 8-thioxo-ATP. Stability constant of Cu(II)-8-thioxo-ATP could not be measured due to reduction of Cu(II) to Cu(I) by the thiolate. The measured stability constants of nucleotides **1-9** with Cu(II) ions remained similar (within 0.3 log unit) to that of the parent Cu(II)-ATP complex, $\log K^{M}_{ML}$ 6.45. Intramolecular equilibrium between the open and the closed species also operates here, as in Cu(II)-ATP, where a macrochelate is formed by the coordination of Cu(II)-triphosphate open complex to the base moiety. The nucleobase binding site is dictated by the nucleotide conformation, thus in *anti* nucleotides, including ATP, macrochelate formation is via N7, and in *syn* nucleotides, via N1. The degree of macrochelate formation is dependent on the basicity of the relevant N site. For example, in 2-$SCH_2C(CH_3)_3$-ATP, **2**, the N7 site of which is more basic than that of ATP, a higher macrochelate formation was observed, 87% vs 71%, respectively. Likewise, in 8-SBu-ATP, **9**, and 8-Br-ATP, **6**, where the basicity of the N1 sites is only slightly different, pK_{a1} 4.16 and 3.82, 73% and 69% of the closed isomers were observed, respectively. ATP analogues where N7 is involved in Cu(II)-chelation, form higher percentages of the macrochelate structure, vs. analogues involving N1 coordination, although N7 is less basic than N1. Specifically, 2-SBu-ATP, **3**, forms 83% macrochelate via N7, and 8-SBu-ATP forms 73% closed isomer via N1 site, implying steric inhibition by C6-NH_2. In the *anti* 8-NHBu-ATP, **5**, N7 coordination is enhanced by the increased basicity due to 8-NHBu substitution, but as it is not sterically favourable, there is an overall reduction in the macrochelate formation, i.e., 58% closed species. To conclude, either C2 or C8 EW or ED substitutions on ATP did not result in a significant impact on $\log K^{M}_{ML}$ values of the corresponding Cu(II)-complexes. Steric effects and basicity of the N site influence the extent of macrochelate formation. The percentages of the closed isomers remained high (70-85% vs. 71% for ATP) although macrochelation occurs via N7 or N1. Yet, in some base substitutions, resulting in a more basic N1H (compared with ATP N1H), a higher $\log K^{M}_{MLH}$, of ca. 1 log unit, was observed compared with the corresponding ATP complex. Our findings are expected to be valuable data for drug designers and biochemists.



Anti



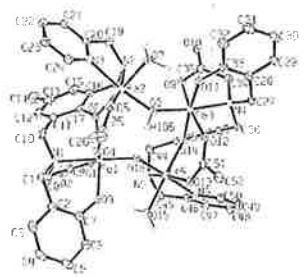
Syn

		X	Y			X
1	ATP	H	H	**6**	8-Br-ATP	Br
2	2-$SCH_2C(CH_3)_3$-ATP	H	$SCH_2C(CH_3)_3$	**7**	8-OMe-ATP	OMe
3	2-SBu-ATP	H	SBu	**8**	8-oxo-ATP	OH
4	2-Cl-ATP	H	Cl	**9**	8-SBu-ATP	SBu
5	8-NHBu-ATP	NHBu	H	**10**	8-thioxo-ATP	SH

Phosphate ester cleavage promoted by a tetrameric iron(III) complex

L. R. Gahan,[1] A. Kantacha,[2] R. Buchholz,[1] S. J. Smith,[1] G. Schenk[1]
1. *The University of Queensland, School of Chemistry and Molecular Biosciences, St. Lucia, QLD 4072, Australia*
2. *Department of Chemistry, Faculty of Science, Thaksin University, 140 Tambon Koaroobchang, Muang, Songkhla 90000, Thailand*

The purple acid phosphatases (PAPs) are the only binuclear metallohydrolases where the necessity for a heterovalent active site (Fe(III)-M(II), (M = Fe, Zn or Mn) for catalysis has been established. The paradigm for the construction of PAP biomimetics, both structural and functional, is that the ligands possess characteristics which mimic the metalloenzyme donor sites and permit discrimination between trivalent and divalent metal ions. The donor atom set of the ligand 2-((2-hydroxy-5-methyl-3-((pyridin-2-ylmethylamino)methyl)benzyl)(2-hydroxybenzyl)amino)acetic acid (H_3HPBA) mimics that of the active site of PAP although the iron(III) complex of this ligand has been characterized as the tetramer $[Fe_4(HPBA)_2(OAc)_2(\mu\text{-}O)(\mu\text{-}OH)(OH_2)_2]ClO_4.5H_2O$.[1] The phosphoesterase-like activity of the complex in 50:50 acetonitrile/water has now been investigated using the substrate bis-2,4-dinitrophenyl phosphate (BDNPP) yielding kinetically relevant pK_as of 5.3, 6.2 and 8.4, with a K_M of 7.4 ± 0.6 mM and a k_{cat} of 1.6 (± 0.2) x 10^{-3} s^{-1}, the latter similar to that of other heterovalent PAP biomimetics. Mechanistic implications of these observations are discussed.



An ORTEP plot of the complex cation of $[Fe_4(HPBA)_2(\mu\text{-}O)(\mu\text{-}OH)(OAc)_2(OH_2)_2]ClO_4.5H_2O$.

Acknowledgements:
This work was funded by a grant from the Australian Research Council (DP0986292).

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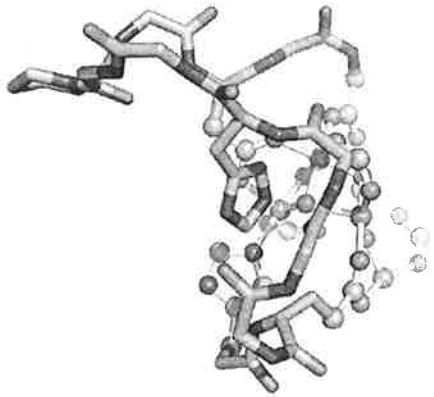
Modelling the Effect of Protein Straps on the Mn4Ca Cluster in Photosystem II: a DFT Study

P. Gatt, R. Stranger, S. Petrie, R. Pace
Research School of Chemistry, Australian National University (Phillip.Gatt@anu.edu.au)

A detailed understanding of the structure and function of Photosystem II (PSII) which is responsible for the light-induced oxidation of water to O2, remains elusive despite the intense scrutiny to which this protein complex has been subjected. At the heart of this system is a metal active site which contains four Mn and one Ca atom. Earlier work involved an extensive DFT study to build up a structural model of the Mn_4Ca cluster in all its catalytically relevant oxidation states, hydration levels and magnetic coupling modes. From this work, a set of model structures **I**, **II** and **III** were derived which differ principally in terms of the spatial relationship between Mn(4) and a generally robust Mn_3Ca tetrahedron. In these model structures, the amino acid residues binding to the metal ions were replaced with simple carboxylate and imidazole groups.[1,2] More recently, we have performed DFT calculations on extended model structures which include the amino acid residues that form the three protein straps linking the Mn ions together. The effect of the structural constraints introduced by the protein straps on the stability of the original model structures, their magnetic coupling modes and water binding site preferences are discussed.

Model structure **I**



Extended model structure **I**

Acknowledgements: I gratefully acknowledge the financial assistance from the Australian National University. I also acknowledge the provision of supercomputer time on the platforms of the National Computer Infrastructure operating through the Australian National University Supercomputer Facility.

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Cytotoxic apoptosis-inducing iridium(III) and rhodium(III) complexes with substituted polypyridyl ligands

Y. Geldmacher, W.S. Sheldrick
Department of Analytical Chemistry, Ruhr Universität Bochum, Universitätsstr. 150, 44780 Bochum, E-Mail: Yvonne.Geldmacher@rub.de

The rhodium(III) and iridium(III) complexes of the types $[(C_5Me_5)MX(pp)]^+$ and $[MX_3(L)(pp)]$ with pp = phen, dpq, dppz, dppn and X = Cl, Br represent new classes of cytotoxic substances. Cytotoxicity and cellular uptake studies on the MCF-7 and HT-29 cell lines have been employed to establish relationships between the structure and the activity of *mer/fac*- $[MX_3(L)(pp)]$ complexes (with L=H_2O, CH_3OH, 1-methylimidazole, DMSO; X=Cl, Br and M=Rh, Ir) [1-2].

Their cytotoxicity increases in dependence on the central atom in the order Ru << Ir < Rh. The biological activity also correlates with the lipophilicity and thereby with the size of the polypyridyl ligand. The IC_{50} values decrease in the series bpy> phen >dpq, dppz. The complexes inhibit angiogenesis, induce specific apoptotic cell death in leukemia and lymphoma cells via the intrinsic mitochondrial pathway and cause regligible nectrotic damage. An influence of the coordination geometry (*mer* or *fac*) and ligands X and L is also apparent. The findings suggest that differences in the cytotoxicity may be related to the extent of cellular uptake and to the differing kinetic stabilities.

As part of our ongoing studies to optimize the activity and therapeutic range of these rhodium(III) complexes, we have been studying the influence of the ligands L and pp. It has previously been shown that there is a significant difference between the cytotoxicities of square planar platinum complexes containing various methylated 1,10-phenanthroline ligands [3].

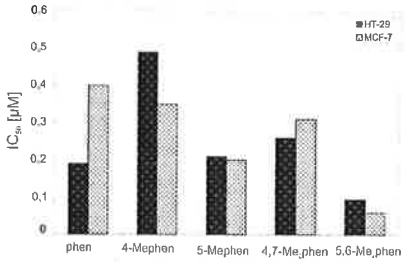

Figure 1: Cytotoxicity of *mer/fac*-$[RhCl_3(DMSO)(pp)]$

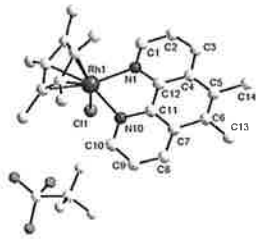

Figure 2: crystal structure of $[(\eta^5\text{-Cp}^*)RhCl(5,6\text{-}Me_2phen)]CF_3SO_3$

Figure 1 demonstrates that a comparable trend is observed for complexes of the type *mer/fac*-$[RhCl_3(DMSO)(pp)]$. Here the *mer/fac*-$[RhCl_3(DMSO)(5,6\text{-}Me_2phen)]$ complex is once again the most active compound and the IC_{50} values for the MCF-7 and HT-29 cell lines decrease in the order 4-Mephen > phen ~ 5-Mephen ~ 4,7-Me_2phen > 5,6-Me_2phen. Results of biological studies are also presented for the analogous Ir and $(\eta^5\text{-}C_5Me_5)Rh$ complexes. To optimize the cell selectivity of the complexes, we are currently further modifing the polypyridyl ligands with suitable substitutents so as to improve their solubility and their uptake into tumour cells.

Acknowledgement: We wish to thank our cooperation partners in the DFG sponsored research group FOR 630 "Biological function of organometallic compounds" for biological and medical measurements.

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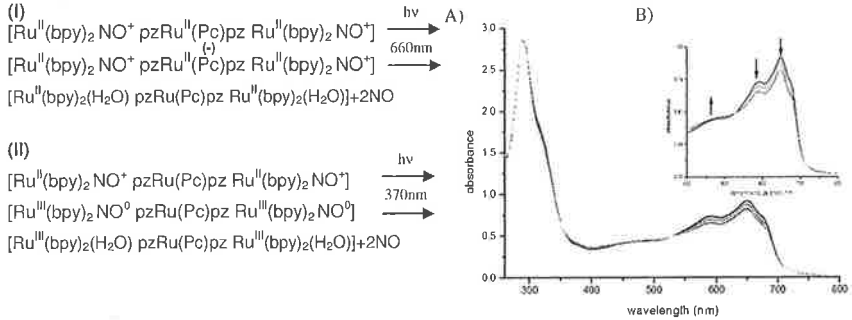
Photochemical reactivity of a new trinuclear phthalocyanine ruthenium complex as nitric oxide donor agent by light irradiation in therapeutic window

T. A. Heinrich (PQ)[1]; J. C. Biazzotto (PQ)[1]; A. C. Tedesco (PQ)[1,2]; R. S. da Silva (PQ)[1].

1. *Departamento de Química e Física da Faculdade de Ciências Farmacêuticas de Ribeirão Preto, Universidade de São Paulo. Av. do Café, s/n CEP: 14040-903, Ribeirão Preto, SP, Brazil. tassiele@usp.br*
2. *Departamento de Química da Faculdade de Filosofia Ciências e Letras de Ribeirão Preto, Universidade de São Paulo. Av. dos Bandeirantes, 3900 CEP: 14040-901, Ribeirão Preto, SP, Brazil.*

Nitric oxide (NO) is an important biological messenger. It has been implicated in many physiological processes, including cardiovascular control, neuronal signaling, defense against microorganism and tumors. It's known depending on the concentration of this molecule (NO) in biological system, it can trigger pro- and antitumor responses[1]. The antitumor effect is pronounced when there are high levels of NO in tumor cells medium[2]. So, the study of NO releasing drugs that can be delivered in different diseased tissues is showing promising results but until remains a challenge. This work describes synthesis, photochemical and photophysical studies of a new nitrosyl ruthenium complex $[\{(Ru(bpy_2)NO)\}_2(pz)Ru(Pc)pz)]$ (I) (where pc=phthalocyanine, bpy= 2,2'-bipyridine and pz=pyrazine ligand) as putative system to improve photodynamic therapy (PDT). Briefly, $[\{Ru^{II}(bpy)_2NO^+\}pzRu^{II}(Pc)pz\ \{Ru^{II}(bpy)_2NO^+\}]$ was prepared by mixing an equimolar ratio of *cis*-$[Ru(NO_2)(bpy)_2(NO)](PF_6)_2$[3], sodium azide ($NaN_3$), and $[Ru(pc)(pz)_2)$ in acetone. This trinuclear compound display ν(NO) at ca. 1942 cm^{-1}, indicating that the nitrosyl group exhibits a sufficiently high degree of nitrosonium ion (NO^+). The electronic spectrum of this complex in aqueous solution displays bands at 290, 320, 590 and 650 nm characteristics of ruthenium phthalocyanines (Figure A). NO photo-release was observed by light irradiation at 370 and 660 nm (Figure B). The photochemical pathway was attributed to two different mechanisms as described below:



We can conclude that the synthesis of this new trinuclear ruthenium complex was photochemically active. The photoinduced NO release with irradiation at therapeutic window prompts us to further investigate its effect *in vitro* and *in vivo* as a putative agent to be used in photodynamic therapy.

Acknowledgements: We thank FAPESP and CNPq to financial support.

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Cell permeable fluorescent Cu(II) complexes for the monitoring of intracellular metal ion behaviour and detection of pathological hallmarks of Alzheimer's disease

J. L. Hickey[1], G. Buncic[1], K. A. Price[2], J. M. White[1], A. G. Wedd[1] A. R. White[2], P. S. Donnelly[1*]

1. *School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, The University of Melbourne, Victoria, Australia 3010. jhickey@unimelb.edu.au*
2. *Department of Pathology, The University of Melbourne, Vic, Australia 3010.*

The biological activity of *bis*(thiosemicarbazone)copper(II) complexes ($^{64}Cu^{II}$(btsc)) is determined by their electrochemistry, in particular the $Cu^{II/I}$ couple.[1,2] Radioactive $^{64}Cu^{II}$(atsm) ((diacetyl-*bis*(4-*N*-methyl-3-thiosemicarbazonato)copper(II)) selectively accumulates in hypoxic tissue and is under investigation as a hypoxia tracer for positron emission tomography (PET). The observed selectivity of $^{64}Cu^{II}$(atsm) is attributed to a $Cu^{II/I}$ couple ($E_{1/2}$ = -0.60V *vs.* Ag/Ag^+) that prevents complex reduction unless in a hypoxic environment.[3] Derivatives of $^{64}Cu^{II}$(atsm) display similar chemical properties including the ability to retain the $Cu^{II/I}$ couple.

Our interest in these systems is to prepare fluorescent Cu^{II}(atsm) derivatives to study cellular uptake *via* confocal fluorescence microscopy. As such, we have synthesised a fluorescent probe incorporating a *bis*-thiosemicarbazone (atsm) ligand conjugated to a 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) fluorophore. The new ligand forms highly fluorescent complexes with Cu^{2+} and Zn^{2+}. The synthesis, electrochemistry, fluorescence spectroscopy,, cellular imaging and the interaction of these new derivatives with protein aggregates associated with neurodegenerative disease will be presented.

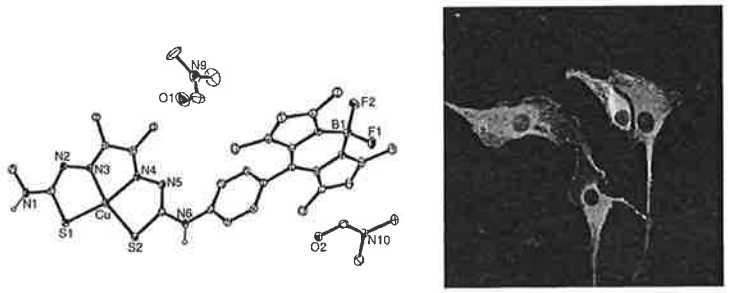

Figure 1. An ORTEP representation of fluorescent Cu^{II}-*bis*-thiosemicarbazone complex Cu^{II}(atsm/*p*-BODIPY) (left) and a confocal fluorescence image of the complex in glial cells (right).

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Synthesis, Carbohydrate- and DNA-Binding Studies of Cationic 2,2':6',2"-Terpyridineplatinum(II) Complexes Containing *N*- and *S*-donor Boronic Acid Ligands

S. S. Hosseini[1], M. Bhadbhade[2], R. J. Clarke[1], P. J. Rutledge[1] and L. M. Rendina[1]*
1. *School of Chemistry, The University of Sydney, NSW 2006, Australia, simin@chem.usyd.edu.au*
2. *Solid State & Elemental Analysis Unit, The University of New South Wales, Sydney, NSW 2052, Australia*

There is considerable interest in the interactions of metal complexes with DNA.[1,2] Water-soluble and stable complexes containing spectroscopically rich metal centres are extremely valuable in the study of biological systems.[3] For example, the DNA intercalation of platinum(II) complexes containing 2,2':6',2"-terpyridine (trpy) first reported by Lippard and co-workers in 1974,[2] has been used extensively since.
An immense variety of boronated compounds have also been synthesized and assessed for DNA binding, for example as potential agents for boron neutron capture therapy (BNCT),[4,5] but very few have been incorporated into DNA metallointercalators.[6] Boronic acids in particular have the unique property of reversibly binding to carbohydrates in solution, which dramatically increases their aqueous solubility and can lead to non-covalent interactions that supplement the DNA-binding of such complexes.
We report the synthesis, characterization, carbohydrate and DNA-binding studies of a series of platinum(II)-trpy complexes of the type $[Pt(trpy)L](NO_3)_n$ (L = 3- or 4-pyridineboronic acid (3- or 4-pyB, respectively), n = 2; HL = 4-mercaptophenylboronic acid (HmpB), n = 1; trpy = 2,2':6',2"-terpyridine) and $[\{Pt(trpy)\}_2(\mu\text{-pzB})](NO_3)_3$ (HpzB = pyrazolylboronic acid). Carbohydrate binding studies revealed that the complexes avidly bind to sugars such as D-fructose and ribose as well as catechol, sorbitol and mannitol to afford 1:1 adducts which possess greatly enhanced water solubility.[7] DNA-binding studies reveal an intercalative interaction between selected platinum(II)-trpy complexes and calf-thymus DNA, as determined by thermal denaturation (T_m) and isothermal titration calorimetry (ITC) experiments. The key results of this work will be presented.

Acknowledgements: We thank Mr Vincent Ching for assistance with the ITC experiments, Dr Ian Luck for assistance with the NMR studies and Dr Keith Fisher for recording the ESI-MS. We are grateful to Johnson-Matthey for the generous loan of $K_2[PtCl_4]$ and the Australian Research Council for financial support.

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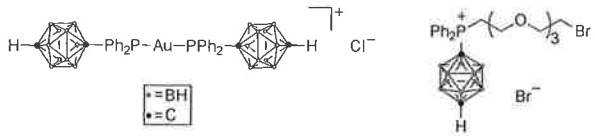
Carborane-Containing Phosphonium Salts and Gold(I)-Phosphine Complexes for Boron Neutron Capture Therapy and Tumour Imaging

J. A. Ioppolo[1], M. Kassiou[1,2,3], L. M. Rendina[1]
1. *The University of Sydney, Sydney, Australia. Email j.ioppolo@chem.usyd.edu.au*
2. *Discipline of Medical Radiation Sciences, The University of Sydney, Sydney, Australia.*
3. *Brain and Mind Research Institute, The University of Sydney, Sydney, Australia.*

Gold(I) complexes (e.g. $[Au(dppe)_2]Cl$) and arylphosphonium salts such as methyltriphenylphosphonium (TPMP) iodide are known to accumulate selectively in the mitochondria of cancer cells. For the latter, *in vivo* and *in vitro* uptake studies have shown a high tumour : healthy tissue ratio (~ 40 : 1) for these agents which is approximately an order of magnitude more selective than clinical agents for Boron Neutron Capture Therapy (BNCT). Gold(I) complexes and phosphonium salts containing containing dicarba-*closo*-dodecaborane(12) (carborane) can act as new cancer-selective, boron delivery agents to mitochondria, organelles that play a critical role in the regulation of apoptosis.[1]

The preparation and characterisation of a number of phosphonium salts and gold(I) complexes containing *closo*-carborane and anionic *nido*-carborane cages are presented. We have recently reported the synthesis, characterisation, and cell-uptake studies of some of these compounds.[2,3] These include Au(I) complexes of the boronated phosphine ligand $1\text{-}PPh_2\text{-}1,12\text{-}C_2B_{10}H_{11}$ as well as boronated phosphonium salts including $[CH_3PPh_2\text{-}1,12\text{-}C_2B_{10}H_{11}]I$ and a highly water-soluble derivative containing a tetraethyleneglycol chain $[PPh_2(1,12\text{-}C_2B_{10}H_{11})((CH_2CH_2O)_3CH_2CH_2Br]Br$. The key results of this work will be presented.

Acknowledgements: We would like to thank the Australian Research Council, Cure Cancer Australia Foundation and the National Breast Cancer Foundation for supporting this research program.



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In –Vitro Cytotoxicity Studies of Vanadyl(VO) Complexes with Hydroxamic Acid Series

K. Kassim [1], H. Bahron[1], S. N. Shotor[1], A. M., Tajuddin[1], S. R. S. Omar[1], F. Z. Yusof[1], S.K. Yong[1] and C.J. Marmion[2]

1. *Department of Chemistry, Faculty of Applied Sciences,Universiti Teknologi MARA, 40450 Shah Alam, Malaysia.*
2. *School of Pharmacy, Royal Collage of Surgeons of Ireland.*

The complexes of V(IV) hydroxamic acids derivatives namely acetohydroxamic acid (AHA), benzohydroxamic acid (BHA) and salicylhydroxamic acid (SHA) have been successfully syhthesized. All the synthesized compounds were characterized using elemental analysis, infrared spectroscopy, NMR spectroscopy and magnetic susceptibility measurement.

Through infrared investigation, it was suggested that the hydroxamic acids coordinated to the metal centeres as O,O bis-bidentate ligands, acting as single deprotonated hydroxamato moieties. The magnetic susceptibilities measurements indicated that the vanadyl(VO) complexes were diamagnetic. Upon *in-vitro* cytoxicity investigation using MTT assay on Chang liver cells, all the ligands were found to be non-toxic whereas the vanadyl(VO) complexes were mildly toxic with the lowest cell viability of 54.9% after 72 hours of exposure to the compounds.

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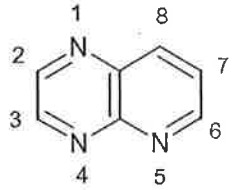
New rigid porous coordination polymers with a mixed-valence Cu as bridging metal

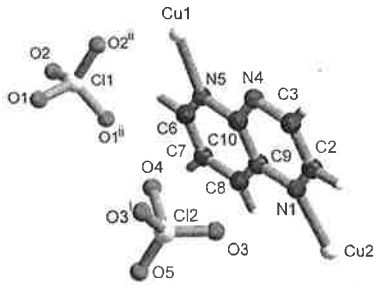
G. A. van Albada,[1] M. Ghazzali,[2] K. Al-Farhan[2] and J. Reedijk[1,2]

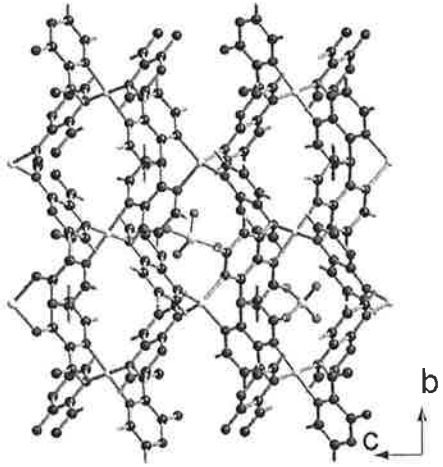
1. *Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands*
2. *College of Science, King Saud University, P.O. Box 2455 Riyadh 11451, Kingdom of Saudi Arabia*

In a search for new rigid coordination polymers we have undertaken a study with the trifunctional, asymmetric ligand 1,4,5-triazanaphthalene (tan). Under aerobic conditions either mononuclear or polynuclear Cu(II) compounds are formed depending on the conditions and used anion [1]. In the polynuclear compounds the ligand either uses N1 and N4 to bridge, or N1 and N5 to bridge between metal ions.



When using Cu(II) and a non-coordinating anion, like perchlorate, with this ligand it was aimed that all 3 N-donor atoms could bind to 3 different metal ions. Surprisingly, however, a red-colored mixed-valent compound of stoichiometry $Cu_2(tan)_4(ClO_4)_3$ is isolated from EtOH, which appeared to be an unprecedented copper species, in which Cu(I) is tetrahedrally coordinated by 4 different ligands via N5, and Cu(II) is square planar coordinated by 4 different ligands via their N1. So each ligand is bridging between a Cu(I) and a Cu(II). The nitrogen N4 is not coordinated. The empty spaces are filled by 3 non-coordinating perchlorates (2 independent ones), leaving 29% of the remaining spaces not filled. Details of the unique 3D structure and the properties of the compound will be presented.





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Studies On Metal Complexes and Metal Capacity of A Newly Synthesized Chelating Resin Bearing (2, 2'–ethylenedithio)diethanol

A. Z. Alasar, A. H. Bu-Olian , and A. El-Dissouky*
Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, State of Kuwait. email: alieldissouky70@yahoo.com

Abstract:
Water contamination by metals is of great importance from a health point of view because of its high toxicity and susceptible carcinogenic effect. The threat to mankind comes from the accumulation of such non-biodegradable ions in water and solid polluted by contaminant from mining and industry. Recently the solid phase extraction (SPE) has emerged as a powerful tool to enrichment/separation because of its advantages[1-4]. The SPE method needs a chelating resins because of their multi-coordinating functions [4,5]. Therefore, 2, 2'– (Ethylenedithio)diethanol (EDTDE) was loaded on Amberlite XAD-16 through -SO_2 linker to give the new chelating resin AXAD-16-EDTDE. Its complexes with, Cu(II), Ni(II),Co(II), Cd(II), Pb(II), Hg(II) and Fe(III) were synthesized and characterized by elemental analyses, spectral (FT-IR, Uv/Vis and ESR, XRD), magnetic studies and thermal behavior. Characterization of the surface modification was also performed with SEM, EDX, EDS, AMF and BET, BJH techniques. The resin was subjected for the separation and determination of the concentration of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Hg(II) and Fe(III) ions from aqueous medium by batch and column methods and the concentration of the metal ions were measured by ICP-OES and ICP-MS. A comprehensive sorption study (kinetic isotherm and thermodynamics) of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Hg(II) and Fe(III) removal from synthetic and real water samples by sorption on AXAD-16-EDTDE was conducted regarding the effects of pH, shaking time, initial metal ion concentration, concentration of eluting agents, flow rate, temperature. recommended method was also successful in determination metal ions down to the limit of ng mL-1. Furthermore, the data showed that AXAD-16-EDTDE can be considered as promising and competent to most of the resins reported for determination and preconcentration of the investigated metal ions.

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The Investigation of New Dinuclear Cobalt Complexes with Redox-Active Ligands

K. G. Alley[1], P. S. D. Robinson[1], C. Ritchie[1], A. Nafady[2], B. Moubaraki[2], K. S. Murray[2], A. M. Bond[2],C. Boskovic[1]
[1] School of Chemistry, University of Melbourne, Victoria, 3010, Australia; kalley@unimelb.edu.au
[2] School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia

Valence tautomerism is a phenomenon observed for certain metal complexes, where a reversible intramolecular electron transfer occurs between a metal centre and a redox-active ligand, resulting in systems that can exist in two tautomeric forms. Temperature, pressure, X-rays and irradiation have been shown to drive the conversion between the tautomers.
[1] These complexes may ultimately find application asmolecular sensors or switches.

Many mononuclear valence tautomeric complexes and a small number of dinuclear valence tautomeric complexes have been reported to date. One of the most interesting is the dinuclear complex, $[Co_2(TPA)_2(dhbq)](PF_6)_3$, (dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone; TPA = tris(2 -pyridylmethyl)amine), which was found to display thermally induced valence tautomerism with a large hysteresis around room temperature.[2] Polynuclear valence tautomeric complexes such as this suggest the possibility of more than two accessible tautomeric states.

Our search for polynuclear valence tautomeric complexes has involved the use of new redox-active ligands as bridges between metal centres. We will present structural, magnetic, lectrochemical and spectroscopic investigations of new dinuclear cobalt complexes bridged by the bis-catecholate ligand 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol ($spiroH_4$) (Figure 1). The significant effect that derivatisation of the TPA capping ligand has on the redox state of the complexes will also be examined.

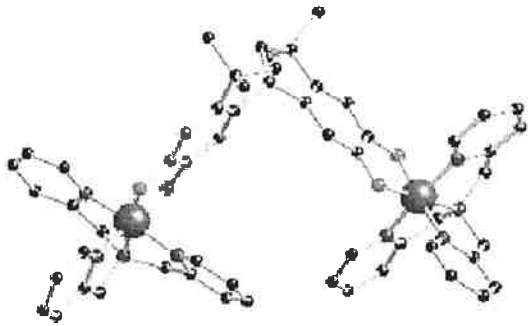

Figure 1. $[\{Co(TPA)\}_2(spiro)]^{2+}$

Acknowledgements: We thank the Australian Research Council and University of Melbourne for funding.

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Quadratic optical nonlinearities of dipolar alkynylruthenium complexes with phenyleneethynylene/phenylenevinylene and oligo(phenyleneethynylene) bridges

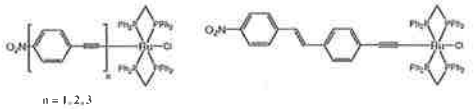
B. Babgi,[1] L. Rigamonti,[2] M. P. Cifuentes,[1] I. Asselberghs,[3] K. Clays,[3] and M. G. Humphrey,[1,*]

1. *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia. Dipartimento di Chimica Inorganica, Metallorganica e Analitica "L. Malatesta", Università degli Studi di Milano, via Venezian 21, 20133 Milano, Italy.*
2. *Department of Chemistry, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium.*

Nonlinear optical (NLO) properties of organometallic materials have attracted significant interest, particularly metal alkynyl complexes for which earlier research studies have explored structure-related NLO properties. Previous studies have shown:

[1] An increase in the second-order nonlinearity when the bridge length increases from n = 1 to 2 and then to 3 for the complex below left.[1]

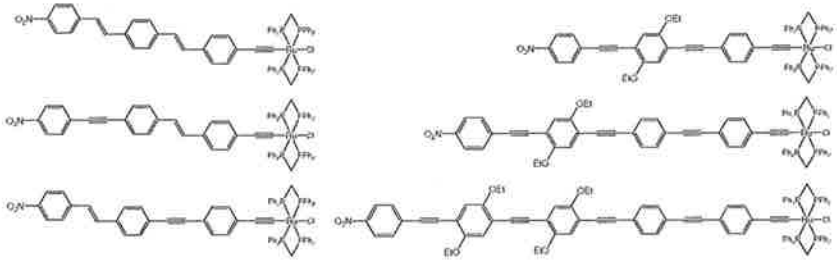
[2] An increase in the second-order nonlinearity upon replacing one ethynyl linkage by an ethenyl linkage for the example where n = 2 in the diagram below right.[1]



We have now extended these studies and have:

[1] examined the effect of extending the chain further (n = 4, 5). Preliminary studies have shown a dramatic decrease in the solubility which necessitates the incorporation of alkoxy groups (solublising groups). The nonlinear optical properties saturate at the trimer.[2]

[2] examined the impact of of replacing ethynyl linkages with ethenyl linkages in different sites on the bridge and the replacement of more than one ethynyl linkage. Such modifications leads to dramatic changes in nonlinear optical properties.[3]



Acknowledgements: We thank the Australian Research Council for support of this work. MGH is an ARC Australian Professorial Fellow, MPC is an ARC Australian Research Fellow, and BB thanks King Abdulaziz University for sponsorship.

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EGTA Complexation with Dioxovanadium(V) at Different Ionic Strengths by Using Bronsted-Guggenheim-Scatchard Specific Ion Interaction Theory

K. Majlesi, A. Rouhzad

Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran, kavoshmajlesi@gmail.com

Metal ion chelators like ethylene glycol-bis(2-aminoethyl)-N, N, N´, N´- tetraacetic acid (EGTA) widely used in experimental protocols and clinical diagnosis. The effect of EGTA on the microhardness of root canal dentin has been reported. EGTA has been also used for stabilizing different shapes of silver nanoparticles. Vanadium complexes show insulin-like effects which have been demonstrated both in vivo and in vitro. Therapeutic use of vanadium complexes is thus promising.

In previous works [1-4] we took into account the interaction of VO_2^+ and MoO_4^{2-} ions with different aminopolycarboxylic acid ligands at different ionic strengths and non aqueous solutions. Now one more ligand has been considered, EGTA, that in addition to the carboxylate donor groups, contains etheric oxygen which can interact as well with the VO_2^+ ion. Both potentiometry at different ionic strengths and UV spectrophotometry have been employed in order to better characterize the species in solution. Two species, VO_2H_3L and VO_2H_2L, were identified. Measurements have been made at 25 °C and different ionic strengths of sodium perchlorate ($0.1 < I / mol.lit^{-1} < 1.0$). Results were analysed in terms of their dependence on the ionic strength dependence by using Bronsted-Guggenheim-Scatchard specific ion interaction theory (SIT). In this research, the classic SIT model was used instead of the two parameter SIT model proposed in the literature, owing to the short ionic strength interval here investigated. Calculations performed using the two parameters model showed no improvement. Finally a comparison with other aminopolycarboxylic acid complexes and thermodynamic models was made.

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Assembling Mixed-valence Complexes: A Strategy toward Molecular Quantum Cellular Automata Cells

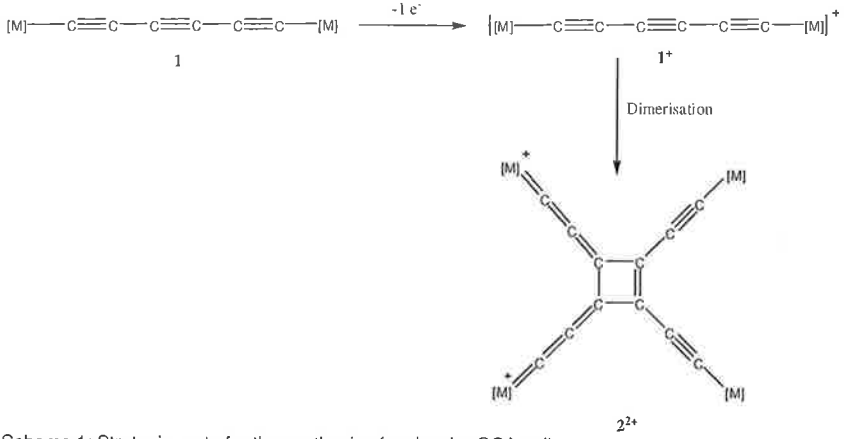
A. Burgun,[1,2] M. I. Bruce,[1] K. Costuas,[2] F. Gendron,[2] J. F. Halet,[2] C. Lapinte[2]
1. *School of Chemistry & Physics, University of Adelaide, South Australia, 5005, Australia*
2. *Laboratoire Sciences Chimiques de Rennes, Université de Rennes1, Campus de Beaulieu, CNRS, 35042 Rennes, Cedex, France. E-mail: alexandre.burgun@univ-rennes1.fr*

Organometallic complexes containing π-conjugated carbon chains linking transition-metal centres are of great interest in contemporary research because of their possible involvement in nanoscale devices as, or as models for, molecular wires[1] or memories.[2]

We are focussing our attention on molecular Quantum Cellular Automata (QCA) Cells which is a new approach to store binary information in the charge configuration of a single molecule. A QCA cell containing two quantum dots is a mixed-valence complex when scaled to molecular sizes.[3] In this context, we are focussing our efforts on the synthesis of organometallic complexes containing metal atoms as dots, and carbon bridges as conjugated linkers (**1**, Scheme 1).

Upon one electron oxidation, mixed-valence states are generated and, depending upon the electronic properties of the metal building blocks, the reactivity of **1**$^+$ can be controlled. Taking advantage of these properties and guided by DFT calculations, intermolecular carbon-carbon bond formation allows access to tetranuclear species like **2**$^{2+}$, which constitute interesting target molecules for models of QCA cells.

The synthesis, characterisation, electronic structures and some properties of these new compounds will be reported.



Scheme 1: Strategic route for the synthesis of molecular QCA cell.

Acknowledgements: A. B. thanks the University of Adelaide and the Université de Rennes1 for a co-tutelle PhD joint program.

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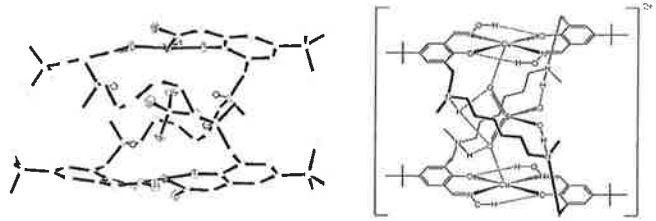
Salicylaldoxime Derivatives as Potential Pressure-Selective Extractants

P. J. Byrne, J. Y. Chang, R. S. Forgan, S. Parsons, P. A. Tasker
School of Chemistry, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, Scotland, EH9 3JJ, UNITED KINGDOM

The progresses from pyrometallurgy into hydrometallurgy have reduced significantly the aerial pollutants in the metal mining operations. Nevertheless, the large consumption of organic and halogenated solvents involved in hydrometallurgy calls for further developments into making the processes more efficient and be more environmentally friendly. Salicylaldoximes account for almost a quarter of the world's production of copper. Their extraction strength is heavily influenced by the 3-substituent of the phenolic ring.[1] In addition, the central coordination moiety of the pseudomacrocyclic ring formed also varies upon the applied pressure.[2]

These phenomena prompted us to investigate whether pressure can impart selectivity in both cation and anion sequestrations using salicylaldoxime-based metal extractants. A bis-salicylaldoxime ligand containing a flexible 6-methylene carbon linkage was prepared for this investigation and at 1:1 stoichiometry, dinuclear complexes of copper(II) and nickel(II) were isolated.[3] The metal-only complex shows extension of the methylene linkages. Upon protonation of the nitrogen donors in the linkage units, the complex contracts around the anion and encapsulates it more effectively as illustrated by x-ray crystallography. Anion chromatography analyses show varying degree of uptakes among the anions as well as uptake preferences between copper(II) and nickel(II). Recently, a hexanuclear complex of copper(II) was reported[4] and is currently under active investigation for its anion binding ability. The syntheses of these novel cage complexes and their corresponding anion uptake studies at ambient pressure will be presented.



Acknowledgements: This work is supported by grants from Engineering and Physical Sciences Research Council (EPSRC).

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A novel Re(IV)-pyrazinecarboxylate complex as building block for polynuclear compounds: X-ray structures and magnetic properties

L. Arizaga[1], D. Armentano[2], G. De Munno[2], M. Novak[3], C. Kremer[1], R. González[1], R. Chiozzone[1].

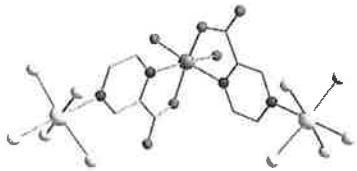
1. *Cátedra de Química Inorgánica, Facultad de Química, Universidad de la República, Montevideo, Uruguay, rchiozzo@fq.edu.uy*
2. *Dipartimento di Chimica, Università della Calabria, Cosenza, Italia*
3. *Instituto de Fisica, Departamento de Fisica da Materia Condensada, Universidade Federal do Rio de Janeiro, Brasil*

Heterobimetallic $Re^{IV}M^{II}$ compounds (M^{II} = divalent first-row transition metal ion) are examples of mixed 3*d*-5*d* systems whose structures and magnetic properties have been subject of investigation during the last decade. A successful strategy for their design has been the rational "complex as ligand" approach, where a fully solvated transition metal cation or a preformed complex whose coordination sphere is insaturated is allowed to react with an inert rhenium(IV) complex containing at least one potential bridging ligand.

We have prepared a stable mononuclear rhenium(IV)-containing building block of formula $[ReCl_5(pyzc)]^-$ (pyzc = 2-pyrazinecarboxylate anion). Pyrazinecarboxylate is a well-known versatile organic ligand which can bridge metal ions to construct discrete or extended structures, as well as mediate magnetic interactions between them.[1]

The use of $[ReCl_5(pyzc)]^-$ as ligand has provided dinuclear $Re^{IV}M^{II}$ (M = Ni, Co) and trinuclear $Re^{IV}M^{II}Re^{IV}$ (M = Ni, Co, Fe) compounds, depending on reactants ratios and auxiliary ligands bonded to the M^{II} ion.

We report here the synthesis and molecular structure of these new compounds. Magnetic properties are discussed on the basis of isotropic exchange and local anisotropy of participant ions.



Perspective drawing of the trinuclear unit $\{[ReCl_5(\mu\text{-pyzc})]_2Fe(H_2O)_2\}^{2-}$

Acknowledgements: To the Comisión Sectorial de Investigación Científica (CSIC-UdelaR) and the Agencia Nacional de Investigación e Innovación (ANII) (Uruguay).

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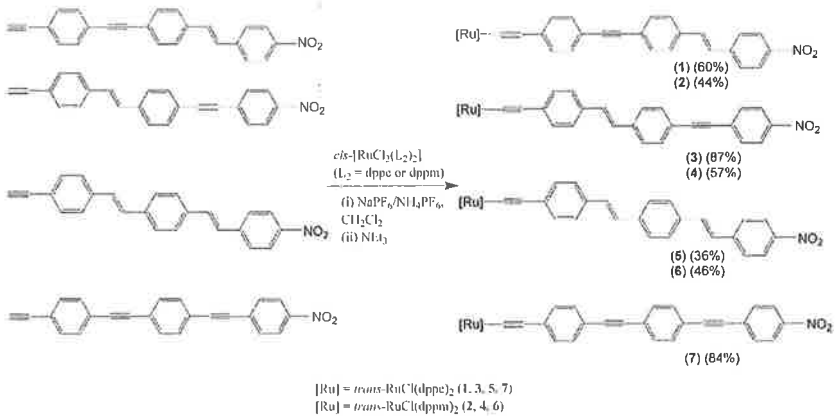
Metal-Containing Oligo(phenyleneethynylene)s: Syntheses and Nonlinear Optical Properties

M. P. Cifuentes[1], M. G. Humphrey[1], M. Samoc[2], B. Babgi[1], G. T. Dalton[1], L. Rigamonti[1]

1. *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia. E-mail: Marie.Cifuentes@anu.edu.au*
2. *Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, 50-370 Wroclaw, Poland.*

Oligo(*p*-phenyleneethynylene)s (OPEs) have been of considerable interest in recent years. Introduction of ligated metal units into an OPE structure can add a new dimension: the resultant transition metal OPE complexes can potentially possess a number of useful properties such as luminescence, reversible redox chemistry and accessible mixed valence states. Such complexes have been examined for molecular electronics and liquid crystal applications, but physical properties of series of systematically-varied metal-terminated OPEs are yet to be explored. We report here syntheses of a series of metal-terminated OPEs (up to a hepta(phenyleneethynylene)), and examples with phenylenevinylene segments (see below), the evolution of linear optical properties in metal-containing OPEs and hybrid OPE/OPVs (oligo(phenylenevinylene)s) upon chain lengthening, and a wavelength-dependence study of the cubic nonlinear optical (NLO) properties of metal-containing OPEs by fs Z-scan measurements.[1-3]



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Synthesis, Structural and Modelling Studies of (η^6-cymene)osmium(II) Complexes

H. S. Clayton[1], D. C. Liles[2], J. R. Moss[3]

1. *Chemistry Department, University of South Africa, Pretoria, 0003, South Africa*
2. *Chemistry Department, University of Pretoria, Pretoria, 0002, South Africa*
3. *Chemistry Department, University of Cape Town, Rondebosch, 7701, South Africa*

Osmium complexes bearing arene ligands have long been known and have been used in the preparation of osmium catalyst precursors for ring-closing, ring-opening and cross-metathesis [1]. These complexes have also been shown to exhibit C-H bond activation behaviour [2] as well as being useful catalysts for the cyclopropanation of olefins [3]. In addition, these complexes have also been shown to exhibit anticancer properties [4].

A series of compounds of the general formula [(η^6-cymene)Os(L)Br_2] (L = PMe_3; PEt_2Ph; PPh_3; $P(OMe)_3$;$P(OEt)_3$; $P(O^iPr)_3$; $P(O^nBu)_3$; $P(OPh_3)$) have been prepared and characterized structurally by single crystal X-ray diffraction[5]. Some computational results of a DFT analysis of the binding of the phosphorus ligands are also reported.

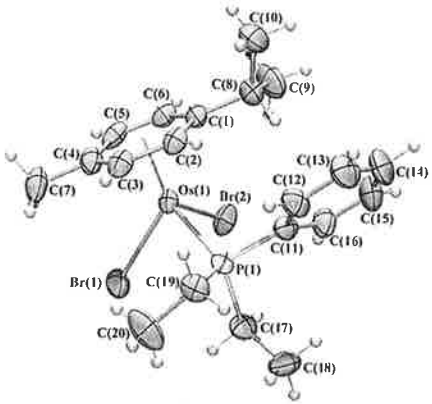

Figure 1. Molecular diagram of (η^6-cymene)Os(PEt_2Ph)Br_2

Acknowledgements: This work was supported by the University of South Africa, the University of Cape Town and the National Research Foundation.

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Towards Versatile Functional Metal-Organic Frameworks

R. S. Crees[1], C. J. Sumby[1], M. L. Cole[2], L. R. Hanton[3]

1. *School of Chemistry & Physics, The University of Adelaide, Adelaide, Australia*
2. *School of Chemistry, University of New South Wales, Sydney, Australia*
3. *Department of Chemistry, University of Otago, Dunedin, New Zealand*

Metal-organic frameworks (MOFs) are recognised as potentially superior to other porous solids such as zeolites and oxides because of their uniformity, high porosity and large internal surface area [1]. These unique characteristics may render MOFs capable of superior performance over existing materials in functions as such as separation, catalysis and storage. The characteristics of a MOF can be targeted pre-assembly by selecting organic 'links' and inorganic 'nodes' to direct the shape, size and chemistry of the framework cavities.

Accordingly, we have designed a set of ligands which feature chemically-active cores flanked by peripheral donor groups for bridging structural metals. The target ligands are based on imidazolium salt cores due to the known activity [2] of N-heterocyclic carbenes (NHCs), as either an organocatalyst or as part of an embedded organometallic catalytic moiety, into which the imidazolium can be converted.

In our hands, the first successful assembly of such a coordination polymer involved the reaction of 1,3-bis(3-carboxyphenyl)imidazolium bromide with zinc nitrate to yield a one-dimensional (1D) MOF containing the intact imidazolium salt [3]. The potentially porous structure, formed from close packing of the 1D necklace-type polymers, contains channels occupied by disordered DMF solvate molecules. A formate anion also bridges the zinc secondary building units in the 1D polymer, which has an undulating structure resulting from the U-shaped conformation of the dicarboxylate imidazolium ligand.

The 4-substituted analogue of this ligand has been synthesised, as have the 3- and 4-cyano substituted derivatives. Work is continuing on assembling MOFs from these related ligands. Extending the series to investigate the effect of introducing steric bulk at the 4,5-positions of the imidazolium ring is also underway.

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Odd-Even Effect Observed in the Bending Alkyl Chain of Asymmetric Quaternary Ammonium Cations of $[Ni(dmit)_2]^-$ Salts in Crystalline State

K. Dai, K. Tomono, K. Miyamura
Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
E-mail: j1307706@ed.kagu.tus.ac.jp

Since physical properties of materials depend on the molecular arrangement in crystals, systematic and thorough research on the molecular design with intra- and intermolecular interaction is required to predict the crystal structure. In this point of view, we have been exploring a method to control $[Ni(dmit)_2]^-$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) arrangement using hydrophobic interaction of cations with alkyl chains. As shown in our previous report [1], two dioctadecyldimethylammonium cations pack in tail-to-tail manner to form biomembrane-like bilayer structure in the crystal of $[Ni(dmit)_2]$ salt. As a result, the crystal of dioctadecyldimethylammonium-$[Ni(dmit)_2]$ salt has been found to be composed of alternate sheets of $[Ni(dmit)_2]^-$ anions and sheets of cations. In other words, the use of hydrophobic interaction is able to control the alignment of molecular anions.

In this study, the crystals of $[Ni(dmit)_2]^-$ salts with asymmetric quaternary ammonium (alkyldimethyloctadecyl ammonium (C18C*n*) ; C*n* = alkyl chain length ; *n* = 1-18) in figure 1a were synthesized and characterized by single crystal X-ray analysis. All complex salts have been found to be composed of alternate sheets of $[Ni(dmit)_2]^-$ anions and sheets of cations. In addition, the conformation of cation significantly changed according with the change of the alkyl chain length. As a result, two types of regions were found depending on the alkyl chain length. In the conformation of cations, the opened structure gradually changed to the closed structure. Whereas the cations with short alkyl chain (C18C1-C7) formed opened structure which is composed of two all-trans alkyl chains; the cations with medium and long alkyl chain (C18C8-C18) formed closed structure in which one of the two long alkyl chains adopted gauche conformation. However, the opened structure differed between two groups of medium (C18C8, C18C9) and long (18C10-C18) alkyl chain length. While the longer chain of two alkyl chain invariably bent in the group of medium alkyl chain, the bending alkyl chain differed between odd and even number of carbon atoms in the group of long alkyl chain (see figure 1b).

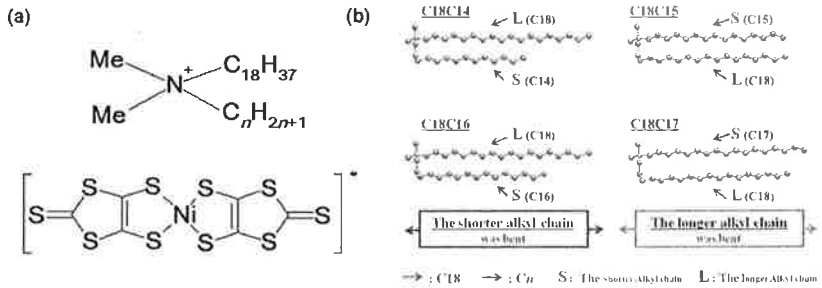

Figure 1. (a) Structural formula of C18C*n*. (b) The conformations of the cations (C18C14-C17) with long alkyl chain.

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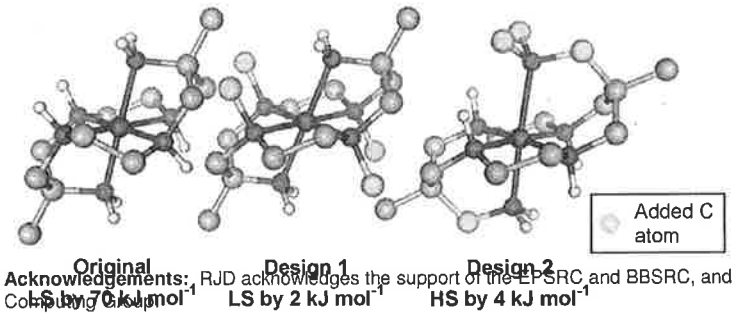
Towards the Rational *in Silico* Design of New Spin-Crossover Materials

R. J. Deeth, A. E. Anastasi and M. J. Wilcockson
Department of Chemistry, University of Warwick, U.K. E-mail: r.j.deeth@warwick.ac.uk

Certain Transition Metal (TM) centres can support more than one spin state. Six-coordinate Fe(II), for example, may be high spin (HS) (S=2) or low-spin (LS) (S=0). With the right ligand, a change in spin state can be effected by varying the temperature and/or pressure, or by absorbing light. The archetypal Fe(II) spin crossover (SCO) complex, $[Fe(NCE)_2(phen)_2]$, E = S or Se, was reported 50 years ago but its SCO behaviour was only discovered accidentally three years later. Since then, more than 400 ligand systems have been reported which support SCO but they virtually all conform to the original FeN_6 paradigm.[1] The reason is simple. SCO, and the related Light Induced Excited Spin State Trapping (LIESST), are very sensitive phenomena. Minor variations in conditions or ligand can shift the SCO regime to an inaccessible temperature. The major drawback of experiment is that the energy of the 'other' spin state is unknown. Hence, we have no way of knowing how far from the SCO divide we are nor what ligand modification might bring us back. Given that the theoretical interpretation of SCO is based on the Tanabe-Sugano diagram for d^6 octahedral systems where the only variable is Δ_{oct}, we are forced to use the ligand set which we know works. Consequently, we are stuck in the existing FeN_6 paradigm. In order to break free, we need to know where the other spin state is. The only practical way forward is to calculate it but this creates a whole new set of problems. Modern quantum chemistry in general, and Density Functional Theory (DFT) in particular, is quite capable of providing a good description of spin-state energy differences in Fe(II) complexes but *ALL* QM methods, including DFT, are relatively slow. Our problem is akin to drug discovery where a typical 'virtual screen' involves hundreds of thousands of compounds. DFT simply is not practical. In response, therefore, we have developed Ligand Field Molecular Mechanics (LFMM)[2] which combines the speed of classical MM with a sophisticated treatment of M-L σ and π bonding based on the Angular Overlap Model of Ligand Field Theory. SCO is a particularly 'ligand field' problem which we have validated against experiment and DFT for a series of Fe-am(m)ine complexes. By training the LFMM parameters against experimental and computed data for representative model complexes including, crucially, DFT estimates of the structures and energies for *both* spin states, LFMM delivers DFT accuracy up to four orders of magnitude faster. We illustrate the potential of LFMM by suggesting modifications to existing Fe-amine complexes which are clearly *not* SCO to give new species which might be. For the first time, we have a viable computational tool for SCO ligand discovery which could pave the way to whole new classes of complex previously thought incapable of supporting SCO. Their potential application in display devices, data storage, and sensors could be enormous.



Acknowledgements: RJD acknowledges the support of the EPSRC and BBSRC, and Chemical Computing Group.

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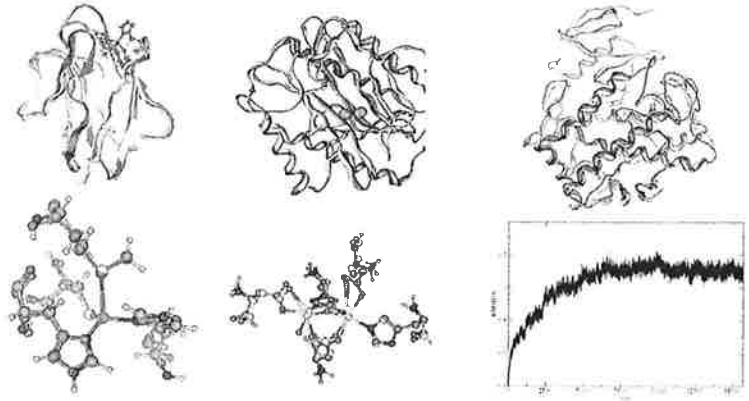
Bioinorganic Molecular Modelling: Transition Metal-Protein Interactions

R. J. Deeth and C. Diedrich
Department of Chemistry, University of Warwick, U.K. E-mail: r.j.deeth@warwick.ac.uk

Transition metal centres are ubiquitous in biology. They mediate diverse functions in electron transport, catalysis, oxygen transport and structural chemistry. Although present in relatively small quantities in living organisms, their distribution and concentration must be very carefully regulated. Many TMs bind readily to bio-macromolecules such as proteins. Proteins are exquisitely complicated and offer unparalleled levels of selectivity and catalysis but, from a coordination chemistry perspective, they are quite simple ligands. They have only a small number of donor types and while their number and disposition may be challenging to mimic in a small-molecule analogue, the essential nature of M-L bonding in metalloproteins is the same as in classical coordination chemistry. Nevertheless, the perception that TM systems are inherently 'difficult' has had a severe effect on theoretical bioinorganic systems. Compared to carbon chemistry, TM systems have high coordination numbers, variable oxidation and spin states, and generally complicated electronic structures. These features appear to demand a quantum mechanical treatment but QM is far too slow to treat systems as large and conformationally flexible as proteins. Even hybrid QM/MM schemes cannot presently be used for much more than geometry optimisation and long molecular dynamics simulations are out of the question. In contrast, classical approaches like Molecular Mechanics (MM) are fast enough but poorly suited to TM systems. Consequently, the biosimulation community largely avoids TM systems. What we need is a model which even for TM systems delivers the same accuracy as (or better than) QM at a small fraction of the computational cost. Ligand Field Molecular Mechanics (LFMM) is such a method. By combining the speed of conventional MM with a physically reasonable model of M-L bonding provided by the Angular Overlap Model from Ligand Field Theory, we get the best of both worlds – QM accuracy at MM prices. This enables LFMM to go where QM cannot easily follow. The power of LFMM is illustrated with respect to oxidised Type 1[1] and Type III copper proteins, including a 16 ns LFMD simulation of tyrosinase,[2] and the dimanganese sites of methionine aminopeptidase (MetAP).[3]



Plastocyanin **MetAP** **Tyrosinase**

Acknowledgements: RJD acknowledges the support of the EPSRC and BBSRC, and Chemical Computing Group.

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The *many faces* of the *silicon in* η^2-olefin-complexes of copper(I) chloride

T. Dużak, V. V. Olijnyk
1. *University of Opole, email: tomasz.duzak@pwr.wroc.pl*
2. *University of Opole, email: wlodzimierz.olijnyk@uni.opole.pl*

The use of alkenylsilanes and alkenylsiloxanes as ligands in d^{10} metal η^2-olefin-complexes attracts a lot of attention ***of*** academics as well as practitioners. It is reasonable to investigate such coordination systems since they serve as reactive precursors for the preparation of ***naked metal*** nanoparticles or catalysts and also as ***sensitive coatings of*** piezoelectric sensors. However, it is complicated or even impossible to structurally characterize such systems as far as they are ***nanosystems***. Therefore, we have made an effort to build a small complexes with mono- and oligomeric silicon-containing ligands as model of alkenyl polysiloxane d^{10} metal adducts. Some of such unsaturated molecules (tetravinylsilane, divinyltetramethyldisiloxane, dimethyltetravinyldisiloxane, tetraallylsilane, diallyldimethylsilane) have been used for the construction of different copper(I) chloride complexes in the present work. The synthesized crystal complexes were examined by X-ray diffraction and IR spectroscopy. The obtained data showed that the silicon ligand changes the efficiency of the Cu…C=C interaction. Thus, the consideration of $d_{Si} \leftarrow \pi^*_{C=C} \leftarrow d_{Cu}$ conjugate system may help to understand the influence π–acceptor properties of silicon on the ***degree of trigonal distortion of the Cu(I) coordination tetrahedron*** as well as on the inorganic part organization. Moreover the importance of the inorganic part and ligand symmetries combined with their conformational abilities on the overall crystal symmetry is discussed. The present studies are aimed at the use of the structure controlled ***nanoparticles supported on alkenyl-modified silicon (or silicone) substrate***.

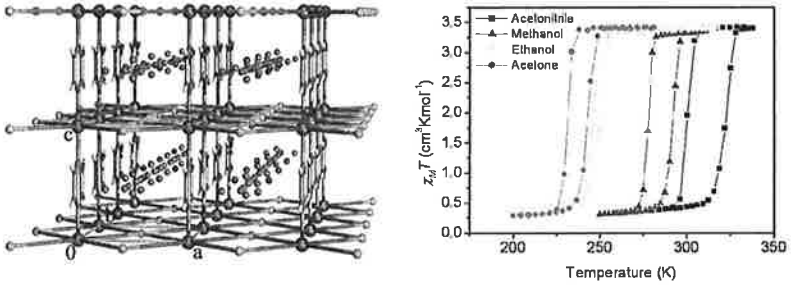
Dynamic Interplay between Spin Crossover and Host-Guest Function in Porous Coordination Polymers

E. A. Fellows[1], P. D Southon,[1] L. Liu,[1] D. J. Price,[1] B. Moubaraki,[2] K. S. Murray,[2] C. J. Kepert[1]
1. *The University of Sydney, New South Wales, Australia, elizabeth.fellows@sydney.edu.au*
2. *Monash University, Victoria, Australia*

Porous coordination polymers (also commonly known as metal-organic frameworks) have received widespread attention due to their rich host-guest interactions and chemical versatility. This field has undergone extensive advancement in recent years with efforts to design framework materials that have highly specific properties, such as selective guest sorption/desorption, electronic and magnetic function, gas storage and negative thermal expansion.[1]

The family of materials $Fe(L)M(CN)_4 \cdot x(guest)$ (M = Ni, Pd, Pt) (Figure 1a) has been investigated for spin crossover (SCO). The incorporation of SCO centres into such framework structures opens the question of whether molecular guests may be encapsulated into these materials, and whether the reversible exchange of these guests may provide a novel mechanism to perturb their electronic switching properties (and vice versa).[2]

By utilizing a number of magnetic, scattering, thermogravimetric and spectroscopic techniques, we have established that these materials show dynamic interplay between the spin transition and its host-guest function (Figure 1b), that is, SCO-induced guest sorption and guest-induced SCO.[3] More recently, we have discovered unprecedented guest-induced physicochemical properties including multistep and unusual hysteresis.



a) b)

Figure 1: a) The crystal structure of $Fe(pyrazine)M(CN)_4.xH_2O$; b) guest-dependent SCO of $Fe(pyrazine)Ni(CN)_4.x(guest)$.

Acknowledgements: EAF would like to acknowledge an AINSE Postgraduate Research Award.

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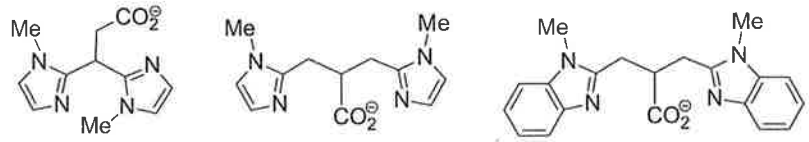
Imidazole based *N,N,O* Ligands

N. V. Fischer,[1] V. Dremov,[2] M. Stocker,[2] U. Mitra,[2] P. Müller,[2] N. Burzlaff[1]

1. *Inorganic Chemistry, Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), University of Erlangen-Nürnberg, Egerlandstraße 1, D-91058, Erlangen, Germany; e-mail: nina.fischer@chemie.uni-erlangen.de*
2. *Department of Physics, University of Erlangen-Nürnberg, Erwin Rommel-Str.1, D-91058 Erlangen, Germany.*

Tripodal, pyrazole-based heteroscorpionate ligands such as bis(pyrazol-1-yl)acetic acid (Hbpza) and its derivatives have been proved to be versatile ligands in the field of coordination chemistry as well as in bioinorganic chemistry.[1] Recently, the work of our group and others has focused on the synthesis of imidazole based tripodal ligands such as bis(*N*-methylimidazol-2-yl)propionic acid (Hbmip) and bis(*N*-methylimidazol-2-yl)ethanol (Hbmie).[2-4] Here, we report on the synthesis of bis(*N*-methylimidazol-2-ylmethyl)acetic acid (Hbmima) and bis(*N*-methylbenzo-imidazol-2-ylmethyl)acetic acid (Hbmima^{bo}) as new tridentate *N,N,O* ligands. Complexes bearing these ligands as well as coordination polymers thereof will be presented and are studied by STM and AFM.



bmip bmima bmima^{bo}

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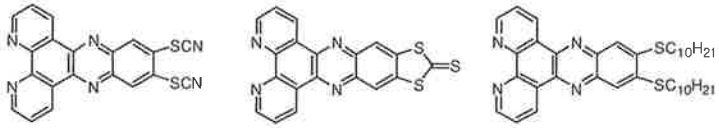
The Effect of Sulfur-based Substituents on the Electronic Properties of Re(I) dppz complexes.

M. Fraser, A. Blackman and K. Gordon
MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, Dunedin, New Zealand

Complexes incorporating dipyrido[3,2-a:2',3'-c]phenazine (dppz) and its derivatives have been the subject of extensive investigation because they possess interesting photophysical properties. One striking example of this is the observation that some dppz complexes exhibit a "light switch effect", being highly emissive in aqueous solution in the presence of DNA but non-emissive in normal aqueous solution.[1] Theoretical and photophysical studies suggest that the excited states of Re(I) complexes with dppz-type ligands contain closely lying ligand centered (LC) and metal-to-ligand charge-transfer (MLCT) states of differing orbital parentage. The orbital parentage of electronic transitions in dppz has been the subject of some early theoretical investigations which remain the current thinking on the electronic structure
of the ligand.[2] A series of sulfur-substituted dipryidophenazine (dppz) -based ligands and their Re(I)(CO)3Cl complexes are reported. The sulfur-substituted ligands (Figure 1) and complexes show interesting electronic properties atypical of dppz-type systems. Substitution of dppz with thiocyanate (SCN) groups results in typical behaviour of an electron withdrawing group. However, substitution of dppz with the electron donating trithiocarbonate (S2CS) or deca-alkylthioether (Sdec) groups confer ICT from the S adduct to the phenazine LUMO. Upon complexation of the substituted dppz ligand to Re(CO)3Cl this ICT red-shifts and increases in intensity.



a) $dppz(SCN)_2$ b) $dppzS_2CS$ c) $dppz(Sdec)_2$

Figure 1. Sulfur substituted dppz based ligands in this study.

This interpretation is supported by the resonance Raman data that shows enhancements of vibrations attributable to the sulfur substituents. The partial oxidation of the metal centre in the mixed excited state results in the absence of the usual carbonyl band enhancement observed in the resonance Raman spectra of Re(I)(CO)3Cl polypyridyl MLCT transitions.

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Magnetically Interesting Pyrimidine-Bridged Dinuclear Iron(II) Complexes

W. Gobeze,[1] V. A. Milway,[1] S. Brooker[1,*]
1. *Department of Chemistry and the MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, PO Box 56, Dunedin 9054, New Zealand; wgobeze@chemistry.otago.ac.nz and sbrooker@chemistry.otago.ac.nz*

Dinuclear iron(II) complexes of heterocyclic ligands, especially ligands that are capable of providing a bridge between the metal centres, are of considerable current interest, in particular with regard to the spin crossover (SCO) effect as they can either switch in one step [HS-HS] ↔ [LS-LS] or more interestingly in two steps [HS-HS] ↔ [HS-LS] ↔ [LS-LS].[1] If the switching is accompanied by hysteresis this endows the system with memory. Heterocycle bridging of the metal ions is of interest due to the potential mutual influence of heterocycle-mediated magnetic exchange coupling and SCO behaviour.

Some pyrimidine-bridged iron(II) complexes exhibit SCO.[2] In 1995 Oshio used a *bis-tetradentate* unsubstituted *pyrimidine*-based ligand, L^{Et-H}, to prepare $[Fe^{II}_2(L^{Et-H})(NCS)_4]$, and reported that it was [HS-HS] down to 50 K.[3] With the aim of generating SCO-active pyrimidine-bridged dinuclear iron(II) complexes we have recently prepared and characterized a family of related complexes, $[Fe^{II}_2(L^{R-Ph})(NCX)_4]$, from *bis-tetradentate phenyl-substituted pyrimidine*-based ligands L^{R-Ph}, which vary in the 'arm' length R (methylene/ethylene/mixed linked pyridyl 'arms', L^{Me-Ph}, L^{Et-Ph}, L^{mix-Ph} respectively, provide differing flexibility and chelate ring sizes), and choice of anion, specifically SCN^-, $SeCN^-$ and $NCBH_3^-$. The results of this study will be presented and discussed.

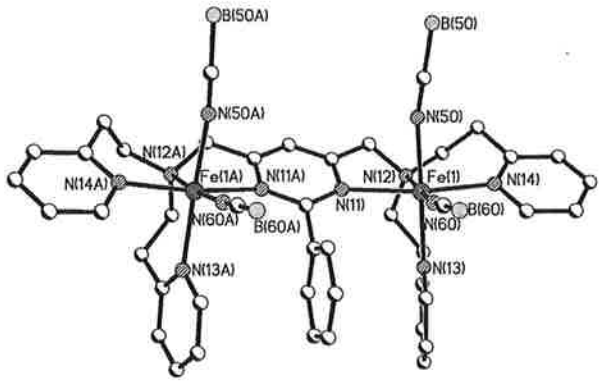

Figure: X-ray crystal structure of $[Fe^{II}_2(L^{Et-Ph})(NCBH_3)_4]$.

Acknowledgements: Support from the University of Otago (including a PhD scholarship to WG) and the MacDiarmid Institute is gratefully acknowledged.

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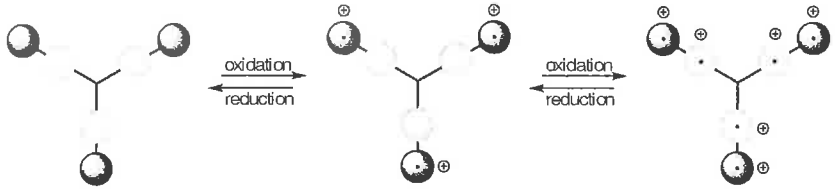
Multi-state octupolar complexes for nonlinear optics

G. Grelaud[1,2], T. Schwich[1], M.G. Humphrey[1], M.P. Cifuentes[1] and F. Paul[2]

1. *Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia*
2. *Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, Rennes, France*

Octupolar complexes are interesting because they may possess significant quadratic and cubic NLO activity[1,2].

We will present some new organometallic octupolar complexes containing different metal centres. These complexes exhibit several reversible redox processes, which allow modulation of the NLO properties between the different oxidation states. Synthesis, electrochemical and optical behaviour of the complexes will be described[3].



Acknowledgements: We thank the Region Bretagne and the Australian Research Council for support of this work. MGH is an ARC Australian Professorial Fellow and MPC is an ARC Australian Research Fellow.

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Tellurium complexes in hydrothermal solutions

P.V.Grundler[1], A. Pring[1], J. Brugger[1], L. Helm[2]

1. *Department of Geology and Geophysics, University of Adelaide, North Terrace, Adelaide SA 5005, Australia, pascal.grundler@adelaide.edu.au*
2. *Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

Tellurium, an element on the edge between metals and non-metals, is a focus of research in different fields, among them geochemistry and nanomaterials.
Although a trace element in natural systems, tellurium is considered to be potentially important in the transport and enrichment processes occurring in the earth's interior which lead to precious metal ore deposits of economic significance.[1]
Carriers of the metals are hydrothermal fluids, mainly composed of water with varying amounts of CO_2, H_2S and chloride. The study of these fluids is challenging for the geochemist due to the extreme conditions of temperature and pressure. Further some fundamental properties of water change with increasing temperature and pressure. Between room temperature and the critical point (T_c = 374 °C, p_c = 220.6 bar) the dielectric constant of water decreases from 80 to about 5, the density decreases by two third and the auto ionization constant varies from 10^{-14} to $10^{-15.5}$ via a minimum value of $10^{-11.2}$ at 250 °C.[2]
The dramatic change in the dielectric constant means that at higher temperature water will become a better solvent for non polar solutes. Therefore the speciation of metals in solution will be influenced by these changes. The nature of the metal complexes, their coordination sphere, will change with increasing temperature.
Experimental work is required to obtain key thermodynamic data which will help in understanding the behaviour of metals in hydrothermal solutions and allow modelling the reactions happening in fluids circulating in the earth's crust.
Currently the data available for tellurium is mainly limited to room temperature. Extrapolation from data available for sulphur and selenium is used at higher temperature which can yield to significant inaccuracies especially as tellurium is a borderline case, showcased for example by it's ability to form chloro-complexes not unlike many metals.[3]
In the present study, the speciation of tellurium as a function of temperature, pressure and solution composition was investigated by ^{125}Te NMR, UV-vis spectrophotometry as well as X-ray absorption and fluorescence spectroscopy (XANES-EXAFS).
In aqueous solutions Te(IV) is the most stable oxidation state. The main species are $Te(OH)_3^+$, H_2TeO_3(aq), $HTeO_3^-$ and TeO_3^{2-}, the distribution being controlled by pH. In presence of chloride, a series of chloro-complexes of the general formula $[TeO_xCl_y(OH)_z]^{4-2x-y-z}$ are formed.
Stability constants for the different species have been determined providing the information required to describe the speciation of tellurium in hydrothermal solutions.
This knowledge is not only relevant to geochemistry but also for example to the field of nanomaterials as shown recently by the preparation of tellurium and tellurides nanotubes from hydrothermal solutions.[4]

Acknowledgements: Financial support from the Australian Research Council (grant DP0880884) is acknowledged.

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Amido Cuprate Bases in Directed *ortho* Metallation

J. Haywood[1] and A. E. H. Wheatley[1]

1. *Dept of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK; jh414@cam.ac.uk*

Directed *ortho* cupration (DoC), the process of replacing the *ortho* hydrogen on a functionalised aromatic with a copper-containing moiety, has only recently been developed. It is of interest due to the possibility of achieving carbon-carbon coupling through oxidation of the metal centre, a process that has not previously been realised using established lithium, zinc or aluminium 'ate bases alone.

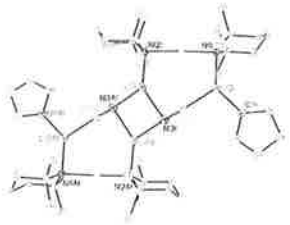
$TMP_2CuLi_2(CN)$•THF, a bisamido cuprate, and RCuTMPLi•*n*S (R = Me, Ph), both organoamido cuprates, have, among others, been shown to be very effective deprotonating agents with respect to a variety of aromatic substrates.[1]

Investigation of the structures of these reagents in the solid state has provided novel structures. The bisamido cuprate takes up a dimeric structure, each monomeric component of which is composed of a seven-membered metallocyclic ring, with bridging occurring via the lithium and nitrogen of the included LiCN unit.[1] Conversely, the organoamido cuprates exist as monomers in the solid state, excluding LiCN.[2]

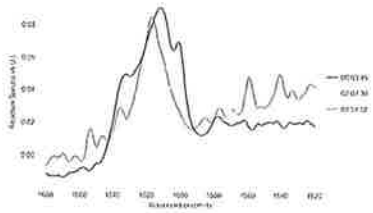
The solid-state structural findings have been mirrored by calculations on the solution state behaviour of model amido cuprate compounds, with the lowest energy states showing LiCN inclusion for a model bisamido cuprate, and exclusion for a model organoamido cuprate. Despite these being the lowest energy conformations, there is a very low barrier to their interconversion, suggesting the importance both structure-types in solution.

Investigation of the equlibrium between the calculated states, one showing inclusion and one exclusion of LiCN, using *in situ* IR spectroscopy has allowed DoC reaction intermediates to be monitored in solution through their effect on an aromatic substrate bearing a carbonyl-containing directing group.

a.



b.



a. Crystal structure of $TMP_2CuLi_2(CN)$•THF showing its dimeric nature and b. an example of the carbonyl stretching region of an *in situ* IR trace

Acknowledgements: Prof. Masanobu Uchiyama, RIKEN, Japan, AstraZeneca Charnwood for use of *in situ* IR facilities and the EPSRC and the Royal Society for funding.

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Identification of Niobium(V) complexes for the possible separation of Niobium and Tantalum

L. Herbst[1], H.G. Visser[1], A. Roodt[1]

1. *Department of Chemistry, University of the Free State, Nelson Mandela Avenue,Bloemfontein 9300, South Africa, E-mail: leandra9herbst@yahoo.com*

Niobium and Tantalum were discovered early in the nineteenth century, barely a year apart, and since then great difficulty has been experienced in separating them.[1] This is a result of their very similar chemical properties. Niobium(V) and Tantalum(V) are both hard metal centres and the halido species are know to readily hydrolyse.

Interesting coordination chemistry are displayed by niobium(V) when utilising bidentate O,O donor ligands, such as oxalate. Šestan *et al.*[2] characterized oxotris(oxalate)niobate(V) structures, and found $Rb_3[NbO(C_2O_4)_3]\cdot H_2O$ to be isotypic with the ammonium analogue, $(NH_4)_3[NbO(C_2O_4)_3]\cdot H_2O$, of Mathern *et al.*[3].

This project is therefore aimed at the investigation and identification of different niobium(V) complexes containing selected hard mono, bi- and multidentate ligands that could potentially be utilized for the selective separation of niobium from tantalum. The focus is primarily on on oxygen and nitrogen electron donating ligands but also includes hard pi-ligands such as cyanide and nitride.

Different aspects of the solid state behaviour and solution chemistry were investigated and will be reported on in this presentation. This includes high temperature sublimation studies, and detailed structural characterization by means of multi nuclear NMR spectroscopy, single crystal X-ray diffraction, powder-XRD and IR-spectroscopy. The various techniques were used to determine the different solid state coordination modes of the ligand spheres as well as packing modes which might induce different distortions. UV/Vis spectrophotometry and stopped flow techniques were utilized to construct a thermodynamic and kinetic reaction scheme for the various complexes of niobium.

Acknowledgements:
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Study of Loha Bhasma Composed Of Doped Iron-Oxide Nanoparticles Synthesized By Traditional Ayurvedic Processes

R. W. Jawale[1], D. G. Kanase[2], R. D. Kankaria[3], Rupali Lad[3], Vividha Dhapte[4], M. P. Wadekar[1] and S. S. Kadam[4].

1. *Y. M. College, Bharati Vidyapeeth Deemed University, Pune – 411 038.*
2. *M. B. S. K. Kanya Mahavidyalaya Kadegaon*
3. *B. J. S. Arts, Science and Commerce College Pune-412 207*
4. *Poona College of Pharmacy Pune – 411 038*

Email: dgkanase@yahoomail.com, shivaji_takale@yahoo.co.in

Loha bhasma, which is an iron-based ayurvedic preparation is a famous traditional drug used all over India since ancient times. It can be synthesized directly from microfined iron powder by the ayurvedic techniques called as bhasmikarana which converts heavy metals into a state called as 'bhasma state'. The exact nature of this 'bhasma state' and the 'mechanism' of bhasmikarana are yet to be explored from chemical point of view. However it is claimed that through bhasmikarana the heavy metals lose their toxicity and significant medicinal properties are induced in the resulting metallic bhasmas. The flow sheet indicating the important steps in the process of bhasmikarana is given in Chart[1] 1.1

The important medicinal properties of loha bhasma include its therapeutic use in the treatment of anemia, dropsy, jaundice, rheumatism, arthritis, eye troubles etc. These properties are quit different than pure iron-oxides[2].

Therefore, to explore the exact nature of loha bhasma, synthesized by following the procedure given in Figure 1.1, its chemical and structural aspects are investigated through EDX, XRD, SEM, IR, UV spectroscopy.

Our study shows that loha bhasma is composed of doped iron-oxide nanoparticles. Its major constituent is a mixture of α -Fe_2O_3 + γ-Fe_2O_3. The minor/trace constituent includes carbon, hydrogen, Na, K, Ca, Mg, SiO_2, S, P. etc is unexpectedly high (9 to 10 %) and its exact nature.

The crystallite size of the particles as determined by XRD and SEM is of the order of 20-30 nm.

Presence of carbon and organic matter is under investigation at present.

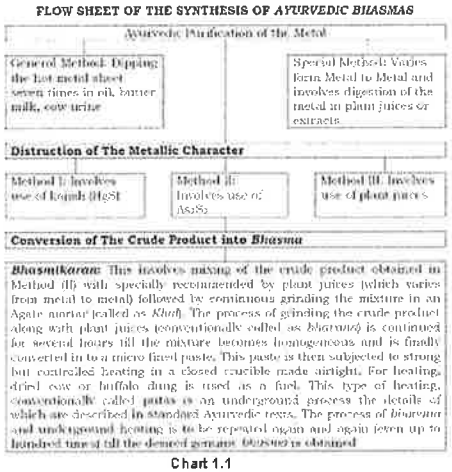

Chart 1.1

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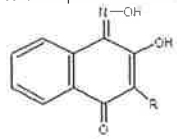
Role of Coordinated water In stabilizing the Geometry of La(III), Sm (III) and Dy (III) chelates of Lawsone monoximates

R. W. Jawale, D. G. Kanase, Pratibha Jadhav, V. B. Jadhav, P. S. Khandagale, V. V. Dhapte and B. A. Kulkarni.

1. *Y. M. College, Bharati Vidyapeeth Deemed University, Pune – 411 038.*
2. *M. B. S. K. Kanya Mahavidyalaya Kadegaon*
3. *Henkel Pvt. Limited. Jajuri, Dist – Pune.*

Lawsone monoxime (I) and its C-3 substituted derivatives constitute an important class of ligands due to their powerful chelating ability, analytical utility and biological activity. Among large number of their metal chelates, lanthanide chelates are of special interest from stereochemical point of view.

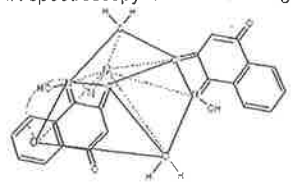


(I)

These lanthanide chelates can be synthesized by mixing metal ligand solutions in the propertion of 1:3 M. Their molecular composition corresponds to $ML_3n.H_2O$ where $M=L^{3+}$, L= ligand and n varies from 2 to 4.

These lanthanide monoximates can be easily precipitated in aqueous medium at pH 5 to 6. But if both metal ions and ligands are dissolved in anhydrous non-donor organic solvents like methanol, ethanol or acetone and mixed in the above proportion, NO PRECIPITATION takes place at all. However, if few drops of pure water are added to this reaction mixture , immediate precipitation takes place indicating the necessity and role of coordination water in the formation of these lanthanides chelates.

IR spectroscopy and TGA investigations support the presence of coordinated water. Therefore, apart from three oxime ligands, at least, two coordinated water molecules are necessary for the stabilization of these chelates. Considering the tendency of lanthanides ions, towards larger coordination number cubic geometry (Fig 1.2) is suggested in which the two water molecules occupy trans position and stabilize the cubic geometry. Our results and conclusions for La (III), Sm (III) and Dy (III) lawsone monoximates will be reported in this communication.



(Fig 1.2)

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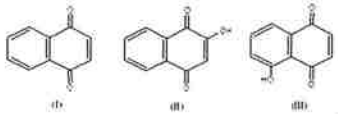
Comparative Study of The Isomeric Chelates Of Zn(II), Cd(II) and Hg(II) with 2.hydroxy and 5.hydroxy 1,4 Naphthquinones.

R. W. Jawale[1], S. D. Gaikwad[2], A. B. Pawar[1], R. G. Sarawadekar[1], B. L. Kahde[1], S. T. Takale[1] and M. P. Wadekar[1].

1. *Y. M. College, Bharati Vidyapeeth Deemed University, Pune – 411 038.*
2. *B. J. S. College of Arts, Science and Commerce, Pune – 412 207.*

Hydroxy derivatives of 1,4 naphthoquinone (I) in which the hydroxyl group is placed adjacent to one of the carbonyl groups constitute an interesting series of the isomeric ligands. Among these, 2-hydroxy 1,4 naphthoquinone (II) and 5-hydroxy 1,4 naphthoquinone (III) are the simplest derivatives. The former is an active constituent of lawsonia alba and is also known as lawsone, while the later is an active constituent of walnut tree and known as juglone. Both these isomeric derivatives are powerful chelating agents which can interact with most of the metal ions forming an attractive series of isomeric chelates. These isomers differ exclusively in their ring size, the lawsonate involving five membered ring chelates while the corresponding juglonates involving six membered ring chelates. This type of isomerism recognized as ring isomerism has significant effects on the properties of isomeric chelates.



In the present work, isomeric lawsonates and juglonates of Zn(II), Cd(II) and Hg(II) are studied to explore the effect of ring isomerism on their chemical, structural and biological properties. The chelates are synthesized by known methods and their comparative study is carried out with the help of EDX, SEM, XRD, XPS, IR and UV spectroscopy. The antimicrobial activities of the ligands and their chelates are studied using disc-assay method against the selected Gram + ve and Gram – ve microorganisms.

The results of chemical, structural and antimicrobial investigations are employed to throw light on the effect of ring isomerism on various properties.

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Polyoxometalate HIV-1 Protease Inhibitors (Inorganic Coordination compounds)

Ali Gharib[1,2,*], Manochehr Jahangir[1], Mina Roshani[1], Ali Jalinous[3]

1. *Department of Chemistry, Islamic Azad University, Mashhad, IRAN*
2. *Agricultural Researches and services Center, Mashhad, IRAN*
3. *Kimigar Toos Pharmaceutical Co., Mashhad, IRAN*

aligharib5@yahoo.com

The principal disadvantage of POMs vis-à-vis medicine is that they are not organic species. Low molecular weight organic species dominate in the pharmaceutical industry (drug discovery, synthesis, and development). An intrinsic counterpoint here involves the vast third world markets and their attendant requirements for pharmaceuticals. Most of the recently developed and optimally efficacious pharmaceuticals including anti-HIV agents are prohibitively expensive for such markets. As POM-based pharmaceuticals are much less expensive and more amenable to scale-up than the great majority of organic pharmaceuticals, their development might positively impact these large and growing markets in the emerging world. When administered to four patients with AIDS, Rozenbaum et al. reported a reduction in the surrogate markers for HIV [1]. These results prompted several groups to develop less toxic POM antiviral agents that could be effective against HIV. This paper examined the pharmacokinetics of three anti-HIV POMs ($K_{12}H_2[P_2W_{12}O_{48}]$, $K_{10}[P_2W_{18}Zn_4(H_2O)_2O_{68}]$, $[NaP_5W_{30}O_{110}]^{14-}$ and $(Me_3NH)_8[Si_2Nb_6W_{18}O_{77}]$) following a single 50 mg/kg iv administration in rats [2]. For example, the Keggin sandwich compound $K_{10}Fe_4(H_2O)_2(PW_9O_{34})_2$ exhibited significant inhibitory activity against influenza A and B, RSV, measles virus, and parainfluenza virus 2, but no inhibitory activity against parainfluenza virus 3 or mumps virus. The most effective POMs against virus infection had Nb or Fe units incorporated into the POM structure. Judd et al. investigated the inhibitory action of Nbcontaining POMs of the Wells-Dawson structure (formula α_1(or α_2)-$K_7[P_2W_{17}(NbO_2)O_{61}]$ and α_1(or α_2)- $K7[P_2W_{17}NbO_{62}]$) against HIV-1 P and used computer modeling to investigate the likelihood of this interaction [3].

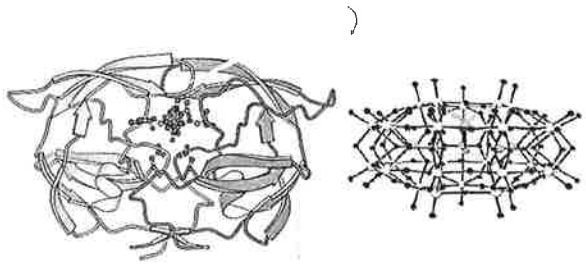

Figure 1. HIV Protease-Polyoxometalate Complex. (Left) The HIV protease is shown with the inhibitor polyoxometalate bound at the active site. (Right) The drug has been rotated to reveal its approximately twofold symmetric conformation.

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Preyssler Heteropolyanions as Homogeneous Catalysts (Coordination Catalysis Compounds)

Ali Gharib[1,2,*], Manochehr Jahangir[1], Mina Roshani[1], Ali Jalinous[3]
1. *Department of Chemistry, Islamic Azad University, Mashhad, IRAN*
2. *Agricultural researches and services Center, Mashhad, IRAN*
3. *Kimigar Toos Pharmaceutical Co., Mashhad, IRAN*
any correspondence: aligharib5@yahoo.com

Polyoxometalates (POMs) are discrete molecular structures composed of metal cations bridged by oxide anions. They are not multi-metal species with metal-metal bonding, one conventional definition of "clusters", but they are clusters in the generic sense of the word. A number of general reviews on POMs have appeared in recent years [1]. Since a great majority of these structures are anionic, and thus salts with obligatory cations, and constituted primarily of early-transition-metal (d-block) elements in their highest oxidation states, the name early-transition-metal-oxygen-anion clusters is generally viewed as appropriate. However, the literature on molecular polyanions is now so large that there are exceptions to each component of this description of polyoxometalates.
Heteropolyacid (HPA) compounds are the objective of research for a long time.The reactions catalyzed By them both in heterogeneous and homogeneous systems have been reviewed by many researchers [2].Catalysis of keggin heteropolyacid has at tracted much interest since seventies.The heteropolyacid possesses the dual catalytic functions of strong acidity and oxidizing ability.HPA will be expected as an alternative acid catalyst to improve several organic processes which employ conventional acids [3].In aqueous solution HPA such as PW, SiW, Preyssler"s anion and PMo are strong fully dissociated acids. HPAs in solution are stronger them the usual mineral acids such as HCl, Sulfuric acid, and etc [4]. teropoly acids (HPAs) are well defined molecular clusters that are remarkable for their molecular and electronic structural diversity and their significance is quite diverse in many areas, e.g., catalysis, medicine, and materials science [3]. HPAs are complex proton acid that incorporate polyoxometalate anions (heteropolyanions) having metal-oxygen octahedra as the basic structural units and catalysis by them is a field of increasing importance [4].
$[NaP_5W_{30}O_{110}]^{14-}$, the socalled Preyssler's anion, Na^+ is encrypted inside a central cavity formed by five PW_6O_{22} units arranged in a crown [5], as shown schematically in Fig. 1.

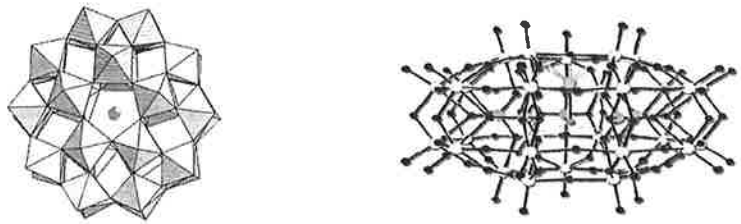

Figure 1. Structure of $[NaP_5W_{30}O_{110}]^{14-}$ polyhedral form showing WO_6 octahedra and the central Na (open circle).

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Crystallographic determination of Ni-α-hydroxyoxime-carboxylic acid synergist complexes

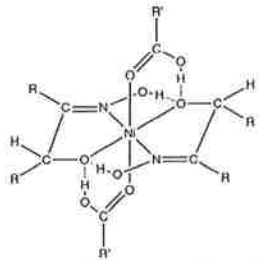
K. R. Barnard[1], G. L. Nealon[2], M. I. Ogden[2], B. W. Skelton[3]
1. *The Parker Centre (CSIRO Minerals Down Under Flagship) Keith.Barnard@csiro.au*
2. *The Parker Centre (Department of Chemistry, Curtin University)*
3. *Chemistry, School of Biomedical and Chemical Sciences, University of Western Australia*

The ability of certain mixtures of reagents to impart a synergistic effect on metal extraction is both of scientific interest and of potential value as a commercial solvent extraction (SX) process. A reagent that has regularly found itself a part of synergistic systems is LIX®63, the active component of which is 5,8-diethyl-7-hydroxydodecan-6-oxime (H_2Ox). Synergism involving LIX®63 and the use of a carboxylic acid (RH) was first reported in 1969.[1] CSIRO has recently rekindled interest in this reagent system for the selective extraction of valuable base metals including Ni, Co, Cu and Zn from gangue metals Mn, Mg and Ca.[2]

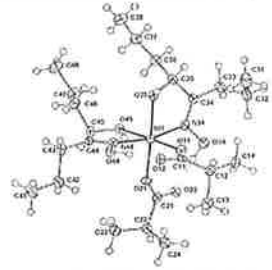
Most past research into this system has focussed on the synergistic effect observed for Ni, Cu and Co extraction. To date, structural information on the species formed in this system has been limited to equilibrium studies and UV-visible analysis. Based on this information an octahedral nickel complex of formula $Ni(HOx)_2(RH)_2$ containing anionic hydroxyoxime ligands was deduced.[3] A structure containing anionic oxime ligands in a square planar configuration and axial carboxylic acid groups, stabilised by intra-molecular hydrogen bonding, was proposed (see below).[4]

The present work has resulted in the X-ray crystallographic determination of three model nickel-α-hydroxyoxime-carboxylic acid structures. In all cases, a short chained (C_8) analog of LIX®63 hydroxyoxime was used, along with either benzoic, isobutyric or acetic acid. All three complexes have the same structure wherein the two acid groups are present in the anionic form and are located *cis* to one another. The two chelated α-hydroxyoxime ligands are uncharged with the oxime nitrogen atoms located *trans* to one another. Intra-molecular hydrogen bonding between each carboxylate carbonyl group and a *cis*-adjacent oxime hydroxyl group is evident. In addition, *inter*-molecular hydrogen bonding between each α–hydroxyl proton and a neighbouring carboxylate carbonyl group is observed within the lattice. Unlike the phenolic-based hydroxyoxime-metal complexes and the previously proposed structure [4], no intra-molecular hydrogen bonding between the hydroxyoxime ligands is apparent.

These structures provide the first definitive structural elucidation of the types complexes formed via synergistic solvent extraction utilising LIX®63 and carboxylic acids. Extension of this work into other metals and reconciliation of spectroscopic data with the commercial system is planned.



Previously-proposed structure [4]



Crystallographically determined structure

Acknowledgements: The support of the Minerals Down Under National Flagship and Parker CRC for Integrated Hydrometallurgy Solutions are gratefully acknowledged.

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Heteropolynuclear molybdenum (V) complexes – precursors of the catalytic clusters of low valence molybdenum with Na, K, Mg as a heteroatom

T. A. Bazhenova[1], D. A. Kuznetsov[1], Yu. V. Manakin[1], T. A. Savinykh[1], K. A. Lyssenko[2]

1. *Institute of Problems of Chemical Physics, Russian Academy of Sciences, bazhen@cat.icp.ac.ru*
2. *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences*

Protonic dinitrogen-fixing systems with participation of molybdenum compound as a catalysts are the most active abiotic systems which catalyze the molecular dinitrogen reduction [1].
The catalytic complexes of low valence molybdenum result from polynuclear Mo(V) compounds reduction. These Mo(V) compounds in turn are formed during the preparation of protonic dinitrogen-fixing systems from $MoCl_5$ in methanol both in the presence and in the absence of magnesium under the action of different bases. The chemical composition, structure and the mechanism of production for both high and low valence polynuclear molybdenum catalysts are not known. The mechanism of their catalytic action in nitrogenase substrates reduction is unknown as well.
It has been shown that the character of the base used proves to be one of the essential factors that predetermine the content and structure of the polynuclear molybdenum complexes, which are formed from molybdenum (V) chloride in methanol under the action of bases.
A few oxo-alkoxide polynuclear molybdenum(V) complexes of different structures, depending on the base nature used for the reaction, have been isolated and characterized with X-ray and other physical and chemical methods. It has also been shown that the base cation may be either included or not included in the content of the molybdenum complex synthesized. At the same time the base anion defines geometric structure of the polynuclear molybdenum complex due to the favorable creation of μ-2, μ-3, μ-4 oxygen-containing bridges depending on the character of the base used. In particular, it has been found that $[Mo(OCH_3)_3Cl_2]_2$, $[Mo(OCH_3)_4Cl]_2$ [2] and $[Na(CH_3OH)][Mo_2O_2(OCH_3)_7$ complexes are formed step-by-step under the action of $NaOCH_3$ (Fig. 1, structures 1, 2). It has been observed that the use of the potassium methylate as a base results in a formation of molybdenum-potassium cluster, containing binuclear Mo-Mo fragments and complicated net of the oxygen-containing μ-2 and μ-3 bridges between molybdenum and potassium (Fig. 1, structure 4). The octa-nuclear neutral molybdenum complex of formula $Mo^V_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2(HOCH_3)_4$ was formed under the action of potassium hydroxide and it turned out that the potassium atoms were not included in this structure (Fig. 1, structure 3). Quantum-chemical calculations of the structure, electronic structure and IR spectra of the isolated $Mo^V_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2(HOCH_3)_4$ complex were made and proved the compliance with the experimental results.

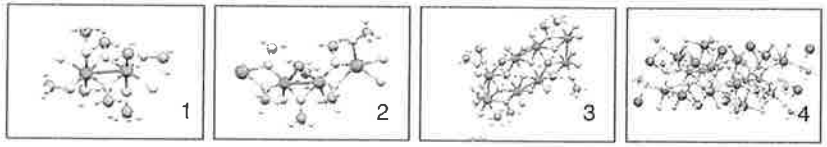

Fig. 1 Molecular structures of polynuclear molybdenum complexes that form under the action of different bases on $MoCl_5$ in methanol

Acknowledgements: This work was supported by Russian Foundation for Basic Research, Grant N° 08-03-00674a and by Ministry of Education and Science of the Russian Federation, Grant N° P 1346

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Small Molecule Chemistry via Lewis Acid-Activated, Multielectron Transformations

L. A. Berben, N. Kazem, and M. Diego Rail
University of California, Department of Chemistry, Davis, CA 95616
email: laberben@ucdavis.edu

The combination of Lewis acidic centers to activate and bind small molecules at low overpotentials, in conjuction with a source of multielectron reducing equivalents is being investigated. For example, the multi-electron reduction of CO_2 into simple products such as formate, formaldehyde and methanol, or into the most basic C-C coupled products such as ethanol remains a challenge in developing renewable sources of fuel and chemicals. Electrocatalysis, as a method for the reduction of small molecules is particularly appealing because the energy and electrons required to cycle a photocathode:electrocatalyst system can be harnessed from sunlight.

In one approach, we are investigating a redox-active ligand in conjuction with a Lewis acidic reaction center. Catalysts obtained by chelation of Lewis acidic metal centers, will be used to activate and bind small molecules. In conjunction with the reducing equivalents stored in the ligands, both activation and reduction is being investigated. We have shown that the ligand naphimpy can be accessed in multiple oxidation states thus supplying multielectron reducing equivalents to a bound molecule such as CO_2.

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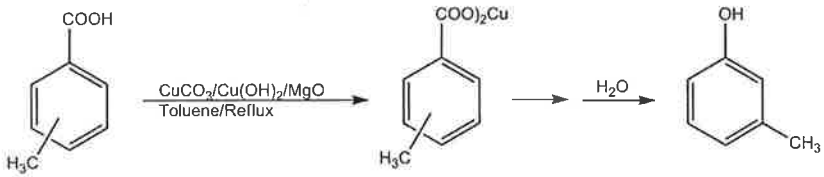
Mechanism of the copper catalysed rearrangement of toluic acids to *meta*-cresol

B.C.B. Bezuidenhoudt, C.A. Sunil, C. Marais, E.H.G. Langner
Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein, 9300, South Africa.
e-mail: bezuidbc@ufs.ac.za.

Cresols (hydroxytoluenes) are important industrial starting materials for many phenolic compounds, and are currently obtained industrially by a three step process from toluene. In a process similar to the one for the production of phenol, toluene is reacted with propylene in the first step to give a mixture of *ortho*-, *meta*-, and *para*-isopropyltoluene, which is subjected to oxidative cleavage (by air) to give the corresponding cresols together with acetone. This mixture then needs to be separated into the pure components by distillation. Due to their close boiling points, *meta*- and *para*-cresol are however not separable by distillation and the only two methods currently available for the direct separation of these compounds are very elaborated adduct crystallization processes or chromatography. All the hassles associated with the production of synthetic *m*-cresol therefore render it a very expensive phenolic starting material.

Since it is known that *meta*-cresol can be produced selectively from either *ortho*- or *para*-toluic acid and that these acids are available from the corresponding xylenes, this was identified as an alternative relatively cheap technology for *m*-cresol production.[1,2,3] A thorough understanding of the Keading process is, however, a prerequisite for the optimal production of *m*-cresol. In this regard the mechanism of the reaction sequence was investigated through the use of thermogravimetric, and X-ray crystallographic, and MS analytical processes.



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Chiral Amines and Diamines from Monosaccharides as Ligands in Transfer Hydrogenation of Acetophenone

M. D. Boege[1], C. Fowelin[2], S. Lerch[2], J. Heck[2]
1. *Institute of inorganic and applied chemistry, university of Hamburg, matthias.boege@chemie.uni-hamburg.de*
2. *Institute of inorganic and applied chemistry, university of Hamburg*

Monosaccharides provide a lot of options for modification and are of high potential as ligands in stereoselective catalysis, since the stereochemistry of the different sugars is well defined. In addition the synthetic pathways to each monosaccharide are often well known.

Former studies in our group have shown that 2,3-diamino carbohydrates are suitable for the chelating complexation of transition metals as chromium, molybdenum and tungsten.[1]

Coordination compounds of rhodium, iridium and ruthenium with chiral amino ligands are utilized as pre-catalysts in asymmetric transfer hydrogenation which often achieves high enantioselectivity.[2]

There is one example for the use of an 2,3-diamino glucoside as ligand in enantioselective transfer hydrogenation.[3] The synthesis of various monosaccharides with amino groups and their coordination compounds with metals from group 8 and group 9 (e.g. see illustration 1) as well as their potential in enantioselective transfer hydrogenation will be reported.

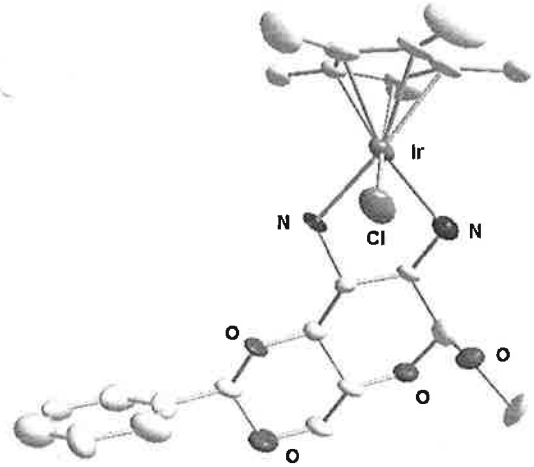

Illustration 1: Molecular structure of chlorido-(methyl-4,6-*O*-benzylidene-2,3-diamino-2,3-dideoxy-*α*-D-glucopyranoside)-η^5-pentamethylcyclopentadiene-iridium(III)-tetrafluoroborate. For clarity only the heteroatoms are labelled. The hydrogen atoms and the counter ion are omitted.

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft.

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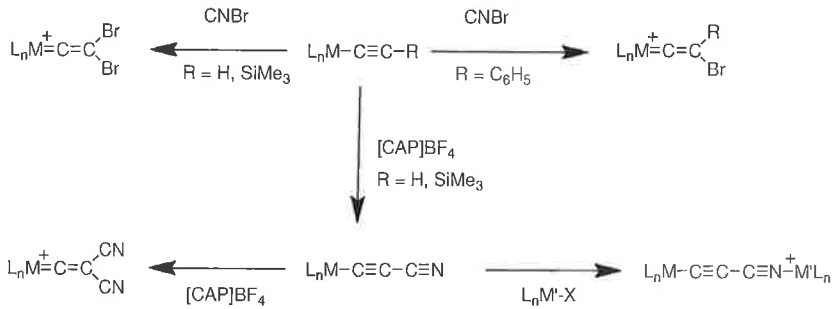
Cyanoligand Chemistry: A Versatile Synthesis of Cyanovinylidenes to Cyanoacetylides

N. J. Brown,[1] E .A. Strickson,[1] M. E. Smith,[1] M. A. Fox,[1] D. S. Yuift,[1] J. A. K. Howard,[1] P. J. Low.[1]
1. *Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, England.*

The cyanide ligand, $[C{\equiv}N]^-$, is almost ubiquitous in coordination chemistry. However, despite the structural and electronic analogies which can be drawn between $[C{\equiv}N]^-$ and $[C{\equiv}CC{\equiv}N]^-$, the chemistry of the cycanoacetylide ligand has remained largely un-touched and routes towards complexes containing this moiety are rare.[1] To this end, we sought to develop a new facile synthetic routes to complexes containing cyanoacetylide ligands.[2] We have recently shown that reactions of $M(C{\equiv}CR)L_n$ (R = H, $SiMe_3$) with cyanogen bromide gave low yields of $M(C{\equiv}CC{\equiv}N)L_n$ complexes, together with di-bromovinylidenes, $M(=C=CBr_2)L_n$.[3]



On the other hand, reaction of $M(C{\equiv}CR)L_n$ with 1-cyano-4-dimethylaminopyridinium tetrafluoroborate, $[CAP]BF_4$, gave cyanoacetylide complexes in high yield.[4] These complexes have been shown to be excellent metalloligands, coordinating to a wide range of metal fragments giving rise to a family of cyanide bridged bimetallic complexes $L_nM(\mu\text{-}C{\equiv}CC{\equiv}N)M'L_n$. In this contribution, these synthetic studies will be described, and the structures of the resulting terminal and bridging cyanoacetylide complexes compared with those of the analogous cyanide species.

Acknowledgements: We thank the EPSRC for support of this work through grant GR /T05271/01

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Controlling the Regioselectivity of Directed Aromatic Metallation

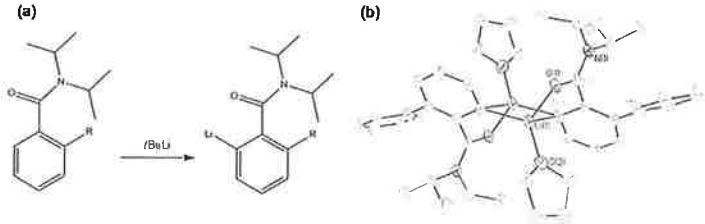
A. M. Campbell Smith[1], A. E. H. Wheatley[1], J. Clayden[2]
1. *Dept. of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK; amc73@cam.ac.uk*
2. *School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK*

Directed metallation is a highly effective way of regioselectively substituting aromatic rings at the *ortho* position,[1] a technique which has been used in many organic syntheses over the past twenty years.[2] Commercial organolithium reagents are very commonly used to provide the metal ion. Of the many substituent groups which can be employed to direct lithiation, secondary and tertiary amides, along with carbamates and oxazolines, are among the most effective due to the ability of their electron-rich oxygen centres to effect the complex-induced proximity effect[3] and to withdraw electron density from the ring.

Little work has been done in investigating the precise structures of the *ortho*-lithiated intermediates formed in these reactions. In 2001 Wheatley *et al.* published the solid state structures of *N,N*-diisopropyl-2-lithiobenzamide-diethyl ether and *N,N*-diisopropyl-2-lithionaphthamide-THF, both of which exist as a dimer in the solid state with coordination of the metal by one solvent molecule per amide molecule.[4] It was found that the large steric bulk of the isopropyl groups caused the amide group to twist significantly out of the plane of the phenyl (47°) or naphthyl (65°) ring. As a result, the lithium ion also lies well outside of the ring plane but is stabilised by further coordination on dimerisation.

Subsequent work has considered how this twist angle is affected by placing a substituent in the 2-position of the aromatic ring (see scheme below).[5] The *ortho*-lithiated product *N,N*-diisopropyl-2-ethyl-6-lithiobenzamide was characterised in the solid state and the twist angle shown to be 60°. Lateral lithiation was also observed in competition to *ortho*-lithiation on addition of the chelating solvent PMDTA (*N,N,N',N'',N''*-pentamethyldiethylenetriamine), allowing characterisation of the monomeric solid state structure of α-lithio-2-ethyl-*N,N*-diisopropyl-1-benzamide-PMDTA.

Further investigation of how modifying the steric bulk of an *ortho* substituent influences the site of lithiation and the twist angle of the *ortho*-lithiated product has been undertaken. The structures of lithiated 2-organyl-*N,N*-diisopropylbenzamide are reported (organyl = isopropyl, phenyl) and reveal the importance of substituent steric effects and choice of solvent in defining the site of metallation.



(a) A generalised ortho-lithiation scheme (b) Solid state structure of the ortho-lithiation product when R = Ph

Acknowledgements: UK Engineering and Physical Sciences Research Council

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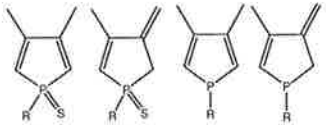
Synthesis and Investigation of Phosphole Isomers as Novel Ligands for Coupling Reactions

A. Ciric[1], F. Mathey[1]

1. *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371 anac0001@ntu.edu.sg*

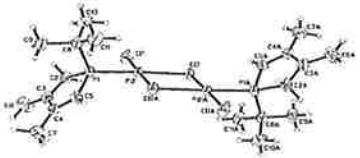
Due to being slightly antiaromatic,[1] phosphole sulfides **(1)** tend to isomerize into their respective products containing one exocyclic double bond **(2)**, which are more stable by 2.4 kcal mol^{-1} (R=Me). On the contrary, the slightly aromatic trivalent phospholes **(3)** are more stable then their isomeric products **(4)** by 3.5 kcal mol^{-1} (R=Me).



(1) (2) (3) (4)

Upon additional theoretical investigation, the data showed that the lone pair at phosphorus is shifted to higher energy by 0.49 eV after the conversion of **(3)** into **(4)**.[2] This destabilization of the lone pair is assigned to the antibonding overlap with the HOMO of the diene unit (see below). This interesting observation led us to examine the different R groups on the phosphole. When R=tBu, the lone pair energy was on the same level as the lone pair of tris(tertbutyl)phosphine, which has been used as a remarkably efficient ligand in a wide range of palladium-catalyzed reactions.[3] This discovery prompted us to synthesize and examine the catalytic activity of palladium complexes of these isomeric phospholes.

Complex shown below confirmed its catalytic activity during Suzuki cross-coupling of aryl chlorides however, the more interesting deboronation/homocoupling[4] was observed in high yield. Current work is focused on the synthesis of derivatives of **(4)** and its uses as ligands for coupling reaction of unactivated and sterically hindered coupling reagents.



Acknowledgements: Nanyang Technological University, Singapore for their financial support.

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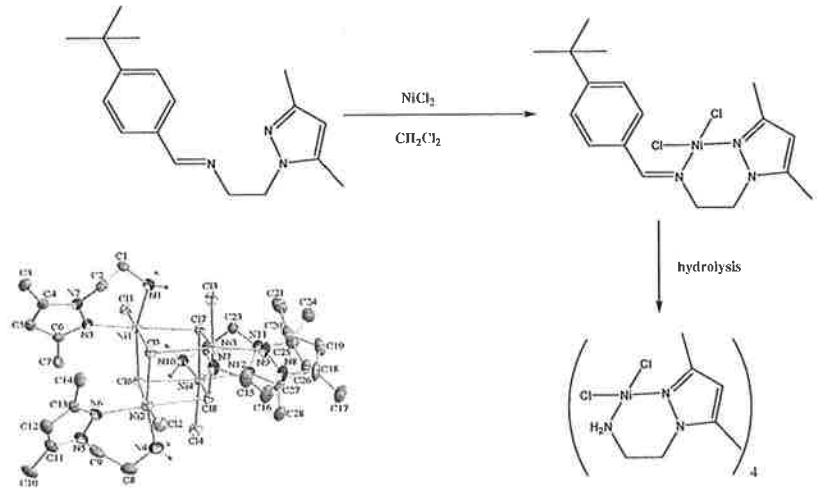
Pyrazol-1-ylsalicylaldimine and imidazolylsalicylaldimine metal complexes: unusual hydrolysis products, and olefin oligomerization and polymerization catalysts

J. Darkwa[1], M. K. Ainooson[1], M. Yankey[1], I. A. Guzei[2]

1. *Department of Chemistry, University of Johannesburg, Auckland Park Kingsway Campus, Auckland Park 2006, Johannesburg, South Africa; e-mail: jdarkwa@uj.ac.za*
2. *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, USA*

Metal complexes with imine ligands have been used extensively as catalysts in ethylene polymerization reactions in recent years.[1] Brookhart has shown that cationic α-diimine palladium complexes are particularly active as ethylene polymerization catalysts because of their highly electrophilic metal centres. But imines are also prone to hydrolysis and readily go back to the aldehyde or ketone and the amine from which the imine was formed.[2] We have recently combined imines with pyrazolyl or imidazolyl groups to prepare ligands that form complexes with a number of transition metals but found that in some instances the pyrazolylimines hydrolyzed when complexed with some first row transition metals. For instance zinc dichloride hydrolyzed the pyrazolylimines to the corresponding pyrazolylamine, while the same ligand is hydrolysed by nickel chloride to the cubane type complex in Scheme 1. This and other nickel complexes are highly active oligomerization catalysts for olefins. However, ligands that contain the imidazolyl unit are less prone to hydrolysis and form stable metal complexes, some of which are good ethylene polymerization catalysts. The extent of hydrolysis in these two types of ligands, as well as their properties as catalysts for olefin polymerization and oligomerization would be discussed.



Scheme 1

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Kinetic and Crystallographic Investigation of Model Iridium(Carbonyl)(Acetylacetonato) Complexes in Olefin Hydroformylation/Transformations

I. Engelbrecht[1], A. Roodt[1], H. G. Visser[1]
1. *Department of Chemistry, University of the Free State, Nelson Mandela Avenue, Bloemfontein 9300, South Africa, E-mail: Engelbrechtl@UFS.ac.za*

Hydroformylation is an important industrial process for the functionilisation of olefins from petroleum sources to aldehydes, and kinetic manipulation by ligand variation which controls linearity and selectivity of product formation is of prime importance. The well-known catalytic system for hydroformylation, hydrogenation and isomerisation of olefins is based on rhodium, where $[Rh(acac)(CO)_2]$ in the presence of tertiary phosphines or phosphites (PR_3) ($PR_3 = PPh_3$, $P(OPh)_3$) is used as catalyst precursor.[1],[2],[3],[4] In the case of hydroformylation, the starting material, $[Rh(acac)(CO)_2]$ in the first step involves the substitution of a CO group by PR_3, yielding $[Rh(acac)(CO)(PR_3)]$,[5],[6] which is eventually converted into the catalytically active hydrido complex, $[HRh(CO)(PR_3)_2]$. Weaker π-acceptors only produce the monosubstituted products even when used in large excess[3],[5],[6] while strong π-acceptor ligands such as $PR_3 = P(OPh)_3$ and $P(NC_4H_4)_3$ generate the di-substituted $[Rh(acac)(PR_3)_2]$.

Iridium compounds are often used as model complexes, since Ir(I) and Ir(III) complexes with similar ligand sets to those proposed in rhodium chemistry, tend to behave in the same way and are isolated more readily than the rhodium analogues. Thus, this study concentrated on ligand effects in square planar $[Ir(LL')(CO)(PR_3)_2]$ complexes (LL' = monocharged bidentate ligand with donor atoms L and L', PR_3 = tertiary phosphine) to determine the importance of electronic factors and steric crowding from the tertiary phosphines for manipulating the reactivity of the Ir(I) centre.[7]

Structural results for different complexes and intermediates [beta-diketonato ring opened example shown below in Figure 1] and a kinetic investigation, illustrating the high reactivity of these complexes, will be presented and discussed.

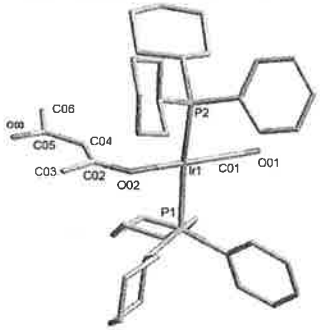

Figure 5: Molecular structure of *trans*-[Ir(acac-*O*)(CO)(PPhCy$_2$)$_2$]

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Formation of Ethylbis(2-pyridylethyl)amineruthenium Complexes Containing an Iminium-ion or a Nitroso Moiety

S. Fukui[1], N. Suzuki[1], T. Wada[2], K. Tanaka[3], H. Nagao[1]
1. *Sophia university, Tokyo, Japan sohei-f@sophia.ac.jp*
2. *Saint Paul's University, Tokyo, Japan*
3. *Institute for Molecular Science, Aichi, Japan*

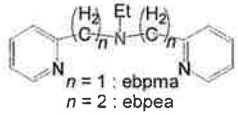


Figure 1. Bis(pyridylalkyl)amine

We have been investigating syntheses of ruthenium complexes bearing a tridentate bis(pyridylalkyl)amine ligand and relationships between their reactivities and geometrical configurations. Ethylbis(2-pyridylmethyl)amine (ebpma), which has $-CH_2-$ arms between the pyridyl and ammine groups as shown in Figure 1 coordinates in both a facial and a meridional configuration with two pyridyl- and one amino-nitrogen atoms. Ruthenium complexes containing the ebpma ligand coordinated in both facial and meridional fashions were synthesized[1] and the difference of their stability of configuration was investigated by DFT calculations. Two $-C_2H_4-$ arms of ethylbis(2-pyridylethyl)amine (n = 2: ebpea in Figure 1) are more flexible than those of the ebpma ligand, and we note difference of structures and properties between the ebpma and ebpea complexes. In this work, formation of a novel (iminium-ion) ruthenium complex, *mer(Cl, Cl, Cl)*-$[Ru^{II}Cl_3\{\eta^2\text{-}N{=}CHCH_2py(C_2H_4py)C_2H_5\}]$ (*mer*-[1]), via a C-H activation reaction of an ethyl group which was connected between the pyridine ring and the amino nitrogen atom occurred during a reaction using a Ru blue solution with ebpea.[2] This complex was characterized by X-ray structural analysis as shown in Figure 2. The N1-C2 distance (1.378(5) Å) was shorter than those of other N-C single bonds (ca. 1.50 Å). The ^{1}H NMR spectrum revealed its diamagnetic property and the coordination mode was a $Ru^{II}(\eta^2$-iminium ion)-type. It was first example of isolation and characterization of the novel iminium-ion ruthenium complex. Reactions of *mer*-[1] in ethanol and 2-propanol afforded *mer*-$[RuCl_3(ebpea)]$ (*mer*-[2]) with acetaldehyde and acetone, respectively. A reverse C-H activation reaction of *mer*-[2] occurred to give a *mer*-[1] under refluxing in an alcohol. The conversion between *mer*-[1] and *mer*-[2] would be used for an oxidation reaction of alcohols by the iminium-ion moiety (Scheme 1).
Formation of nitrosoruthenium complex, *cis*(N_3, N_3)-$[Ru(N_3)_2(NCH_2CHN(O)py(C_2H_4py)C_2H_5)]$ (*cis*-[3]), via an alternative C-H activation reaction of the $-CH_2-$ moiety at next to the pyridyl group occurred during a reaction using nitrosylruthenium complexes, $[RuX_2(NO)(ebpea)]^+$ (X = Cl^-, ONO_2^-), with N_3^-. The structure was shown in Figure 3. Distances of Ru-N1, N1-O1, and N1-C1 were 1.8689(14), 1.2504(19), and 1.514(2) Å, respectively. The angle of Ru-N1-O1 was 136.71(12)°. These parameters indicated that the Ru-N(O)C- moiety was nitroso group.

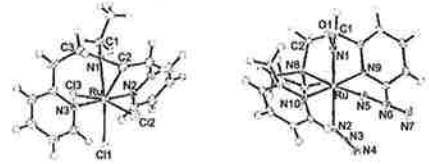
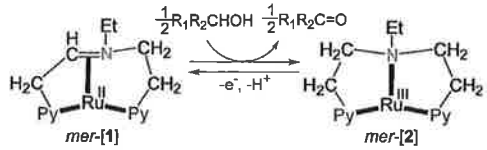


Figure 2. Strucutre of *mer*-[1] and *cis*-[3]



Scheme 1. Conversions between *mer*-[1] and *mer*-[2]

Acknowledgements: This work was supported by the Joint Studies Program (2009) of the Institute for Molecular Science.

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Synthesis, Characterization and Reactivity of Iridium Complexes Containing Bis(ditertiaryphosphine) Ligands

S. Garcia, S. Schreiner
Department of Chemistry, Randolph-Macon College, Ashland, VA 23005, USA
(stephanygarcia@students.rmc.edu)

The coordination chemistry of iridium complexes containing bis(diphenylphosphino)methane (dppm) has been explored to a great extent, and results show that both mono- and binuclear compounds[1] have been able to activate small molecules[2,3,4]. However, little is known about the reaction chemistry of iridium complexes stabilized by bulkier ligands such as bis(dicyclohexylphosphino)methane (dcpm).

Here we wish to describe the synthesis and spectroscopic characterization of mono- and bimetallic iridium complexes stabilized by bis(ditertiaryphospines) ligands such as dppm and dcpm. The reactivity of these complexes towards small molecules such as CO, HCl, O_2 and SO_2 will also be reported.

The reaction of $[Ir(Cl)(CO)(PPh_3)_2]$ (**1**) with dcpm in non-polar solvents in a 1:2 ratio yielded the ionic complex $[Ir(CO)(dcpm)_2]Cl$ (**2**) in 92% yield as a pale yellow solid. This complex readily undergoes decarbonylation when refluxed under N_2 gas, yielding $[Ir(dcpm)_2]Cl$ (**3**) as an orange solid in a 67% yield. Iridium complex (**3**) has shown reactivity towards small molecules including carbon monoxide, acids, primary silanes, oxygen and hydrogen.

Synthesis of $[Ir_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}dcpm)_2]Cl$ (**4**) is achieved through the reaction of $[Ir_2(Cl)_2(COD)_2]$ (COD = cyclooctadiene) with dcpm in a 1:2 ratio in the presence of CO. Using similar synthetic procedures, the reaction of $[Ir_2(Cl)_2(COD)_2]$ with dppm yielded $[Ir_2(Cl)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$[1] (**5**) in about 80% yield. (**5**) undergoes decarbonylation when refluxed in THF yielding the anionic trans species, trans-$[Ir(Cl)_2(CO)_2(\mu\text{-}dppm)_2]$[1](6). Under N_2, the reaction of $[Ir_2(Cl)_2(COD)_2]$ with dcpm yielded mononuclear complexes via ligand exchange with cyclooctadiene, [Ir(COD)(diphoshine)]Cl (diphosphine = dcpm (**7**) or dppm (**8**)). All complexes were characterized by IR and multinuclear NMR spectroscopy. The reactivity of all mono- and binuclear complexes towards activation of small molecules will be detailed.

Acknowledgements: This work is supported by the Schapiro Undergraduate Research Fellowship, the Virginia Foundation for Independent Colleges, the National Science Foundation and the Jackson Endowment.

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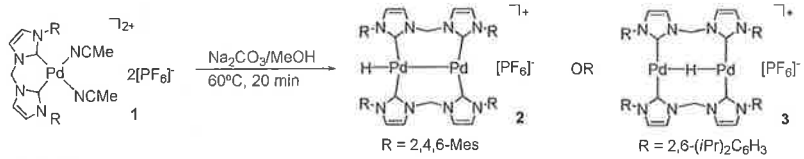
Reduction of Chelating Bis(NHC)Pd(II) Complexes to $[\{\mu\text{-bis(NHC)}\}_2Pd_2H]^+$: Novel Pd(I)-Pd(I) Bonded Species with a Terminal Hydride and a Pd(I)-H-Pd(I) Complex Lacking a Pd-Pd Bond

M A. Riapanitra[1], P.D.W. Boyd[1], A.J. Edwards[2], M.G. Gardiner[1], M.-H. Lemée-Cailleau[3], D.S. McGuinness[1], D.N. Stringer[1], and B.F. Yates[1]

1. *School of Chemistry, Private Bag 75, University of Tasmania, Hobart TAS 7001, Australia. Michael.Gardiner@utas.edu.au*
2. *Bragg Institute, ANSTO, Menai NSW 2234, Australia.*
3. *Institut Laue-Langevin, B.P.156, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France.*

Mechanistic debate in the area of Pd based C-C coupling reactions using *N*-Heterocyclic Carbene (NHC) ligands has spanned the in situ generation of active NHC complexes from the reaction of simple Pd(0) or Pd(II) species with imidazolium-based ionic liquid solvents, through to the opposite extreme of NHC complexes acting as precatalysts to NHC-free colloidal Pd materials that partake in heterogeneous catalysis.

Herein we report the base assisted reduction of chelating bis(NHC)Pd(II) complexes **1** to the $(Pd_2H)^+$ species **2** and **3** stabilised by sterically demanding, bridging bis(NHC) ligands, Scheme **1**. The terminal hydride ligand has been established by neutron crystal structure analysis for **2**. In contrast, the more bulky analogue **3** lacks a Pd-Pd bond (3.3944(12) Å) and the hydride ligand, purportedly, bridges the Pd centres in linear fashion (hydride not located by X-ray diffraction). The bonding interactions in the $(Pd_2H)^+$ cores of **2** and **3** have been studied by DFT calculations and the fluxional nature of **2** in solution has been examined by NMR spectroscopy.



Scheme 1.

Complexes **2** and **3** are the first Pd(I) NHC complexes and the first low valent Pd NHC complexes (I or 0) prepared by reduction of Pd(II) complexes to be structurally authenticated. NHC ligand binding mode changes and reduction to palladium black for less bulky ligands is of great catalytic relevance for catalysis with bis(NHC) ligands. The performance of the Pd(I) complexes in C_2H_4/CO copolymerisation and various C-C coupling reactions has been investigated.

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New Coordination Materials for Energy Applications – Indolizino[2,3-b]quinoxaline-derived Ligands

W. M. Bloch[1], J. C. Morris[2], C. J. Sumby[1]

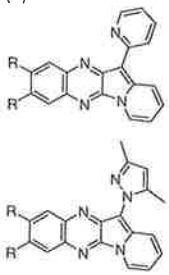
1. *School of Chemistry and Physics, University of Adelaide, Adelaide, Australia witold.bloch@adelaide.edu.au*
2. *School of Chemistry, UNSW, Sydney, Australia*

A new class of conjugated heterocyclic ligand bearing an indolizino[2,3-b]quinoxaline core (Figure 1a) have been synthesized and their properties examined[1]. These ligands chelate via formation of a six-membered chelate ring to a range of transition metals and, when complexed to ruthenium, show absorptions spanning the UV and visible regions (Figure 1b). Hence, ruthenium complexes of these ligands may show promise as dyes for Dye-sensitized Solar Cells.

New compounds (Figure 1a) of this class have been synthesized from active methylene compounds, e.g. 2-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]pyridine, and 2,3-dichloroquinoxaline or 6,7-dimethyl-2,3-dichloroquinoxaline. By computational methods and NMR spectroscopy, it has been found that when the heterocycle in the 5-position of the indolizino[2,3-b]quinoxaline core is 3,5-dimethylpyrazole the compounds possess a steric clash which impedes on their ability to chelate to metal centres. This was confirmed by X-ray crystallography for silver(I) or copper(I) complexes of the ligand 5-(3,5-dimethyl-1H-pyrazol-1-yl)-8,9-dimethylindolizino[2,3-b]quinoxaline.

The synthesis of bridging ligands bearing an indolizino[2,3-b]quinoxaline core has also been investigated.

(a)



R = H or Me

(b)

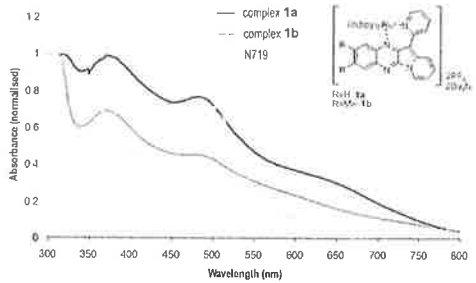


Figure 1. (a) Structures of the type of heterocyclic ligand under investigation and (b) UV-visible absorbance spectra for ruthenium(II) complexes 1a and 1b.

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Surface binding and corrosion inhibition on iron of some cobalt(III) complexes

R. T. Jane[1], R. M. Hartshorn[1], P. A. Tasker[2], R. J. Cooper[2]

1. *Department of Chemistry, University of Canterbury, New Zealand, rtj17@uclive.ac.nz*
2. *School of Chemistry, University of Edinburgh, UK*

The treatment of metal surfaces by chromates has been used in industry since the early 20th century to impart properties such as increased resistance to corrosion and improved adhesion of coatings.[1] However, its use is being increasingly restricted due to the toxicity of chromium in high oxidation states.[2] Chromate surface treatment is generally thought to occur by the formation of highly insoluble, polymeric chromium(III) oxide-hydroxides at the interface of the substrate (Figure 1A).[3] Many of the properties of chromium(III) complexes that contribute to the formation of these layers (kinetic inertness, preference for an octahedral geometry and ability to form hydroxide-bridged polynuclear complexes) are shared by complexes of cobalt(III). We have therefore undertaken a study of the binding of cobalt(III) complexes to metal oxide-hydroxide surfaces. This will occur through displacement of the exchangeable ligands by the surface bound oxide and/or hydroxide groups. This would result in the formation of complexes in which the metal oxide-hydroxide surface is a polydentate ligand (Figure 1B).

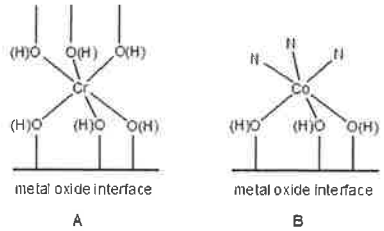

Figure 1: Possible attachment to a metal oxide layer of A) a polymeric chromium(III) oxide-hydroxide and B) a cobalt(III) amine complex.

High surface area goethite was used as a model for the surface of iron. The uptake of cobalt(III) complexes bearing exchangeable ligands was followed by measuring the decrease in cobalt content from aqueous solution by ICP-OES. From the resulting adsorption isotherms, it can be seen that complexes with a greater number of exchangeable ligands show better binding to the goethite surface. This supports the binding model in Figure 1B, with more bridges to the surface providing greater stability. When no exchangeable ligands are present, the uptake is very low, which may be explained by low background physisorption. The inhibition of corrosion on iron by cobalt(III) complexes was also investigated. It was found that all the complexes tested reduced the rate of corrosion. However, the observed inhibition does not appear to be related to the number of exchangeable ligands.

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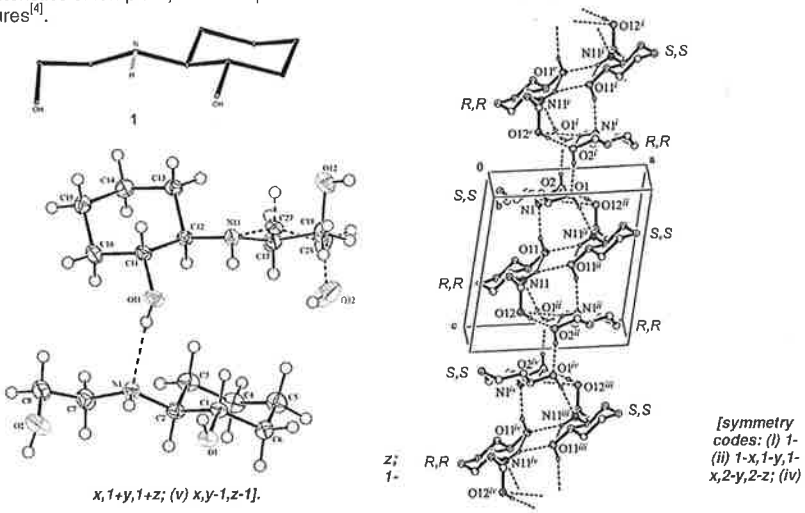
Hydrogen Bonding in Anion Assisted Self-Assembly of Amino Alcohols

A. S. de Sousa[1], Z. Hlam[1], H. M. Marques[1]
1. *School of Chemistry, University of the Witwatersrand, Johannesburg, Private bag3, Wits 2050, South Africa*

Work on solid state structures of reinforced β-amino alcohols, where cyclohexyl bridges are fused into pendent hydroxyethyl groups, has suggested these compounds are able to form self-assembled structures[1]. Structures of relatively simply amino alcohols, such as diethanolamine weakly assemble into tubular stacks, through linking of ring motifs via N-H...O hydrogen bonds, defining internal cavities of a predominantly hydrophilic nature[2]. Tubular stacks are preferentially formed when stronger O-H...O intermolecular hydrogen bonds are favoured. Grafting a cyclohexyl bridge across hydroxyethyl groups favours intermolecular O-H...O hydrogen bonds[1]. The cyclohexyl bridge, between the amine nitrogen and a single hydroxy oxygen donor atom, promotes stronger intermolecular O-H...O hydrogen bonds that link ring motifs[3] into elaborate tubular stacks in the reinforced diethanolamine derivative (2-[(2-hydroxyethyl)amino]cyclohexanol) (**1**). Hydrophilic inner cores arise from the stereospecificity of intermolecular O-H...O hydrogen bonds, dependent on the cyclohexyl conformation defining a surrounding hydrophobic outer surface.

Investigating self-assembled amino alcohol structures as molecular hosts requires modulation of the hydrophilic inner core through N-alkyl and C-alkyl substitution of hydroxyalkyl pendents. Hydrochloride salts of β-amino alcohols present a convenient starting point. The chloride ion, as for other halide ions, are typically strong hydrogen bond acceptors and O-H...Cl and N-H...Cl interactions effectively stabilize crystallization of these salts. These interactions are often attributed the characteristics of ion-pairs; closer inspection reveals their alternative role in self-assembled structures[4].



x,-y,-z; (iii)

x,1+y,1+z; (v) x,y-1,z-1].

z; 1-

[symmetry codes: (i) 1-(ii) 1-x,1-y,1-x,2-y,2-z; (iv)

Acknowledgements: National Research Foundation (South Africa), University of the Witwatersrand and the Mellon Postgraduate Mentoring Programme.

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Manganese phthalocyanine: variety of coordination forms

O. V. Dolotova[1], G. A. Meerovich[2], V. M. Negrimovsky[1], O. L. Kaliya[1]
1. *FSUE "SSC "NIOPIK" (Organic Intermediates and Dyes Institute), Moscow, Russia, oldolotova@yandex.ru*
2. *A.M. Prokhorov Institute of General Physics of Russian Academy of Sciences, Moscow, Russia*

Since the first publication about interaction of manganese phthalocyanine (PcMn) with dioxygen [1], any derivatives of PcMn attract steady attention of scientists due to unordinary coordination and catalytic chemistry.
Synthesis of substituted in benzene ring derivatives of PcMn soluble in inert organic solvents allowed to clarify fundamental aspects of PcMn coordination chemistry[2].
A number of thiosubstituted PcMn were synthesized and characterized by elemental analysis data and electronic absorption spectra in the present work. Main bands positions and intensity are represented in the table for various PcMn's coordination forms.

№	Compound	λ_{max}, nm (lg ε)			
		PcMn(III)Cl in chloroform	**(PyPcMn(III))$_2$O** in pyridine	**PcMn(II)** in benzene	**PcMn(II)** in pyridine
I	3-(t-BuS)$_4$-PcMn	359 (4.59), 528 (4.08), 745 (4.85)	330, 654	350, 685	350, 483, 525, 568, 668, 840, 889
II	4-(t-BuS)$_4$-PcMn[2]	352 (4.57), 516 (4.04), 731 (4.86)	335, 635	355, 685	350, 470, 520, 570, 660, 820, 860
III	3-(t-BuS)$_4$-5-(t-Bu)$_4$-PcMn	367 (4.63), 535 (4.15), 751 (4.80)	340, 651	360, 689	350, 487, 524, 568, 668, 838, 887
IV	4-(BuS)$_4$PcMn	337 (4.59), 449 (4.41), 525 (4.28), 750 (4.85)	330, 640	350, 685	350, 482, 530, 581, 670, 850, 911
V	4,5-(SDec)$_8$-3,6-Cl$_8$PcMn	300 (4.28), 522 (3.71), 785 (4.18)	335, 683	304, 723	354, 487, 695, 855
VI	4,5-(PhS)$_8$PcMn	330 (4.63), 464 (4.43), 524 (4.34), 773 (4.87)	325, 662	350, 450, 712	493, 550, 622, 627, 687, 868, 916

The most essential dependence of band position on the nature and location of substituents was observed for Mn(III) complexes.
In the presence of organic bases complexes Mn(II) exhibit multiband spectra corresponding to the mixture of: PyPcMn(II), Py$_2$PcMn(II), PyPc$^+$Mn(I) and Py$_2$Pc$^-$Mn(III)[2].
It was shown that some of the investigated manganese phthalocyanines are perspective as potential contrast agents for magnetic resonance imaging.

Acknowledgements: We thank Moscow Government for financial support.

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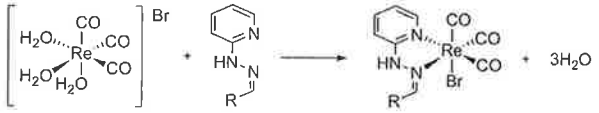
Development of radiotracers to assist in the diagnosis of Alzheimer's disease.

D. J. Hayne[1,2], S. Lim[1,2], J. M. White[1,2], P.A. Lay[3], K. J. Barnham[2,4], P. J. Barnard[5], P. S. Donnelly**[1,2]

1. *School of Chemistry, The University of Melbourne, Victoria, Australia 3010; d.hayne@pgrad.unimelb.edu.au*
2. *Bio21 institute, University of Melbourne, Victoria, Australia 3010*
3. *School of Chemistry, The University of Sydney, NSW, Australia 2006*
4. *Department of Pathology, The University of Melbourne, Vic, Australia 3010*
5. *Department of Chemistry, La Trobe University, VIC, Australia 3086*

A radiotracer suitable for the detection and imaging of the pathological hallmarks associated with Alzheimer's disease (AD), particularly β amyloid (Aβ) plaques, would assist in early diagnosis along with the evaluation and use of interventional therapies. With the necessary infrastructure for single photon emission computed tomography (SPECT) already present in many hospitals, a radiotracer suited to this technique presents as being of particular clinical relevance.

The radionuclide ^{99m}Tc is used for the majority of SPECT imaging. In the absence of a non-radioactive Tc isotope, Re complexes are often synthesised as surrogates to the corresponding ^{99m}Tc analogues for preliminary assessment. Rhenium has been used extensively for this as it provides a coordination environment very similar to Tc. An oxidation state of +1 was chosen for the Re centre giving the metal a low spin d^6 configuration to help stabilise complexes. The precursor used to prepare complexes was $[Re(H_2O)_3(CO)_3]^+$. Adding to the attraction of using a Re^I centre is the equivalent Tc precursor can be easily produced from $[TcO_4]^-$ using kit preparations.[1] The ligands used were bifunctional, in that they were designed to both coordinate to the metal and bind specifically to Aβ plaques. The reagent 2-hydrazinopyridine was used as the basis for the ligands because it can be functionalised by condensation with the appropriate aldehyde then coordinate in a bidentate fashion through two sp^2 hybridised nitrogen atoms. To increase brain uptake, incorporation of additional functionality that could be used to enhance passive uptake or make use of endogenous active transport mechanisms across the blood brain barrier (BBB) was also investigated.



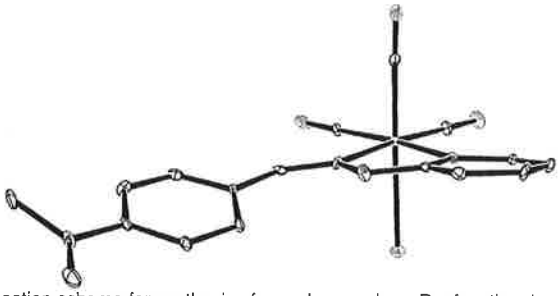


Figure 6 Top: Reaction scheme for synthesis of complexes, where R = functional group that binds specifically to Aõ plaques; bottom: An ORTEP-3 representation showing an example of the type of complex synthesized, hydrogen atoms are omitted for clarity.

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Mechanism for the reaction of Head-to-Head pivalamidato-bridged *cis*-diammine-platinum(III) binuclear complex with isoprene

Koji Ishihara[1], Jun Nagashima[1], Satoshi Iwatsuki[2], Kazuko Matsumoto[3]

1. *Graduate School of Advanced Science and Engineering, Waseda University, Tokyo, Japan*
2. *Department of Chemistry of Functional Molecules, Konan University, Kobe, Japan*
3. *Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan*

The Head-to-Head pivalamidato-bridged platinum(III) binuclear complex, HH-$[Pt(NH_3)_4((CH_3)_3CCONH)_2(NO_3)_2](NO_3)_2$ (**1**) reacts with organic compounds such as ketone and olefin to produce ketonyl-Pt(III) complexes and β-hydroxy-alkyl-Pt(III) complexes, respectively,[1] and the latter complex produces ketones, aldehydes, epoxides, and 1,2-diols by water attack. On the other hand, the reaction of complex **1** with isoprene (2-methyl-1,3-butadiene) gives two alkyl complexes (**2** and **3** in Scheme 1), of which molar ratio ([**2**]/[**3**]) is different from that of their reaction products ([**4**]/[**5**]). We have already studied the mechanisms for the reactions of the amidato-bridged Pt(III) binuclear complexes with halide ions and olefins.[2] In this study, we studied kinetically the title reaction to clarify the precise formation mechanism of the diols (**4** and **5**), and to show why the ratio of the products differs from that of the parent complexes.

Kinetic study was performed using UV-vis spectrophotometry and ^{1}H NMR spectroscopy. The title reaction proceeded consecutively in four steps. It was clarified that when the reaction was followed by UV-vis spectrophotometry, isoprene π-coordinates preferentially with its double bond having methyl group to the $Pt(N_2O_2)$ atom in step 1, the rate-determining π-coordination of another isoprene molecule occurs to the $Pt(N_4)$ atom followed by nucleophilic attack of water molecule to the π-coordinated isoprene on the $Pt(N_2O_2)$ atom to form two σ-complexes accompanying the release of the π-coordinated isoprene on the $Pt(N_4)$ atom in step 2, reductive elimination of the σ-complexes occurs to form two diols and the HH pivalamidato-bridged Pt(II) binuclear complex in step 3, and the acid decomposition reaction of the Pt(II) binuclear complex occurs to form monomers in step 4. On the other hand, when the slower two steps (step 3 and step 4) were followed by ^{1}H NMR spectroscopy, the reductive elimination of the σ-complexes occurs in step 3 (Figure 1), and in step 4 occurs the isomerization from 1,4-diol to 1,2-diol. Therefore, the reason why the ratio of the products (diols) differs from that of the parent σ-complexes is the acid-catalyzed isomerizations (between σ-complexes 2 and 3, and between diols 4 and 5).

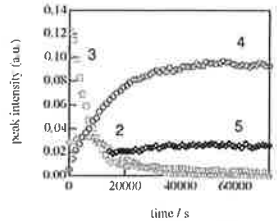
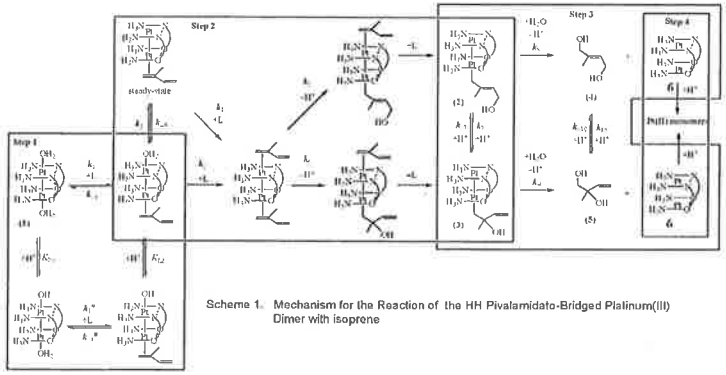


Figure 1. Change in ^{1}H NMR peak intensity with time in step 3 for the reaction of complex 1 with excess isoprene at 30°C and pD = 2.8.



Scheme 1. Mechanism for the Reaction of the HH Pivalamidato-Bridged Platinum(III) Dimer with isoprene

References:

[1] K. Matsumoto et al., *Adv. Inorg. Chem.*, **1999**, *49*, 375.

[2] N. Saeki et al., *J. Am. Chem. Soc.*, **2003**, *125*, 3605.

Solvent extraction of silver(I) ion with 9-aza-3,6,12,15-tetrathiaheptadecane derivatives: effect of *N*-substituents on extraction behavior

S. Iwatsuki[1], A. Ichiyama[1], K. Chayama[1]
1. *Department of Chemistry of Functional Molecules, Konan University,Kobe Japan*
E-mail: iwatsuki@center.konan-u.ac.jp (SI) and chayama@konan-u.ac.jp (KC)

Cyclic and acyclic polythioether compounds are known to extract selectively class *b* metal ions. We have demonstrated that the extraction of silver(I) with acyclic tetrathioethers is more effective than that with the corresponding cyclic thiacrownethers.[1] We also succeeded in preparation of monoazatetrathioether, 9-aza-3,6,12,15-tetrathiaheptadecane (ATH, Chart 1) which extracted selectivity some soft metal ions, e.g., Ag(I), Cu(I), Pd(II), etc. Here, we show the preparation of a series of ATH derivatives with *N*-substituents, *N*-R-ATH (R = $PhCH_2$, 4-NO_2PhCH_2, Ph_2CH), and the extraction behaviors of Ag(I) in water/1,2-dichloroethane (DCE) systems.

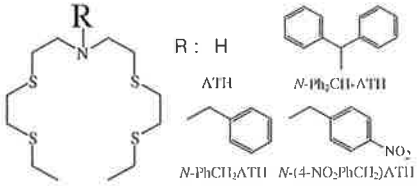


Chart 1. The structure of *N*-R-ATH.

ATH was synthesized via the reaction of 2-mercaptodiethylsulfide with bis(2-chloro-ethyl)amine in basic ethanol solution. *N*-R-ATHs were obtained by Mannich reaction[2] of ATH with R-Br with yields of 40 – 70%.

The water/DCE distributions of ATH and *N*-R-ATHs were examined at various pH of aqueous phase (Figure 1). It was found that ATH and *N*-$PhCH_2$ATH transferred from DCE to water at pH < 5 and pH < 3, respectively while *N*-(4-NO_2PhCH_2)-, and *N*-Ph_2CH-ATH did not transfer even at pH 1. This result suggests that *N*-R-ATH is more hydrophobic than ATH under acidic conditions. Acid dissociation constants of *N*-$PhCH_2$-, 4-NO_2PhCH_2- and Ph_2CH-ATH were also determined in aqueous 1,4-dioxane solution (50v/v%) to be pK_a = 5.26±0.06 (R = $PhCH_2$), 3.74±0.02 (4-NO_2PhCH_2), and 3.11±0.03 (Ph_2CH), respectively. These values are much lower than that of ATH (pK_a = 11.0±0.5 determined by an extraction method). The tendency of the pK_as of *N*-R-ATHs relates to the distribution behavior: *N*-R-ATH with the lower pK_a is hard to transfer to the acidic aqueous phase compared to that with the higher pK_a.

The water/DCE extraction of Ag(I) with ATH and *N*-R-ATH were examined under the various conditions of aqueous phase. It was found that the extraction efficiencies (%E) of ATH and *N*-R-ATHs at various pHs (Figure 2) were in the order of R = $PhCH_2$ > 4-NO_2PhCH_2 > Ph_2CH >> H at pH > 2. This clearly indicates *N*-R-ATHs are better extractants for Ag(I) than ATH, which would be due to hydrophobic nature of *N*-substituents.

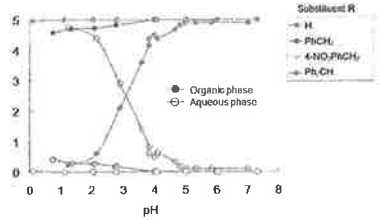


Figure 1. Distribution of *N*-R-ATH between water/DCE at various pH of the aqueous phase.

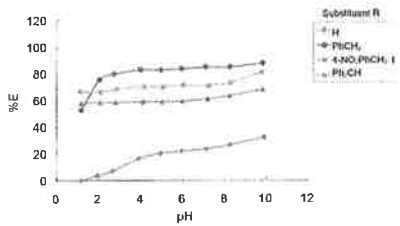


Figure 2. The %E vs. pH plots for the water/DCE extraction of Ag(I) with *N*-R-ATH.

Acknowledgements: This research was partly supported by the Grants-in Aid for Scientific Research (Grants Nos. 20550089 and 21750082) from MEXT and JSPS, Japan.

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[1] K. Chayama and E. Sekido, *Anal. Chim. Acta*, **1991**, *248*, 511; *Anal. Sci.*, **1990**, *6*, 883; *Bull. Chem. Soc. Jpn.*, **1990**, *63*, 2420; *Anal. Sci.*, **1987**, *3*, 535.
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Reactions of Ruthenium Complexes Bearing Pyridyl-containing Ligands With Hydrazine Derivatives

N. Kanesaka, A. Kajihara, S. Okawa, H. Nagao
Sophia University, Tokyo, JAPAN. n-kanesa@sophia.ac.jp.

Ruthenium complexes bearing nitrogen-containing compounds are stable due to affinity of the ruthenium center toward a nitrogen-donor. We have been studying conversions of nitrogen-containing compounds on ruthenium complexes bearing pyridyl-containing compounds as supporting ligands.[1] Pyridyl-ligands such 2,2'-bipyridine (bpy) and 2,2':6',2"-terpyridine have been interested in connection with their electro- and photochemical properties.

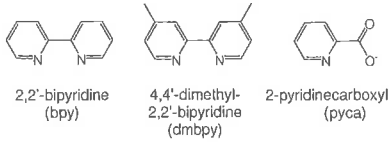


Figure 1. Pyridyl-containing ligands

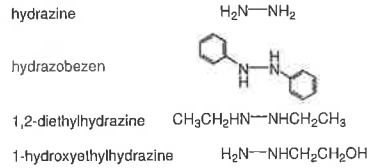
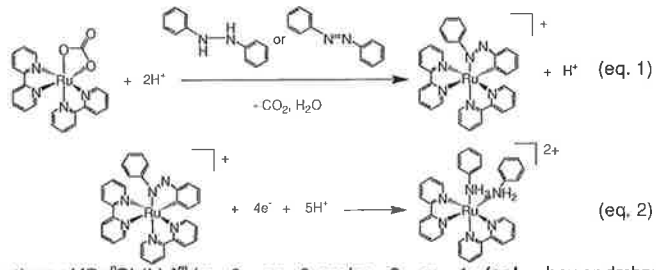


Figure 2. Hydrazine and hydrazine derivatives

A reaction of $[Ru^{II}(CO_3)(bpy)_2]$ with hydrazobenzen or azobenzen afforded $[Ru^{II}(C_6H_4N{=}NPh)\text{-}(bpy)_2]^+$, in which the nitrogen atom of the azo group and the anionic carbon atom at *ortho*-position of the phenyl group coordinated (eq. 1). The nitrogen-nitrogen double bond of the *ortho*-metalation complex was cleaved by a reduction under strong acidity condition to give $[Ru^{II}(NH_2Ph)_2(bpy)_2]^{2+}$ (eq. 2). The UV-vis spectra of $[Ru^{II}(C_6H_4N{=}NPh)(bpy)_2]$ in low-pH regions changed with pH, indicating that the initial stage of this reaction was protonation at the complexes.



Reactions of $[Ru^nCl_2(L)_2]^m$ (n = 2+, m = 0, and n = 3+, m = 1+ for **L** = bpy or dmbpy, and n = 3+, m = 1- for **L** = pyca), with hydrazine and hydrazine derivatives such as 1,2-diethylhydrazine and 1-hydroxylethylhydrazine have been also investigated. $[Ru^{II}Cl_2(bpy)_2]$ reacted with hydrazine, and a mixture of $[Ru^{II}Cl(NH_3)(bpy)_2]^+$ and $[Ru^{II}(NH_3)_2(bpy)_2]^{2+}$ was obtained (eq. 3). A reaction of $[Ru^{III}Cl_2(pyca)_2]^-$ with hydrazine in methanol gave a mixture of $[Ru^{III}(NH_3)_2(pyca)_2]^+$ and $[Ru^{II}(NH_3)_2(pyca)_2]$ (eq. 4). We are investigating reactions of $[Ru^{II}Cl_2(dmbpy)_2]$, $[Ru^{III}Cl_2(dmbpy)_2]^+$ and $[Ru^{III}Cl_2(pyca)_2]^-$ with hydrazine and hydrazine derivatives such as 1-hydroxyethylhydrazine to elucidate the reaction mechanisms.

$$[Ru^{II}Cl_2(bpy)_2] + H_2NNH_2 \longrightarrow \begin{cases} [Ru^{II}Cl(NH_3)_2(bpy)_2]^+ \\ [Ru^{II}(NH_3)_2(bpy)]^{2+} \end{cases} \quad \text{(eq. 3)}$$

$$[Ru^{III}Cl_2(pyca)_2]^- + H_2NNH_2 \longrightarrow \begin{cases} [Ru^{III}(NH_3)_2(pyca)_2]^+ \\ [Ru^{II}(NH_3)_2(pyca)_2] \end{cases} \quad \text{(eq. 4)}$$

Reference:

[1] H. Nagao, T. Kikuchi, M. Inukai, A. Ueda, T. Oi, N. Suzuki, M. Yamasaki, *Angew. Chem. Int. Ed.*, **2006**, *45*, 31

Effectiveness of CPL Spectroscopy for Investigating the Diastereopurity of Chiral Ln(III)-Containing Complexes

G. Muller, K. Do, A. J. Ingram
Department of Chemistry, San José State University, San José, CA, USA

Circularly polarized luminescence (CPL) is a useful tool for obtaining chiral structural information about selected systems in their excited state, while circular dichroism (CD) spectroscopy is for probing the same molecules in their ground state.[1] One advantage of CPL spectroscopy is to identify whether the Ln(III) complex solution contains a mixture of diastereomeric/enantiomeric species or whether this complex solution is a racemic mixture.[2]

It is worth mentioning that NMR is often used for assessing the diastereopurity of chiral systems. In addition to the sample requirement for NMR measurements, it is often the case that Ln(III)-containing complexes, namely Eu(III) and Tb(III), cannot be investigated in this way due to their strong paramagnetic nature.

From this standpoint, we will demonstrate that the CPL technique may be suitable for a detailed examination of the diastereopurity of chiral Ln(III) systems.

[1] G. Muller, *Dalton Trans.*, **2010**, 9692. J. P. Riehl, G. Muller, in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 43* (Eds.: K. A. Gschneider, J.-C. G. Bünzli, V. K. Pecharsky), North-Holland Publishing Company, Amsterdam, **2005**, p. 289.
[2] K. Do, F. C. Muller, G. Muller, *J. Phys. Chem. A*, **2008**, *112*, 6789.

Anion directed formation of metallo-macrocyclic complexes and coordination polymers incorporating flexible amide ligands

M. Abdul-Kadir[1], L. R. Hanton[2] and C. J. Sumby[1]
1. *School of Chemistry and Physics, The University of Adelaide, Adelaide, SA 5005, Australia*
2. *Department of Chemistry, University of Otago, Dunedin, New Zealand*

Anion-directed self-assembly is topical area in metallo-supramolecular chemistry and crystal engineering.[1-2] By using combinations of organic ligands and transition metal ions, new metallo-supramolecular species can be prepared and the self-assembly process modulated by the choice of anion. Our studies have focused on the incorporation of flexible monoamide ligands into metallo-supramolecular assemblies to study the interactions of such assemblies with anions. The syntheses and structures of these amide ligands have been previously reported.[3]
Herein, we report studies of metallo-macrocyclic complexes and coordination polymers containing two amide ligands, *N*-6([3-pyridylmethylamino)carbonyl]-2-pyridinecarboxylate (**L1**) and *N*-6([4-pyridylmethylamino)carbonyl]-2-pyridinecarboxylate (**L2**), respectively (Figure 1). The methyl ester groups in both ligands can easily undergo hydrolysis *in situ* to form free carboxylic acids and ONO chelating sites. The reaction of copper salts with **L1** gives rise to three closely related discrete metallo-macrocyclic complexes, $[Cu_2(NO_3)_2(\mathbf{L1\text{-}CH_3})_2]$ (**1**), $[Cu_2Cl_2(\mathbf{L1\text{-}CH_3})_2].H_2O$ (**2**) and $[Cu_2(\mathbf{L1\text{-}CH_3})_2(CH_3OH)_2](ClO_4)_2$ (**3**) with cleft-shaped structures.

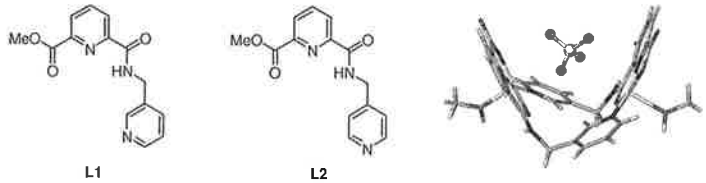


Fig. 1: The structures of **L1** and **L2**. A perspective view of the metallo-macrocyclic copper complex **3**.

A change in the nitrogen position within the pendant pyridine ring when changing from **L1** to **L2** leads to the formation of a coordination polymer, $\{[Cu(\mathbf{L2})(\mathbf{L2\text{-}CH_3})](ClO_4)]\}_n$ (**4**), with $Cu(ClO_4)_2$. Further polymeric compounds were obtained from the reaction of **L2** with other metal salts. These initial results have shown that ligands **L1** and **L2** are suitable for the synthesis of metallo-macrocyclic species capable of interactions with anions, either as part of metallo-supramolecular assemblies or coordination polymers.

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[1] R. Vilar, *Eur. J. Inorg. Chem.* **2008**, 3, 357–367.
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[3] C.J. Sumby, L. R. Hanton, *Tetrahedron*, **2009**, 65, 4681– 4691.

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Preparation and polarized electronic spectra of hybrid materials of chiral Schiff base Ni(II) and Cu(II) complexes and photochromic compounds in PMMA films

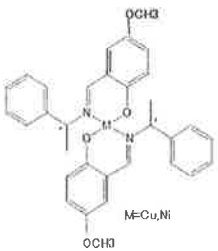
T. Akitsu[1], Y. Miura[1]

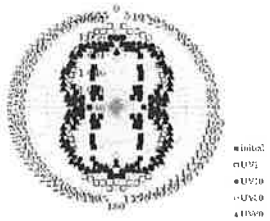
1. *Department of Chemistry, Faculty of Science, Tokyo University of Science, akitsu@rs.kagu.tus.ac.jp*

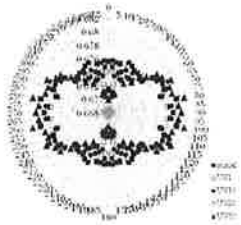
Previously we have successfully observed conformational changes of a chiral Schiff base Ni(II) complex accompanying with cis-trans photoisomerization of azobenzene in supramolecular solution systems[1]. This is due to intermolecular interactions, since not only flexibility of metal complexes but also steric factors of chiral Schiff base ligands are important for this effect[2]. Moreover, we investigated organic/inorganic hybrid materials in PMMA cast films of chiral Schiff base metal complexes and azobenzene to compare matrix environment[3]. Herein we have prepared new hybrid materials containing (1) related Ni(II) and Cu(II) complexes having electron donating MeO-groups instead of electron withdrawing 3,5-Cl-groups to compare electronic effects associated with flexibility of metal complexes and (2) different photochromic compounds, azobenzene and disperse red 1, to compare optical anisotropy by Weigert's effect (not cis-trans photoisomerization).

New Ni(II) and Cu(II) complexes were prepared according to usual methods and new hybrid materials were also assembled by using them and azobenzene or disperse red 1. We measured polarized electronic spectra as a function of angles of polarizers after irradiation of polarized UV light. We investigated optical anisotoropy by Weigert's effect of photochromic compounds based on their ő,-ő * and ŋ-ő * bands and molecular alignment and conformation of metal complexes based on their ő,-ő * and d-d bands.

Circular diagrams of optical anisotropy for a hybrid material of disperse red 1 [left] new Cu(II) complex and disperse red 1 [right] are shown, which indicate not only optical anisotropy by Weigert's effect but also enhancing optical anisotropy by intermolecular interaction.







Acknowledgements: This work was supported by Kato Foundation for Promotion of Science.

References:

[1] T. Akitsu, Y. Einaga, *Polyhedron*, **2005**, *24*, 1869.
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[3] T. Akitsu, T. Itoh, *Polyhedron*, **2010**, *29*, 477.

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Polarized electronic and IR spectra of hybrid materials of chiral Mn(II) complexes and photochromic compounds exhibiting Weigert's effect

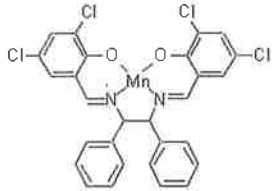
T. Akitsu[1], R. Tanaka[1]

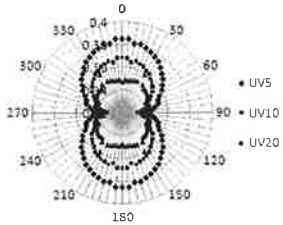
1. *Department of Chemistry, Faculty of Science, Tokyo University of Science, akitsu@rs.kagu.tus.ac.jp*

Recently, we have prepared organic/inorganic hybrid materials consisting of photochromic organic compounds and metal complexes. For example, we have successfully observed conformational changes of chiral Schiff base metal complexes through intermolecular interaction[1] and magnetic changes of typical Mn_{12} single molecule magnet accompanying with states of aggregation[1]. Furthermore, we could find gradual increasing of optical anisotropy of the Mn_{12}[3] and chiral Schiff base metal complexes[4] in PMMA cast films, which restricted molecular motion and alignment, by alternate irradiation of polarized UV and visible light. Herein we attempted that (1) improvement of optical anisotropy by Weigert's effect using irradiation of polarized UV light. (2) separated observation of changes of conformation and alignment of metal complexes and/or components of organic/inorganic hybrid materials by using polarized IR spectroscopy as well as polarized electronic spectroscopy.

We prepared some organic/inorganic hybrid materials containing azobenzene, stilbene, and spiropyrans, exhibiting different properties, and several new chiral Schiff base Mn(II) complexes as PMMA films. Optical anisotropy was investigated based on circular diagrams by electronic (and corresponding CD) and IR spectra.

For example, electronic spectra of a hybrid material of the Mn(II) complexes and azobenzene after irradiation of polarized UV light for 3 min x up to 20 times are shown. The corresponding circular diagram exhibited that improvement of optical anisotropy by Weigert's effect comparing with in the case of cis-trans photoisomerization of azobenzene. Detailed results will be reported in the conference.





Acknowledgements: This work was supported by Kato Foundation for Promotion of Science.

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[4] T. Akitsu and T. Itoh, *Polyhedron*, **2010**, *29*, 477.

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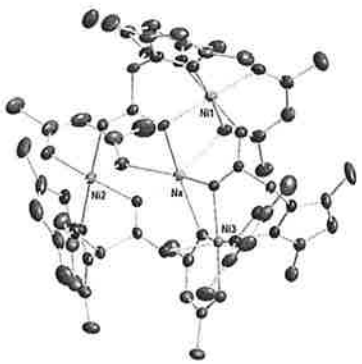
Controlled buildup of supramolecular structures by alkali metal induced self assembling of transition metal(II) complexes

A. Beyer[1], N. Burzlaff[1]

1. *Inorganic Chemistry, Department of Chemistry and Pharmacy & Interdisciplinary Centre for Molecular Materials (ICMM), University of Erlangen-Nürnberg, Egerlandstraße 1, D-91058, Germany.*

Controlled buildup of supramolecular assemblies starting from single molecular building blocks is a topic of great interest and exhibits high potential for catalysis, enzyme mimicking and the design of sensors and optics. Here, we report on a self assembling reaction of Ni(II), Co(II) and Mn(II) complexes bearing 3,5-bis(dimethylpyrazol-1-yl)acetic acid and acetyl acetonate ligands. For this purpose different alkali metal and transition metal ions are used as templates. The resulting products and their properties will be discussed.[1]



Acknowledgements: Generous financial support by the Deutsche Forschungsgemeinschaft DFG (SFB 583) and the Graduate School of Molecular Science (GSMS) is gratefully acknowledged.

References:

[1] A. Beyer, G. Türkoglu, M. v. Gernler, K. Gieb, F. W. Heinemann, T. Drewello, P. Müller, N. Burzlaff, to be submitted.

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Targeted Long Lived Luminescent Lanthanide Ion Probes for Live Cell Imaging

R. Brooks, D. Brooks, S. E. Plush

School of Pharmacy and Medical Sciences, Sansom Institute, University of South Australia (brord004@students.unisa.edu.au)

Accurate visualisation of biological processes in live cells is at the forefront of many recent advances in cell biology. Advanced imaging optics and instrumentation allow for increasingly detailed studies of dynamic processes at the molecular level. However, these processes can only be visualised with tools capable of reporting at a sub-cellular level. The application of luminescent lanthanide complexes to cellular imaging has produced a new generation of probes capable of easily resolving signal from background fluorescence, whilst photobleaching is significantly reduced.[1] Uptake of luminescent lanthanide probes into sub cellular compartments has recently been achieved, though the internalisation and localisation was not targeted and therefore not specific.[2] The challenge in the field is to control both the method of internalisation and the targeting of these probes towards specific organelles. A series of long-lived luminescent lanthanide probes has been developed using a macrocyclic cyclen system (Figure 1, left). This framework allows for the conjugation of cell specific targeting motif that promote endocytic uptake of the probes, and allow their traffic to be directed into specific sub cellular compartments in live cells (Figure 1, right).

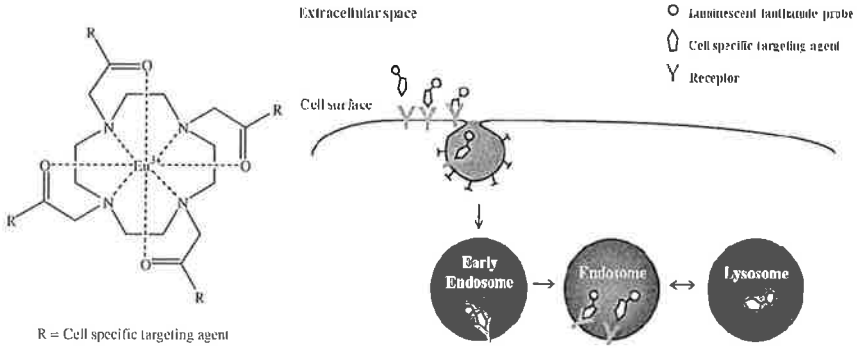

Figure 7: Structure of a cyclen based luminescent lanthanide probe (left), Uptake of the probe into sub cellular compartments (right).

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Designing in Porosity: Metal-Organic Frameworks incorporating Cyclodextrin Ligands

D. B. Cordes[1], R. S. Forgan[2], R. A. Smaldone[2], H. Furukawa[3], J. J. Gassensmith[2], A. M. Z. Slawin[1], J. F. Stoddart[2], and O. M. Yaghi[3]

1. *School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife, KY16 9ST, UK. dbc21@st-andrews.ac.uk*
2. *Center for the Chemistry of Integrated Systems, Department of Chemistry, Northwestern University, Evanston, IL 60208, USA*
3. *Center for Reticular Chemistry, Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, USA*

Metal-Organic Frameworks (MOFs) are crystalline, often porous materials that have emerged over the last ten to fifteen years as potential contenders for a wide variety of materials applications. We have recently discovered a series of MOFs prepared using γ-cyclodextrin under mild conditions, referred to as CD-MOFs (Figure 1). The cyclic nature of the cyclodextrin molecule in these extended structures leads to their inherent porosity, with potentially accessible surface areas of up to 1200 m^2g^{-1}. As such, they show the capacity for the storage of small molecules. Furthermore, due to the use of the FDA-approved cyclodextrins as ligands, and the use of biorenewable ligand systems, CD-MOFs are promising targets both as encapsulating agents for the delivery of small molecules within the human body, and materials for use in green energy or pollution control applications. As such, we are actively pursuing further examples of these and related interesting CD-MOF materials.

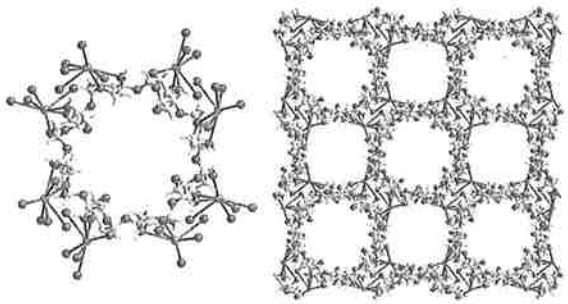

Figure 1. Views of a Cs^+ CD-MOF showing (left) the coordination behaviour of the cyclodextrin, and (right) the porous three-dimensional network formed.

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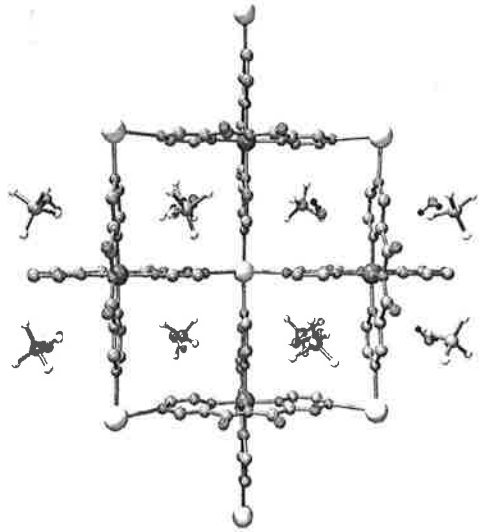
Discrete Coordination Compounds as Building Blocks for Metal Organic Frameworks

M.G. Cowan[1], S. A. Brooker[1,*]

1. *Department of Chemistry and MacDiarmid Institute for Advanced Materials, University of Otago, PO Box 56, Dunedin 9054, New Zealand. Tel: 00 64 3 479 7906. E-mail: mcowan@chemistry.otago.ac.nz; sbrooker@chemistry.otago.ac.nz*

Metal Organic Frameworks (MOFs) have received a large amount of recent attention due to their potential to store small molecules (such as hydrogen or carbon dioxide) and activity as catalysts. Both of these functions arise from the extremely high surface area of these porous structures.[1]

Following from our successes using 2,3- and 2,5-diamide-substituted pyrazine ligands to assemble [2x2] grids,[2] our focus has moved to replacement of the 'terminal' pyridine moieties in those ligands by pyrazine moieties. This provides a 'spare' nitrogen donor which is available as a 'secondary assembly' site, allowing the initially formed complexes to be used as building blocks. Proof of this principle was established recently.[3] Here we describe extension of this concept to larger arrays. Specifically, we have shown that symmetric, mononuclear pyrazine based complexes can be connected into extended three dimensional networks through *pseudo*-octahedral silver(I) links. The resulting aesthetically pleasing MOFs are generated from *discrete* mononuclear complexes using *secondary assembly instructions*, rather than the typical method of production from a single ligand/metal complexation reaction. We discuss the advantages and disadvantages of these relatively unexplored systems vs traditional MOFs.



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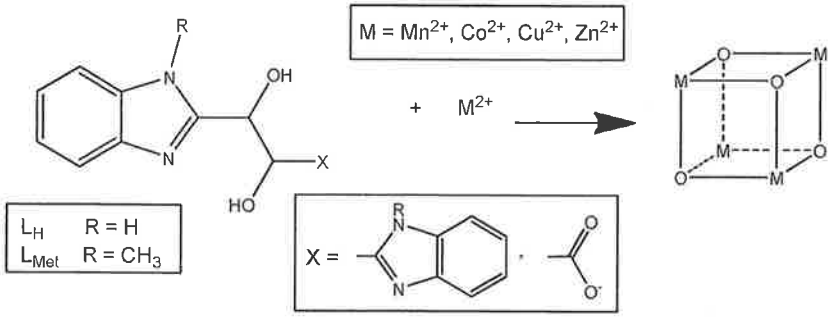
Tetranuclear complexes of transition metals with ligands containing benzimidazole, alcohol and carboxylic acid groups

C. Deville[1], A. Spyratou[1], A. F. Williams[1]

1. *Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland. Claire Deville@unige.ch*

Cubane-like structures are common in transition metal chemistry and one is believed to be present at the active site of the oxygen evolving centre of photosynthesis[1]. Bis-benzimidazole and benzimidazole derivatives of tartaric acid generate cubane-like structures with different transition metal ions[2]. One of the two hydroxyl groups may be deprotonated and serves as a bridge between three metal ions in the core of the cubane (see figure). We show the use of the Pseudoisotopic Molecule Mass Spectrometry (PIMMS) method [3] using methylated or non methylated ligands to establish the formation of the cubanes. The substitution kinetics may also be followed by this method, and are surprisingly slow for formally labile metal ions.



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Development of luminescent lanthanide probes to visualise the distribution of molecules with pharmacological activity in live cells

Z. Du, D. A. Brooks and S. E. Plush

Sansom Institute, Division of Health Science, University of South Australia, SA, 5000, Australia. Email: duyzy004@students.unisa.edu.au

Luminescent lanthanide probes have significant potential in a range of cellular imaging applications. Cellular probes based on luminescent lanthanide ions possess large stokes' shifts, sharp emission bands and long luminescence lifetimes.[1, 2] All these features make lanthanide probes ideal for live cell imaging compared with traditional fluorescence probes.

Both David Parker and Jean-Claude Bünzli have shown that luminescent lanthanide probes can be visualised in live cells. The aim of this work is to develop luminescent lanthanide probes to visualise the distribution of molecules with pharmacological activity in live cells. A serious of luminescent lanthanide probes have been designed based on the following features: (a) a Eu(III) ion which emits a detectable light signal; (b) a cyclen moiety with functional pendent arms for ion coordination and (c) a molecule which exhibits pharmacological activity.

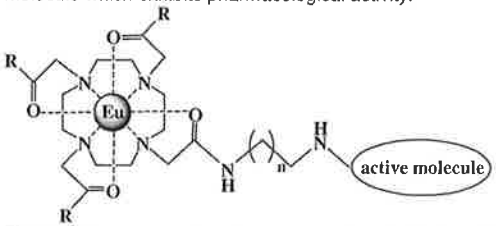

Figure 1 A luminescent lanthanide probe coupled to a molecule with pharmacological activity.

Financial Source: University President's Scholarship of University of South Australia

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Tuneable Negative Thermal Expansion in Cyanide-Bridged Lanthanoid Coordination Frameworks

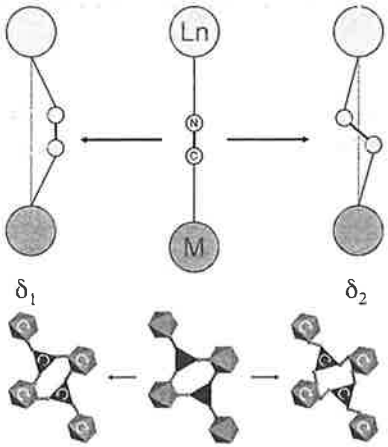
S. G. Duyker[1], V. K. Peterson[2], C. J. Kepert[1]

1. *School of Chemistry, The University of Sydney, NSW, Australia s.duyker@chem.usyd.edu.au*
2. *Bragg Institute, Australian Nuclear Science and Technology Organisation, NSW, Australia*

Negative thermal expansion (NTE, contraction upon heating) of unprecedented magnitude has recently been discovered in a broad family of three-dimensional metal-cyanide frameworks.[1,2] These materials possess two-atom (M-CN-M') linkages instead of the single-atom (M-O-M') linkages of previously studied oxide NTE materials. The NTE behaviour in both classes of materials originates from the transverse thermal vibrations of the linkers, and the diatomic nature of the cyanide molecule gives rise to increased structural flexibility and new kinds of vibrational modes.[1]

Using variable temperature diffraction methods to monitor the crystal structure over a broad temperature range, we have discovered anisotropic NTE throughout the $Ln^{III}M^{III}(CN)_6$ series of cyanide frameworks (Ln = La-Lu, Y; M = Fe, Co, Ir) and revealed a relationship between the composition and the magnitude of the NTE. In the structurally analogous $KLn^{III}Fe^{II}(CN)_6$ series, K^+ counter-ions in the centres of the framework's pores interact with the cyanide linkers, disrupting their transverse vibrations and producing positive thermal expansion (PTE). A similar reversal is observed when guest water molecules are present in the framework. The materials' effective linear coefficients of thermal expansion span a range of values from -14.7×10^{-6} K^{-1} to $+14.8\times10^{-6}$ K^{-1}.

These results demonstrate that the thermal expansion behaviour can be dramatically altered by the presence of guest molecules or pore cations, and subtly tuned by substitution at the lanthanoid, transition metal, or counter-cation sites. We plan to synthesise a zero thermal expansion (ZTE) material by striking a balance between two of the opposing influences.



Two of the possible low energy transverse modes responsible for NTE (top), and the corresponding rigid unit modes in a metal-centred polyhedral representation of the $LnM(CN)_6$ framework (bottom).

Acknowledgements: This research was supported by an Australian Research Council Federation Fellowship and by the Australian Synchrotron Research Program.

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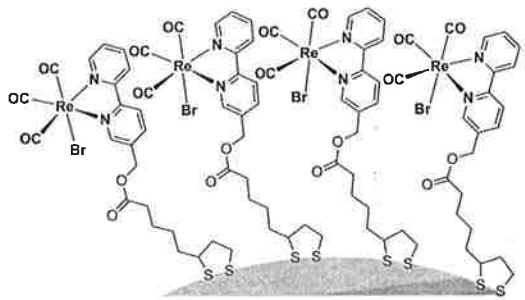
A Modular Approach to Rhenium(I) Sensors

N. C. Fletcher,[1] H. J. Montgomery,[1] D. Pelleteret[1] and S. J. Bell[1]

1. *Queen's University Belfast, School of Chemistry and Chemical Engineering, Stranmillis Road, Belfast BT9 5AG, UK. email: n.fletcher@qub.ac.uk*

Investigation of the photophysical properties of transition metal polypyridine complexes has attracted considerable attention due to their application in molecular sensing and light emitting diodes. Initially concentrated on the ubiquitous $[Ru(bpy)_3]^{2+}$ motif, the family of photoactive organometallic complexes has been extended to include osmium(II), platinum(II) acetylene, cyclometallated iridium(III) and rhenium(I) tricarbonyl complexes, giving rise to a wealth of new luminescent materials.[1] In recent years, we have been considering the use of such compounds for molecular recognition, either by tagging them to selected recognition groups, surfaces or additional chromophores. To achieve this, we have been exploring a modular "metal as ligand" synthetic approach, which has led to some interesting and complex molecular configurations.[2]



We report here a series of rhenium(I) bipyridine tricarbonyl complexes, which include a disulphide group on the end of an alkyl chain which has allowed the study of these compounds on a silver colloid. The Resonance Raman and SERS spectra of the complexes are distinct for each compound, providing detailed information about the component parts. Concentration studies suggest that at higher concentration, the surface coverage is sufficient to prevent the metal collapsing onto the surface (Figure), while the disulphide is crucial to anchor the rhenium complexes to the surface, enabling concentrations as low as 10^{-6} M to be observed. This methodology will permit a modular approach to be used in surface modification to create highly sensitive sensors for biological activity.

Acknowledgements: ESF/DEL(NI) are also gratefully acknowledged for funding.

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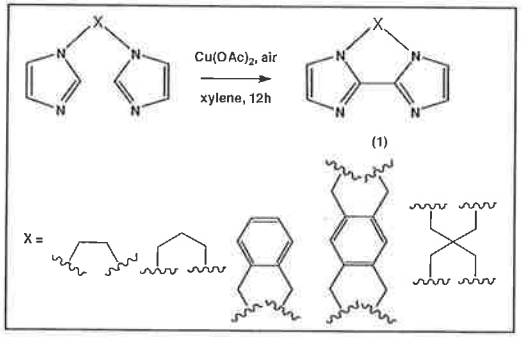
Cu(II) catalysed coupling of imidazoles: synthesis and new supramolecular topologies using biimidazoles.

J. L. Gulbransen[1], C. M. Fitchett[1]

1. *Chemistry Department, University of Canterbury, Christchurch, New Zealand; jlg61@student.canterbury.ac.nz*

Supramolecular complexes of heterocyclic chelating ligands have been intensively studied, and are of interest in various medical and industrial applications. 2,2'-bipyridine complexes are the most widely studied, whilst the supramolecular chemistry of other heterocyclic chelating ligands remains largely unexplored. Although 2,2'-biimidazoles with various backbones have been synthesised previously from 2,2'-biimidazoles and the appropriate halo-substituted backbone, our efforts have focused on the preparation of a series of 2,2'-biimidazoles and bibenzimidazoles, such as (1), through an intramolecular Cu(II) catalysed coupling of bis-imidazoles and benzimidazoles, as shown in the scheme below. The oxidative, intermolecular C-H bond activation and C-C bond formation at the 2-postion of azoles using a Cu(II) catalyst with air as the oxidant has been recently reported.[1] This negates the need for multi-step syntheses of appropriately functionalised starting materials used in traditional transition metal catalysed C-C bond formation. The coordination and supramolecular chemistry of such bridging 2,2'-biimidazoles and bibenzimidazoles is relatively unexplored; changes in the backbone of (1) are expected to potentially allow new topologies and coordination modes.



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Metallo-Supramolecular Actuation with Dynamic Pincer Ligands

L. R. Hanton, A. K. Blackburn and S. C. Moratti

Department of Chemistry, University of Otago, P. O. Box 56, Dunedin 9054, lhanton@chemistry.otago.ac.nz

Actuators are used extensively in everyday life to convert some form of input energy into mechanical energy as motion. One such input energy which is currently of interest accompanies the dramatic change in shape on the binding of metal ions by certain dynamic ligands. If these ligands were to be incorporated into polymer gel network, a metallo-supramolecular activated polymer gel actuator could be developed.[1] The design of the ligand is therefore crucial. Ideally the ligand would be initially linear and flexible so that there is an impact on the skeleton of the compound once it is coordinated to a metal ion. Pincer ligands have been used extensively throughout metallo-supramolecular chemistry to facilitate reactions as they have a pre-organized backbone and are therefore able to act as chelating agents (Figure 1). A small class of pincer ligands, however undergo a change of noticeable magnitude in the shape of the ligand when binding to a metal ion (Figure 1).[2]

Figure 1. The action of pincer ligands. (a) In a traditional pincer ligand the metal ion (grey) slots into the binding cavity on coordination with no obvious change in geometry. (b) In a "dynamic" pincer ligand a change in geometry of the ligand is observed on the coordination of a metal ion (grey).

Two ligands have been designed, **L1** and **L2**, which show this dynamic pincer action (Figure 2). Terminal CH_2OH groups have been incorporated into both ligands to allow them to be polymerised into a gel at a later stage. Some issues were encountered with **L1** due to the presence of H_2O solvent molecules which were tightly bound in the binding pockets of the ligand. These ligands were reacted with Pb(II) ions where they showed the desired pincer binding, resulting in a decrease in the size of the ligand of 50 %. More interestingly, when **L2** was reacted with Cu(II) ions, double helical Cu(II)-Cu(II) and Cu(II)-Cu(I) systems were observed. The results from this investigation are discussed in more detail.

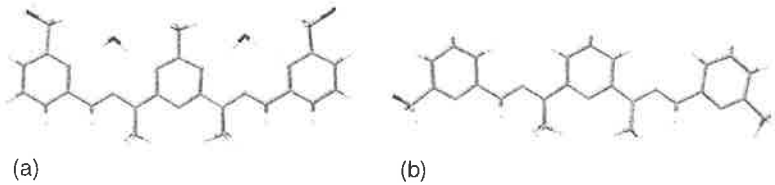

Figure 2. Ligands (a) **L1** and (b) **L2** in their uncoordinated, linear geometries.

Acknowledgements: The authors would like to acknowledge the Department of Chemistry, University of Otago, and the New Economic Research Fund of the Foundation for Research, Science and Technology (NERF Grant No. UOO-X0808).

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Formation of Metal-Assisted Stable Double Helices in Dimers of Cyclic Bistetrapyrroles that Exhibit Spring-like Motion

T. Hashimoto[1] and H. Maeda[1,2]

1. *Institute of Science and Engineering, Ritsumeikan University, Kusatsu 525–8577, Japan.*
2. *PRESTO, Japan Science and Technology Agency (JST), Kawaguchi 332–0012, Japan. E-mail: maedahir@ph.ritsumei.ac.jp*

The control of chirality in metal-assisted assemblies is an important issue. In many cases, chirality in metal-ligand clusters can be controlled by auxiliaries such as the chiral substituents of ligand molecules. On the other hand, metal coordination itself affords racemic forms of chiral assemblies on the basis of achiral ligands. In most cases, the optical resolution of such racemic mixtures is not easy to achieve, especially in the case of metal-assisted helices, because of the fairly weak metal-ligand interactions. Various metal complexes including [2 + 2 (ligands + metal ions)]-type Zn^{II}-assisted double helices can be fabricated by using linear tetrapyrrole ligands *bidipyrrins*, directly linked dimers of dipyrrins,[1] as candidate building subunits of helical assemblies. However, preliminary experiments have shown that bidipyrrin-based double helices are not very robust. Therefore, stimulated by the fascinating but almost unexplored properties of bidipyrrins, we have investigated the formation, topological control, and properties of optically resolved and stable helical structures.

Covalently linked cyclic bis-bidipyrrin (**cBDPR**) was obtained by using oxidative biaryl coupling reaction and subsequent demetallation of Ni^{II}-nanorings (***mmm*-DPR$_2$·Ni$_2$**).[1b] By treating **cBDPR** with $Zn(OAc)_2$, we obtained Zn^{II}-bridged [2 + 4]-type dimer (**cBDPR$_2$·Zn$_4$**; Figure 1), which are suggested by various spectroscopic methods. The VT-NMR spectra of **cBDPR$_2$·Zn$_4$** showed temperature-dependent upfield shifts of external pyrrole-CH of **cBDPR$_2$·Zn$_4$** similar behavior to those of the pyrrole-CH of the [2 + 2]-type bidipyrrin Zn^{II} complex, whose helical structure was revealed by single-crystal X-ray analysis. XAFS revealed that the distances between two neighboring Zn^{II} in **cBDPR$_2$·Zn$_4$**, thereby suggesting the formation of double helices. Interlocked complexes **cBDPR$_2$·Zn$_4$** had stable double helices; therefore, they could be optically resolved by using chiral HPLC. The VT-CD spectral changes of each enantiomer of **cBDPR$_2$·Zn$_4$** revealed stronger Cotton effects at low temperatures because of a possible fastening of the pitches of the Zn^{II}-bridged double helices as springs (Figure 2a); these changes were correlated with the corresponding UV/vis absorption (Figure 2b) and fluorescence spectral changes. The fluorescence lifetimes of **cBDPR$_2$·Zn$_4$** at variable temperatures were estimated TCSPC measurements. At high temperatures, **cBDPR$_2$·Zn$_4$** had two decay components, and at low temperatures, the lifetime of **cBDPR$_2$·Zn$_4$** increased with the disappearance of the fast decay component. From these observations, it is concluded that the fast decay component of **cBDPR$_2$·Zn$_4$** can be derived from the flexible spring-like motion, which can be controlled by external stimuli.[2]

Figure 1

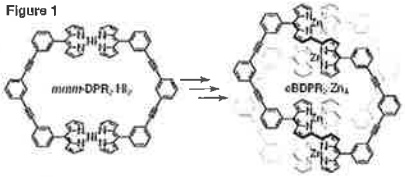
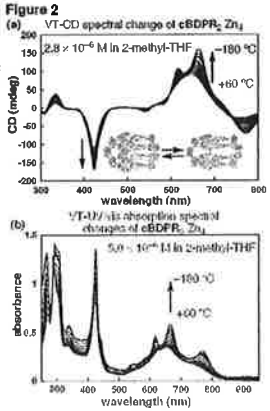


Figure 2



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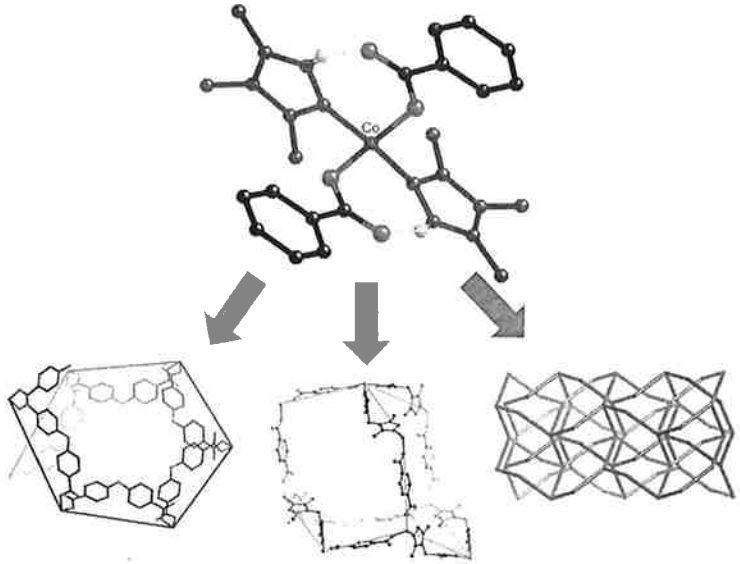
Pyrazole-carboxylate mixed ligand systems as building blocks in cobalt(II) coordination polymers

C. S. Hawes[1], C. M. Fitchett[1], S. R. Batten[2], P. E. Kruger[1]

1. *Department of Chemistry, University of Canterbury, Christchurch, New Zealand chris.hawes@pg.canterbury.ac.nz*
2. *School of Chemistry, Monash University, Melbourne, Australia*

Pyrazoles have been widely studied as ligands in discrete coordination compounds[1], however relatively few examples have been thoroughly examined as linkers in coordination polymers or Metal-Organic Frameworks (MOFs)[2]. When coordinating in a monodentate fashion, 1H-pyrazoles have the ability to rigidify the coordination sphere by taking part in hydrogen bonding with other nearby ligands, such as carboxylic acids[3]. Utilising this motif **1**, we have used the semi-flexible linker (4,4'-methylenebis)-3,5-dimethyl-1H-pyrazole to prepare several examples of cobalt(II) coordination polymers. Altering the geometry and flexibility of the carboxylate co-ligand gives rise to significant variation in overall network topology from 3-dimensional networks to 2-dimensional interpenetrating sheets, while retaining the same geometry within the cobalt (II) coordination sphere[4]. Building on observations from the coordination in **1**, a new family of pyrazole and mixed pyrazole-carboxylate ligands have been prepared, with emphasis given to tuning the conformational freedom between the binding sites.



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Synthesis, Structures, and Intermolecular Interactions of Fully and Partially Fluorinated β-Diketonato Complexes

A. Hori,[1,2] K. Naganuma,[1] Y. Akimoto
1. *School of Science, Kitasato University, Kitasato 1-15-1, Minami-ku, Sagamihara, Japan, hori@kitasato-u. ac.jp*
2. *PRESTO, JST*

The importance of aromatic electrostatic interactions is widely recognized, *e.g.* π-π, CH-π, cation-π (Fig. 1a), anion-π, arene-perfluoroarene (Fig. 1b), to understand the intermolecular force in biology and chemistry. These aromatic interactions can design various coordination complexes and control the strength of the interactions by estimating quadrupole moments for the fluorine substitutions.[1] Such an idea prompted us to design the fluorine substitution to a very common ligand, dibenzoylmethanide (**1**).[2,3] Here, we have synthesized partially fluorinated compounds, bis(3,5-difluorobenzoyl)methanide (**3**), bis(2,4,6-trifluorobenzoyl)methanide (**4**), and bis(2,3,5,6-tetrafluorobenzoyl)methanide (**5**) metal complexes and studied the complexation behavior, metal properties, and intermolecular interactions, compared with the previously reported fully fluorinated ligand (**6**).

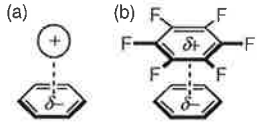
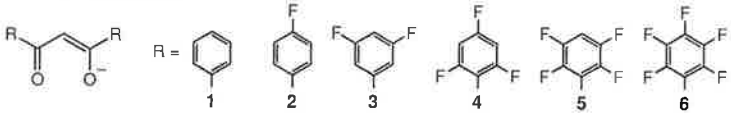
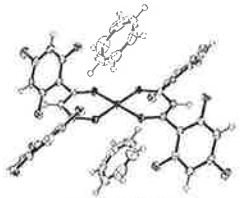


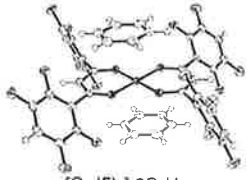
Fig. 1 Weak π interactions



In synthetic process, the ligands were prepared as those Al^{3+} complexes for [Al(**3**)$_3$], [Al(**5**)$_3$], and [Al(**6**)$_3$], which previously reported as the vinyl acetate method.[3] On the other hand, bis(2,4,6-trifluorobenzoyl)methane (**4**-H) was obtained in the same procedure. Typically, the reaction was employed from corresponding fluorinated benzoyl chloride and vinyl acetate in 1,1,2,2-tetrachloroethane in the presence of anhydrous $AlCl_3$. The Al^{3+} complexes were also useful as a starting material for the complexation with valuable transition metals, in this case, Cu^{2+} ion; the Al^{3+} complexes (or ligands) and $Cu(OAc)_2{\cdot}H_2O$ were combined in an ethanol/CH_2Cl_2 solution to give green powders of mononuclear Cu^{2+} complexes, [Cu(**L**)$_2$] (**L** = **1**-**6**). Interestingly, unique benzene-recognition by fluorinated complexes was observed in the crystallization from a CH_2Cl_2/benzene solution. Herein we report the crystal structures of [Cu(**4**)$_2$]·2C_6H_6, [Cu(**5**)$_2$]·2C_6H_6, and [Cu(**6**)$_2$]·3C_6H_6, in which benzene molecules are interacted to the Cu^{2+} complexes through electrostatic interactions, *i.e.* cation-π and arene-perfluoroarene interactions. Especially, cation-π interactions between Cu^{2+} ion and benzene molecules clearly depend on fluorine substitutions. The crystals of [Cu(**L**)$_2$] (L = **1** and **2**) did not include the benzene molecules.



[Cu(**4**)$_2$]·2C_6H_6



[Cu(**5**)$_2$]·2C_6H_6

Additionally, we report the co-crystallization of two complexes. As a good example, two CH_2Cl_2 solutions of [Cu(**1**)$_2$] and [Cu(**6**)$_2$], respectively, are combined together, pure 1:1 co-crystals of [Cu(**1**)$_2$]·[Cu(**6**)$_2$] was obtained through arene-perfluoroarene interactions.[2] These arene-perfluoroarene interactions are not observed for [Cu(**L**)$_2$] (**L** = **1**-**5**).

Acknowledgements: This work was supported in part by a Kitasato University Research Grant for Young Researchers.

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[3] A. Hori, A, Shinohe, S. Takatani, T. K. Miyamoto, *Bull. Chem. Soc. Jpn*, **2009**, *82*, 96.

Syntheses and Crystal Structure and Solution Chemistry of Ruthenium(II) Dimethyl Sulfoxide Complexes with Methylamine. [$RuCl_2(NH_2Me)_2$(dmso-*S*)$_2$], [$RuCl_2(NH_2Me)$(dmso-*S*)$_3$], and [$RuCl_2(NH_2Me)(CH_3CN)$(dmso-*S*)$_2$]

M. Toyama, T. Kushida, and N. Nagao
Department of Applied Chemistry, Meiji University, Kawasaki 214-8571, Japan
nori@isc.meiji.ac.jp

The synthesis and crystal structures of di- and mono-ammine complexes, *trans*(Cl),*cis*(S)-[$RuCl_2(NH_3)_2$(dmso-*S*)$_2$] and *trans*(Cl,S),*fac*(S)-[$RuCl_2(NH_3)$(dmso-*S*)$_3$], had been reported by E. Alessio group.[1] However, the substitution and summarization reactions of the di- and mono-ammine complexes had been mentioned little. In this presentation, we will report the syntheses, crystal structures, and substitution and isomerization reactions of bis- and mono-methylamine complexes, [$RuCl_2(NH_2Me)_2$(dmso-*S*)$_2$], [$RuCl_2(NH_2Me)$(dmso-*S*)$_3$], and [$RuCl_2(NH_2Me)(CH_3CN)$-(dmso-*S*)$_2$].

The reaction of *trans*(Cl)-[$RuCl_2$(dmso-*S*)$_4$] with methylamine (NH_2Me) in a mixture of THF-H_2O (15 : 1) at 275 K for 7 h afforded bis-(NH_2Me) complex *trans*(Cl)-[$RuCl_2(NH_2Me)_2$(dmso-*S*)$_2$] (**1**) in a high yield (85%). The mono-(NH_2Me) complexes were prepared from the bis-(NH_2Me) complex **1** as precursor. A solution of **1** in CH_3CN was heated to reflux for 3 h. The mixture was evaporated to dryness and the residual was treated with EtOH to obtain the yellow precipitate *trans*(Cl,N_{CH3CN}),*cis*(S)-[$RuCl_2(NH_2Me)(CH_3CN)$(dmso-*S*)$_2$] (**2**). A solution of **1** in DMSO was heated at 393 K for 2 h and the mixture was treated with EtOH and ether to precipitate *trans*(Cl,S),*fac*(S)-[$RuCl_2(NH_2Me)$(dmso-*S*)$_3$] (**3**). A solution of **2** in DMSO was irradiated by Xe lamp for 16 h to form a yellow precipitate, *trans*(Cl)-[$RuCl_2(NH_2Me)$(dmso-*S*)$_3$] (**4**). The solution of **4** in CH_3CN was allowed to stir for 0.5 h at room temperature. The mixture was evaporated to a few ml and was treated with ether to form a yellow precipitate, *trans*(Cl),*cis*(S)-[$RuCl_2(NH_2Me)(CH_3CN)$-(dmso-*S*)$_2$] (**5**). The crystal structures of all complexes **1** ~ **5** were determined. The substitution and isomerization reactions of **1** ~ **5** were investigated by means of H NMR spectroscopy.

The crystal structures of **1** and **2** are shown in Fig. 1. Both **1** and **2** have a similar intramolecular interaction that is a hydrogen bond between H atom in NH_2Me and O atom in dmso ligand. The hydrogen bond anchors the NH_2Me ligand, which does not dissociate. The substitution and summarization reactions of **1** ~ **5** are summarized in Fig. 2. In all complexes **1** ~ **5**, the hydrogen bond of NH_2Me and dmso causes them to behave themselves like a bidantate ligand.

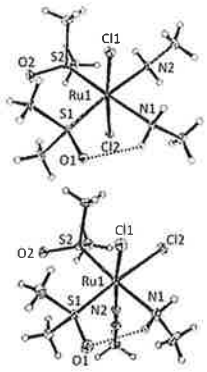

Fig. 1. ORTEP drawings of **1** (top) and **2** (bottom).

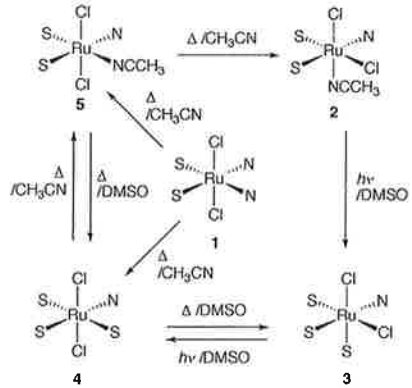

Fig. 2. Substitution and Isomerizention reactions of **1**, **2**, **3**, **4**, and **5** in DMSO and CH_3CN.

References:

[1] M. Henn, E. Alessio, G. Mestroni, M. Calligaris, and W. M. Attia, *Inorg. Chim. Acta,* **1991**, *187, 39.*

Syntheses and Crystal Structures of Ruthenium(II) Complexes with One (3-chloro-6-pyridazyl)(2-pyridyl)amine (Hcpdpa)

M. Toyama, T. Ishida and N. Nagao
Department of Applied Chemistry, Meiji University, Kawasaki 214-8571, Japan
mari@isc.meiji.ac.jp

The (3-chloro-6-pyridazyl)(2-pyridyl)amine (Hcpdpa), which is an analogues of di-2-pyridylamine (Hdpa), was prepared by a base-catalyzed coupling reaction of 3,6-dichloropyridazine and 2-aminopyridine. We have previously reported the syntheses, structures, and isomerization reaction of two mono(Hdpa)ruthenium(II) complexes *trans*(Cl),*cis*(S)- and *cis*(Cl),*cis*(S)-[$RuCl_2$(Hdpa)(dmso-*S*)$_2$].[1] In this presentation we will report the syntheses and structures of some mono(Hcpdpa)ruthenium(II) complexes.

In H_2O-THF at room temperature the reaction between *trans*(Cl)-[$RuCl_2$(dmso-*S*)$_4$] and Hcpdpa afforded mono(Hcpdpa)ruthenium(II) complex *trans*(Cl),*cis*(S)-[$RuCl_2$(Hcpdpa)(dmso-*S*)$_2$] (**1**) in high yield (95%). A suspension of **1** in a mixture of EtOH and DMSO (9 : 1) was refluxed for 3 hours. While refluxing, **1** gradually dissolved and *cis*(Cl),*trans*(S,N_{py})-[$RuCl_2$(Hcpdpa)(dmso-*S*)$_2$] (**2**) was appeared. Although for [$RuCl_2$(Hcpdpa)(dmso-*S*)$_2$] two kinds of *cis*(Cl)-isomers (*cis*(Cl),*trans*(S,N_{py})- and *cis*(Cl),*trans*(S,N_{pd})-isomers) are possible due to the asymmetry of Hcpdpa ligand, only one *cis*(Cl),*trans*(S,N_{py})-isomer has been obtained in good yield (85%). These structures of **1** and **2** were determined by the ^{1}H NMR spectroscopy and X-ray crystal analysis.

The ORTEP drawing of **1** was shown in the left of Figure 1. The asymmetric unit of **1** contained two crystallographically independent molecules, Ru(1) and Ru(2). The structures of molecule Ru(1) and Ru(2) were quite similar. In Figure 1, only a Ru(1) molecule was shown. Both Ru ions in **1** possess a slightly distorted octahedral geometry with two *trans*(Cl) atoms (*trans*(Cl),*cis*(S)-isomer). The Ru-Cl and Ru-S distances (Ru-Cl; av. 2.402 Å, and Ru-S; av. 2.288 Å) were similar to the corresponding distances in the analogous Hdpa complex *trans*(Cl),*cis*(S)-[$RuCl_2$(Hdpa)(dmso-*S*)$_2$] (Ru-Cl; av. 2.405 Å, Ru-S; av. 2.277 Å). The Ru-N_{pd} distances (2.087(6) and 2.096(6) Å) were shorter than the Ru-N_{py} distances (2.128(6) and 2.132(6) Å), which were similar to those in analogous mono(Hdpa)ruthenium(II) complex (2.131(4) and 2.123(4) Å). This suggests that the coordinated pyridazine ring has less bulkiness on the β-position than the pyridine ring, that is, the space of the lone pair on an N atom of β-position of pyridazine ring is smaller than that of the C-H unit of pyridine ring.

The ORTEP drawing of **2** was shown in the right of Figure 1. The crystal structure of **2** was revealed that the Ru ion had a slightly distorted octahedral geometry with two *cis*(Cl) atoms, and the S atom of one dmso ligand *trans* to the N atom of a pyridine ring on an Hcpdpa ligand (*cis*(Cl),*trans*(S,N_{py})-geometry). The bulky dmso-*S* ligand in the equatorial plane was on the *cis* position of a pyridazine ring. The Ru-N_{pd} distance (2.056(3) Å) in **2** was significantly shorter than those in **1** (2.087(6) and 2.096(6) Å). This also suggests that the β-position of a pyridazine ring (an N atom) on an Hcpdpa ligand is less bulkiness than the corresponding part of a pyridine ring (a C-H unit).

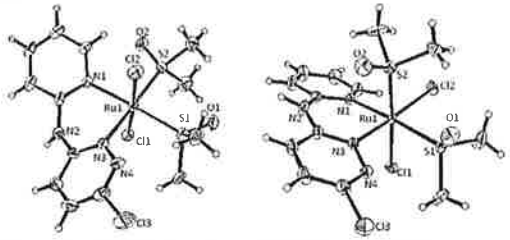

Figure 1. ORTEP drawings of **1** (left) and **2** (right).

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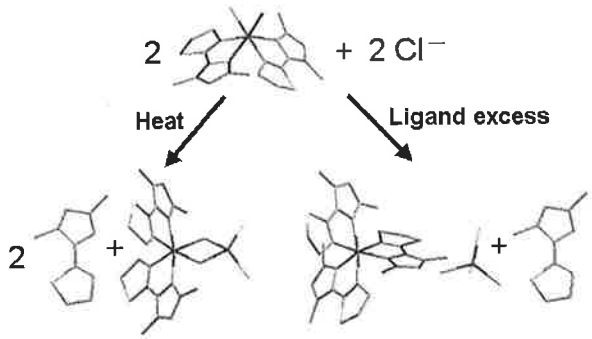
Disproportionation reaction for a mononuclear octahedral cobalt(II) complex with N-(3,5-dimethylpyrazol-1-yl)-2-thiazoline (DMPyTn). Experimental evidences.

F. J. Barros-García[1], R. Pedrero-Marín[1], F. Luna-Giles[1], A. Bernalte-García[1], E. Viñuelas-Zahínos[1]
1. *Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Badajoz, Spain, fergaba@unex.es*

The process of disproportionation through which the pink solutions of cobalt(II) chloride change to blue when heated, is known since ancient times. This blue colour is attributed to the presence of the complex species $CoCl_4^{2-}$.[1]

$$2\,[Co(H_2O)_6]Cl_2 + \text{Heat} \rightarrow Co[CoCl_4] + 12\,H_2O$$

We report here the synthesis and characterisation of [CoCl(DMPyTn)$_2$(H_2O)]Cl (**1**), as well as, the isolation and structural determination of two Co(II) complexes obtained from the previous complex. These results support that for (**1**) it takes place a disproportionation process similar to aforementioned.



Acknowledgements: We would like to thank the Junta de Extremadura (III PRI+D+I) and the FEDER [Project PRI08A022] for financial support.

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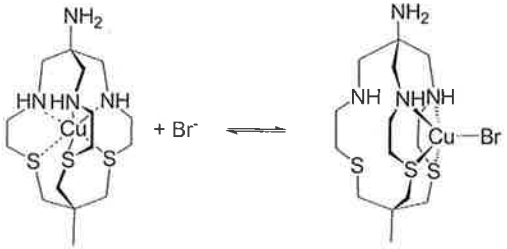
Reversible Rearrangements of a Caged Copper(II) Complex

P. V. Bernhardt,[1] C. A. Bell,[1] L. R. Gahan,[1] M. Martínez,[2] M. J. Monteiro,[1] C. Rodríguez[2] and C. A. Sharrad[1]

1. *School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane 4072, Australia. Email: p.bernhardt@uq.edu.au*
2. *Departament de Química Inorgànica Universitat de Barcelona Martí i Franquès 1-11E-08028 Barcelona, Spain*

The mixed donor cage ligand 1-methyl-8-amino-3,13,16-trithia-6,10,19-triaza-bicyclo[6.6.6]-eicosane (AMME-N_3S_3sar) may coordinate as either a hexadentate (N_3S_3) or tetradentate (N_2S_2) ligand in complex with copper(II). In the absence of coordinating anions, the ligand adopts a conventional hexadentate N_3S_3 coordination mode in the complex [Cu(AMME-N_3S_3sar)]$(ClO_4)_2$ to yield a trigonally and tetragonally distorted Cu(II) complex. However, in the presence of bromide ions (in DMSO) rapid and quantitative conversion to a five-coordinate bromido complex [Cu(AMME-N_3S_3sar)Br]$^+$ is observed featuring a novel tetradentate (N_2S_2) form of the ligand.



The mechanism of this reversible interconversion between the 6- and 5-coordinate copper(II) complexes has been studied and the reaction has been resolved into several steps. Electrochemistry of both [Cu(AMME-N_3S_3sar)]$^{2+}$ and [Cu(AMME-N_3S_3sar)Br]$^+$ in DMSO shows that upon reduction, they share a common five-coordinate monovalent form where the ligand is bound to copper in a tetradentate manner. Both the hexadentate and tetradentate coordinated Cu(II) complexes have been characterised structurally and spectroscopically.

References:

[1] Bell, C.A.; Bernhardt, P.V.; Gahan, L.R.; Martínez, M.; Monteiro, M.J.; Rodríguez, C.; Sharrad, C.A. *Chem.- Eur. J.*, **2010**, 16, 3166-3175.

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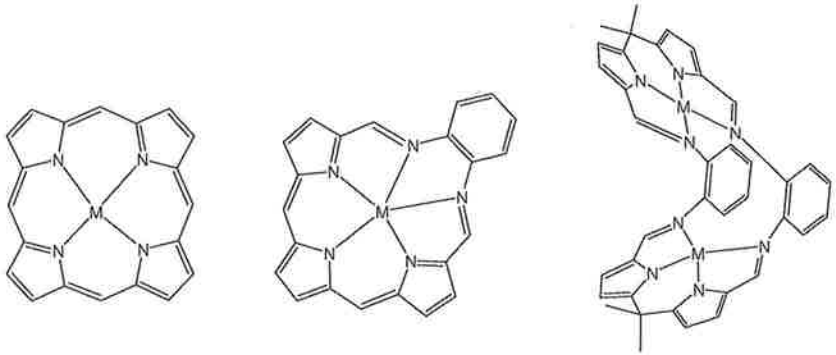
Towards New Families of Expanded Porphyrin-like Ligands and Complexes

S. A. Cameron, D. S. Larsen and S. Brooker*
Department of Chemistry, Univeristy of Otago, PO Box 56, Dunedin
scameron@chemistry.otago.ac.nz

Some of the most important biomolecules in nature are N_4 porphyrin based macrocyclic complexes (I). There are also countless examples of simple synthetic porphyrin based transition metal complexes, many which exhibit interesting properties such as catalytic or single molecule magnet behaviour. Larger N_5 "expanded porphyrins" have also been developed (II). In these systems larger (typically lanthanide series) metal ions can be accommodated, and the resulting complexes have found use as photodynamic therapy and MRI contrast agents.[1] Alternatively, two smaller first row transition metal ions can be accommodated. Related dimetallic complexes (III) have been shown to bind oxygen and it is hoped that natural systems such as cytochrome c oxidase may be modelled by such structures.[2]



I II III

Previously 2,5-diformylpyrrole,[3] and subsequently pyrrole-2,5-diacetaldehyde[4] were thought to be good candidates for making related families of macrocyclic metal complexes. However, neither system was suitable due to incorrect binding geometries and decomposition/stability problems. A promising alternative that addresses these issues will be discussed.

Acknowledgements: We are grateful for the award of a University of Otago Postgraduate Scholarship to SAC.

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Phosphorous acid labilization in *trans*-$[Ru(NO^+)(NH_3)_4P(OH)_3]^{3+}$.

D. W. Franco[1], D. R. Truzzi[1], A. G. Ferreira[2]
1. *University of São Paulo, São Carlos, Brazil.* douglas@iqsc.usp.br
2. *Federal University of São Carlos, São Carlos, Brazil.*

Due to the high *trans* influence and *trans* effect of the phosphorus ligand, compounds type *trans*-$[Ru(NO^+)(NH_3)_4P(III)]^{3+}$ are able to deliver NO efficiently in the presence of suitable reductors [1]. For instance, the specific rate constant for NO dissociation from the ion *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OEt)_3]^{3+}$ is 0.98 s^{-1}, at 25°C and pH = 5.0. In addition, this compound is water soluble and exhibit low citotoxicity thus being a very interesting pro-drug model [2]. However, in neutral medium *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OEt)_3]^{3+}$ undergoes an undesirable nucleophilic attack by hydroxyl ions on the phosphorus ester. To circumvent this inconvenient the phosphorous acid was used as a potential ligand. The complex *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OH)_3](Cl)_3$ was synthesized through $Ru^{II}(H_2O)(NH_3)_5]^{2+}$ and H_3PO_3 reaction. The solid obtained was characterized by spectroscopic (^{31}P NMR, δ=71 ppm for *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OH)_3]^{3+}$ and δ=65 ppm for *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(O)(OH)_2]^{2+}$) and spectrophotometric techniques (λ=241nm - ε=1385 L mol^{-1} cm^{-1}, λ=319 nm - ε=773 L mol^{-1} cm^{-1}, λ=500 nm - ε=20 mol L^{-1} cm^{-1}; ν_{NO+}=1892 cm^{-1} for *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OH)_3]^{3+}$, ν_{NO+}=1879 cm^{-1} for *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(O)(OH)_2]^{2+}$). The pK_a value of 0.74 ± 0.05 for the *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OH)_3]^{3+}$ was determined through Vibrational Spectroscopy in aqueous solution. The E_{NO^+/NO^0} was determined by Cyclic Voltammetry as -0.52 V *vs.* SCE (0.5 mol L^{-1} CF_3COOH, 25°C). As judged from UV-vis, Cyclic Voltammetry and Vibrational Spectroscopy the ion *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OH)_3]^{3+}$ undergoes an aquation reaction yielding free phosphorous acid and the ion complex *trans*-$[Ru^{II}(NO^+)(NH_3)_4(H_2O)]^{3+}$ (λ = 322 nm - ε = 297 L mol^{-1} cm^{-1}; E_{NO^+/NO^0}=- 0.40 *vs.* SCE; ν_{NO+} = 1893 cm^{-1}) [3].

$$trans\text{-}[Ru^{II}(NO^+)(NH_3)_4P(OH)_3]^{3+} + H_2O \xrightarrow[\text{pH 3.0}]{k_{obs}=2.1\times10^{-4}\,s^{-1}} trans\text{-}[Ru^{II}(NO^+)(NH_3)_4(H_2O)]^{3+} + P(O)(H)(OH)_2$$

The ^{31}P NMR spectra at pH 3.0 solution presented a signal at 0.7 ppm confirming the phosphorous acid dissociation. The H_3PO_3 ligand dissociation, followed through ^{31}P NMR, is dependent of the hydrogen ion concentration of the medium (pH 1.0 – $k_{obs}=1.0\times10^{-6}$ s^{-1}, pH 2.0 – $k_{obs}=3.2\times10^{-5}$ s^{-1}, pH 3.0 – $k_{obs}=2.1\times10^{-4}$ s^{-1} at 25°C). ^{31}P NMR and Vibrational Spectroscopy data suggest that, before the H_3PO_3 dissociation, occurs the formation of linkage isomers in which the phosphorous acid is coordinated to the metal center by the oxygen atom (δ=48 and 42 ppm; ν_{NO+}=1874 cm^{-1}).

Acknowledgements: FAPESP, Capes and CNPq for financial support.

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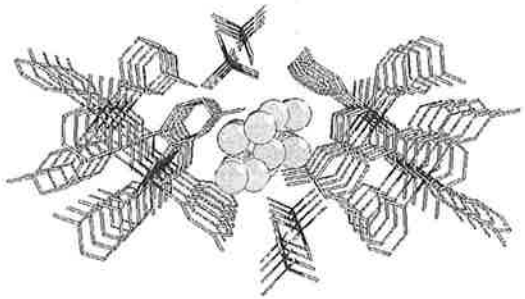
Rhodium complexes with pyridine-type heterocyclic ligands

S.V.Korenev, D.B. Vasil'chenko, A. B. Venediktov
Nikolaev Institute of inorganic chemistry SB RAS, korenev@niic.nsc.ru

Continuous interest to the chemistry of rhodium(III) complexes with heterocyclic ligands is based on the fact that chemical transformations of these compounds lead to derivatives manifesting pronounced photochemical and catalytic properties, as well as promising for medicines. However, despite of numerous studies devoted to this class of complexes, only few of them concern chemical transformations.

This contribution reports the data on the synthesis and characterization (powder X-ray diffraction, chemical analysis, IR and UV-VIS spectroscopy, NMR) of complex salts of the general formula trans-$[RhL_4Cl_2]X$, where L = pyridine, γ-picoline (γ-Pic), β-picoline (β-Pic); X= Cl^-, ClO_4^-, ReO_4^- etc. Systematic study of crystal structures of the prepared compounds has been carried out, and the factors determining their isostructurality have been revealed. Thorough examination of thermal properties made possible to determine fundamental parameters of solid state transformations and develop the methods of preparation of tri-amine rhodium complexes with quantitative yields. Due to high chemical stability of $[RhPic_4Cl_2]^+$ cations, they were used for examination of oxidation of coordinated picoline to isonicotinic acid, the coordination core being preserved.



Perspective view of the crystal structure of trans-$[Rh(\beta\text{-}Pic)_4Cl_2]ClO_4$• DMFA adduct, space group P1. The DMFA molecules are represented in Van der Waals radii (grey balls).

The studies have been carried out on the synthesis, characterization and investigation the properties of similar Rh(III) complexes with such bidentate ligands as isonicotinic acid (i-NicH) and 4-hydroxypyridine. The cationic, neutral and anionic forms of trans-$[RhL_4Cl_2]$ where L = isonicotinic acid or its acid residue have been isolated and characterized. Non-coordinated oxygen donor atoms of the carboxylic or hydroxy-groups have been used as ligands towards other metal cations with the aim to prepare heterometallic systems possessing polymeric or oligomeric nature. By the using of this reaction bimetallic compounds with Cu^{2+} and Ag^+ ions have been obtained and thoroughly studied.

Simultaneous preparation of a seven-coordinate molybdenum(VI) cation and a hexamolybdate(VI) anion.

K. Unoura[1], S. Inomata[2], S. Hoshi[1], and M. Date[1]
1. *Yamagata University, Yamagata, Japan. (unoura@sci.kj.yamagata-u.ac.jp)*
2. *Fukushima University,Fukushima, Japan.*

Several interesting reactions of *cis*-dioxobis(dithiocarabamato)molybdennum (VI) $[MoO_2(R_2dtc)_2]$ have been investigated. The oxygen atom transfer reactions of *cis*-dioxobis(dithiocarbamato)-molybdenum(VI) $[MoO_2(R_2dtc)_2]$ has been interested as a model reaction of oxotransferases such as a sulfite oxidase and a xanthine oxidase and so on[1]. The unique substitution reaction of oxo ligands of $[MoO_2(R_2dtc)_2]$ have been also studied[2]. These rich reactions are ascribed to the fact that $[MoO_2(R_2dtc)_2]$ is made from a *cis*-dioxomolybdenum(VI) core *cis*-MoO_2^{2+}, which is thought to be a hard acid, and a dithiocarbamate ligand which behaves as a relatively soft base.

In this paper, we reported a novel substitution reaction between $[MoO_2(R_2dtc)_2]$ and a soft Pt(II) complex $K_2[PtCl_4]$ to give $[MoO(i\text{-}Bu_2dtc)_3]_2[Mo_6O_{19}]$ (**1**) and $[Pt(i\text{-}Bu_2dtc)_2]$ (**2**). We also reported molecular structure of a new salt **1**, which was consist of a seven-coordinate molybdenum(VI) cation and a hexamolybdate(VI) anion, and a platinum(II)-dithiocarbamate complex **2**.

The reaction between $[MoO_2(i\text{-}Bu_2dtc)_2]$ and $K_2[PtCl_4]$ in dichloromethane afforded to isolate only the novel orange salt **1** as a single crystal. The salt consists of two $[MoO(i\text{-}Bu_2dtc)_3]^+$ cations and one $[Mo_6O_{19}]^{2-}$ dianion in the crystalline state. The structures of the cation and the anion were shown in Figs, 1a and 1b, respectively. On the other hand, only the Pt(II) yellw complex **2** was isolated from the reaction between $[MoO_2(i\text{-}Bu_2dtc)_2]$ and $K_2[PtCl_4]$ in DMF, which was characterized by X-ray structural analysis as shown in Fig. 1c. Further, crystals of **1** and **2** were isolated by the reaction between $[MoO_2(i\text{-}Bu_2dtc)_2]$ and $K_2[PtCl_4]$ in acetone. Accordingly, the stoichiometry of the reaction between $[MoO_2(i\text{-}Bu_2dtc)_2]$ and $K_2[PtCl_4]$ seems to be expressed as the following chemical equation.

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The dianion $[Mo_6O_{19}]^{2-}$ should be formed by the subtraction reaction of dithiocarbamate ligands from $[MoO_2(i\text{-}Bu_2dtc)_2]$, which seems to be caused by the soft metal center Pt(II). It is interesting to note that $[MoO(i\text{-}Bu_2dtc)_3]^+$ should be simultaneously generated by the substitution reaction of an oxo ligand of $[MoO_2(i\text{-}Bu_2dtc)_2]$ to a dithiocarbamate ligand.

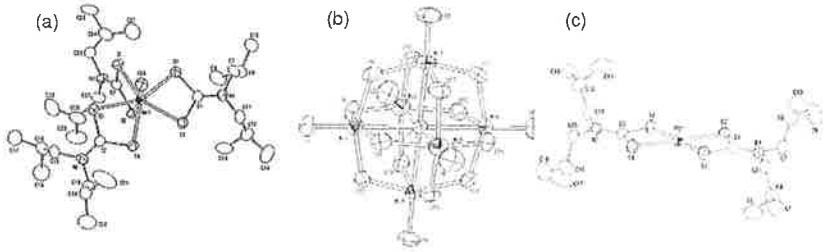

Fig.1. ORTEP diagrams of (a) $[MoO(i\text{-}Bu_2dtc)_3]^+$, (b) $[Mo_6O_{19}]^{2-}$, and (c) $[Pt(i\text{-}Bu_2dtc)_2]$ at 50 % probability. H atoms are omitted for clarify.

References:

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Poster Session 2
Abstracts 301 – 400

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Simultaneous preparation of a seven-coordinate molybdenum(VI) cation and a hexamolybdate(VI) anion.

K. Unoura[1], S. Inomata[2], S. Hoshi[1], and M. Date[1]

1. *Yamagata University, Yamagata, Japan. (unoura@sci.kj.yamagata-u.ac.jp)*
2. *Fukushima University,Fukushima, Japan.*

Several interesting reactions of *cis*-dioxobis(dithiocarabamato)molybdennum (VI) $[MoO_2(R_2dtc)_2]$ have been investigated. The oxygen atom transfer reactions of *cis*-dioxobis(dithiocarbamato)-molybdenum(VI) $[MoO_2(R_2dtc)_2]$ has been interested as a model reaction of oxotransferases such as a sulfite oxidase and a xanthine oxidase and so on[1]. The unique substitution reaction of oxo ligands of $[MoO_2(R_2dtc)_2]$ have been also studied[2]. These rich reactions are ascribed to the fact that $[MoO_2(R_2dtc)_2]$ is made from a *cis*-dioxomolybdenum(VI) core *cis*-MoO_2^{2+}, which is thought to be a hard acid, and a dithiocarbamate ligand which behaves as a relatively soft base.

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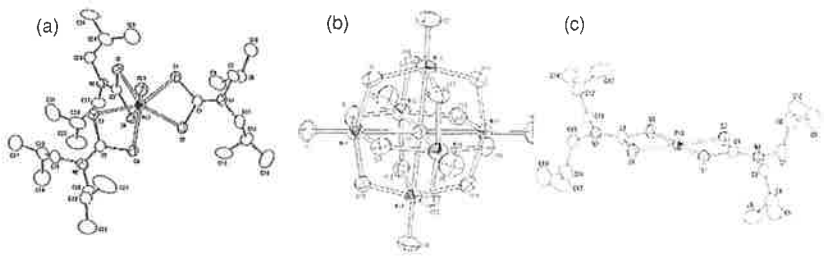

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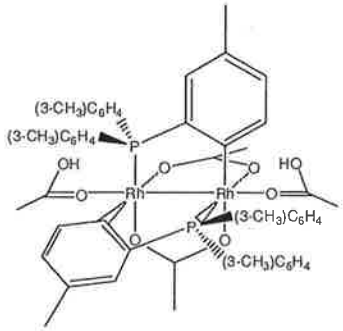
Kinetico-mechanistic information about the reversibility of carbon monoxide coordination on dirhodium(II) cyclometallated complexes adsorbed on silica

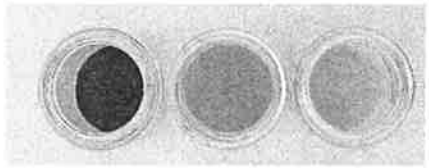
J. Esteban,[1] M. Dolores Marcos,[1] M. Martínez,[2] R. Martínez-Máñez,[1] F. Sancenón,[1] J. Soto,[1] J. Ros-Lis.[1]

1. *Instituto de Reconocimiento Molecular y Desarrollo Tecnológico. Centro Mixto Universitat Politècnica de València-Universitat València. Departamento de Química, Universitat Politècnica de Valencia, Camino de Vera s/n, 46022, Valencia, Spain.*
2. *Departament de Química Inorgànica. Universitat de Barcelona, Martí i Franquès 1-11 E-08028 Barcelona. E-mail: manel.martinez@qi.ub.es*

The use of silica immobilised cyclometallated dirhodium(II) complexes as reversible naked-eye CO sensors has been reported very recently.[1]



4·$(CH_3COOH)_2$



4·$(CH_3COOH)_2$ **4**·$(CH_3COOH)(CO)$ **4**·$(CO)_2$

Our involvement in kinetico-mechanistic studies on the substitution and cyclometallation reactivity on these type of Rh^{II}_2 complexes,[2] as well as in the transfer of mechanistic aspects of solution chemistry to immobilized systems,[3] has prompted us to study the reversibility of this process from a kinetico-mechanistic perspective.

The controlled heating of complexes **n**·$(CO)_2$, generated on CO uptake on silica beads containing immobilized **n**·$(RCOOH)_2$, produced extremely well-behaved kinetic processes. From their changes with temperature, the relevant thermal activation parameters could be extracted by the use of the standard Eyring plots. Results indicate that the CO-expelled carboxylic acid groups remain in close neighbourhood of the axial dirhodium(II) compounds. The facile reversible character of the reaction can thus be explained with the very negative values obtained for $\Delta S^{\ddagger}$.

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[1] J. Esteban, J. V. Ros-Lis, R. Martínez-Máñez, M. D. Marcos, J. Soto, F. Sancenon. *Angew. Chem. , Int. Ed.*, in the press.
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Synthesis, Characterization and Biological studies of Metal(II) complexes of Unsymmetrical Schiff Base Complexes

A. A. Nejo[1], G. A. Kolawole[1], A. R. Opoku[2]

1. *Department of Chemistry, University of Zululand, Kwadlangezwa, South Africa; E-mail: gayokola@pan.uzulu.ac.za*
2. *Department of Biochemistry and Microbiology, University of Zululand, Kwadlangezwa, South Africa*

A new series of metal(II) complexes with unsymmetrical Schiff bases derived from 2-hydroxy-1-naphthaldehyde, phenylenediamine and substituted salicylaldehyde have been synthesized and characterized by their elemental analyses, melting points, ^{1}H-NMR, magnetic susceptibility, IR and electronic spectral measurements. Elemental analyses revealed that the ligands and metal complexes were pure. ^{1}H-NMR spectral data on the ligands confirm that the Schiff bases are unsymmetrical. The comparison of the IR spectra of the Schiff-bases and their metal complexes indicated that the Schiff bases acted as tetradentate ligands. Electronic spectra indicate a square-planar geometry for all the cobalt(II), nickel(II) and copper(II) complexes. The Schiff bases and their complexes were screened for their *in vitro* antibacterial activities against ten human pathogenic bacteria and the minimum inhibitory concentration and zones of inhibition revealed enhanced activity on coordination. Both the free ligands and some complexes exhibit antibacterial activities against some strains, which in a number of cases were comparable to or higher than that of chloramphenicol.

Keywords: Unsymmetrical Schiff base; Cobalt(II); Nickel(II); Copper(II); Biological studies.

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Counter-ion and solvent effects on the primary coordination sphere of copper(II) - bis(3,5-dimethylpyrazol-1-yl) acetic acid coordination compounds

B. Kozlevčar[1], N. Kitanovski[1], J. Reedijk[2]

1. *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia; bojan.kozlevcar@fkkt.uni-lj.si*
2. *Leiden Institute of Chemistry, Leiden University, The Netherlands*

In the last decade, the ligand bis(3,5-dimethylpyrazol-1-yl) acetic acid (Hbdmpza) has been used to prepare model compounds mimicking the active site of certain zinc- and iron-containing enzymes.[1-3] Copper may be coordinated as well by this ligand, yielding biomimetically interesting compounds that further illustrate the coordination versatility of Hbdmpza.

Several copper(II) coordination compounds from this ligand have been synthesized, namely $[Cu(bdmpza)_2]$ (**1**), $[Cu(bdmpza)_2]\cdot 2H_2O$ (**2**), $[Cu(Hbdmpza)_2]\cdot 2HSO_4$ (**3**), $Cu(Hbdmpza)_2Cl_2$ (**4**), $Cu(bdmpza)_2(CH_3COOH)(H_2O)$ (**5**), $\{Cu(bdmpza)_2\}\{Cu_2(O_2CCH_3)_4\}$ (**6**), $[Cu_4Cl_8(Hbdmpza)_2]$ (**7**), of whose certain single crystal X-ray structures and properties have been reported.[4,5] Within these compounds, the ligand is found to act as neutral Hbdmpza. or as deprotonated bdmpza. The typical species obtained is a mononuclear octahedral CuL_2 compound with the ligand acting as a tridentate anionic *N, N, O* scorpionate ligand. The two nitrogen atoms of the two pyrazole rings are usually strongly coordinated, while the coordination distance of the carboxylic(lato) group varies significantly, as the result of its possible interaction (H-bond) with solvent molecules and/or counter ions. Hence, this oxygen atom may be coordinated, semi-coordinated or even non-coordinated. In $[Cu_4Cl_8(Hbdmpza)_2]$ (**7**), each copper(II) ion is coordinated by one sole ligand, in contrast to compounds **1**-**6**, for which a CuN_4O_2 chromophore formed by two ligands is observed. For the preparation of compound **6**, a high concentration of $CuCl_2$ has been used in acetonitrile. The suggested preliminary formulae $\{Cu(bdmpza)_2\}\{Cu_2(O_2CCH_3)_4\}$ for compound **6** arises from the two-step magnetic susceptibility $\chi_M \cdot T$ versus T plot, as well as from its spectroscopic data that notably differ from those of related coordination compounds. Therefore, the application of different solvents and counter ions plays an important role on the primary coordination sphere, which in turns affects the secondary coordination sphere.

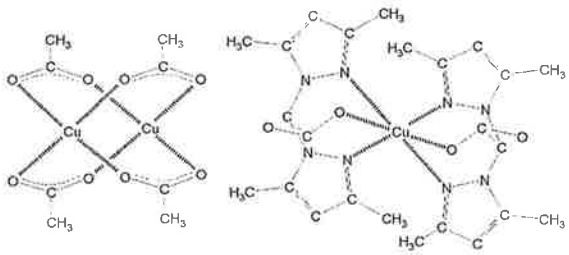

Figure 1: Suggested motif for compound **6** characterized by the co-crystallization of dinuclear copper(II) acetate *paddle-wheels* and mononuclear $Cu(bdmpza)_2$ moieties.

Acknowledgements: We thank R. de Gelder and Z. Jagličić for their help with the crystallographic and the magnetic susceptibility analyses.

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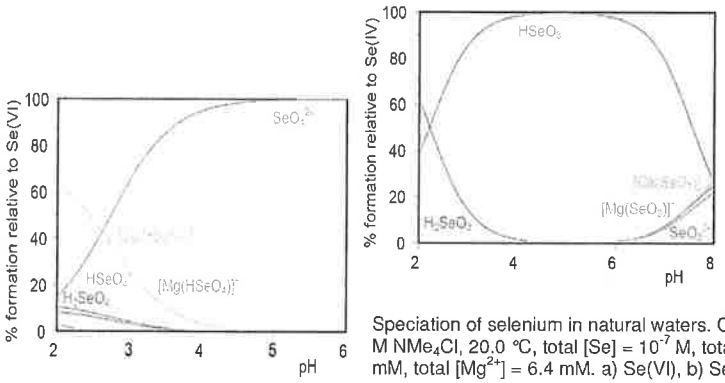
Interactions of selenite and selenate with metal ions: thermodynamic modelling in natural waters

E. Kremer[1], J. Torres[1], V. Pintos[1], L. Gonzatto[1], C. Kremer[1], S. Domínguez[2]

1. *Cátedra de Química Inorgánica, DEC, Facultad de Química, Uruguay. ekremer@fq.edu.uy*
2. *Departamento de Química Inorgánica, Universidad de La Laguna, Canary Islands, Spain*

Reliable thermodynamic data measured under adequate experimental conditions are required in any work focused on developing models for describing aqueous speciation. This is of the utmost importance in the environmental chemistry. Chemical speciation determines the mobility and toxicity of the metal ions. Indeed, the bioavailability of a chemical element in natural aquatic environments is based on the activity of a particular species and certainly not on the total element concentration. Naturally ocurring trace element anions, whose cuantification and chemical behaviour studies are very recent, have been poorly studied. This is the case for selenium, a naturally occurring trace element essential to life, but toxic at high concentration. It is only in recent times that selenium has been identified as an element of concern, arousing interest in the chemical modelling of soluble selenium species in aquatic systems. As selenite and selenate are the predominant water-soluble anionic species of selenium, it becomes important to have experimental data about thermodynamic equilibria between these species and cations. A literature review shows few available data on these systems, with significant differences between old and recent values, even in comparable experimental conditions. Moreover, there are scarce experimental data on thermodynamic parameters that could be used for chemical modelling of selenium in natural aquatic media, most notably those on medium and low ionic strength matrixes.

In this work, we have dealt with the potentiometric study of the interaction of selenite and selenate with metal(II) cations: Ca, Mg, Sr, Ba, Mn, Cu, Zn and Cd, among which some are really relevant from an environmental point of view. Experimental conditions were chosen to simulate those frequently encountered in natural waters media. A proper chemical model includes the values of the thermodynamic equilibrium constants, those referred to infinite dilution, and a procedure for the estimation of the variation of the equilibrium constant in the different media. So, we have studied the influence of ionic strength values on chemical speciation. The stoichiometry and the stability constants of the species formed were measured. The results show that divalent cations are bound by selenium species to a considerable extent, especially in conditions of metal ions excess.



Speciation of selenium in natural waters. Conditions: 0.5 M NMe_4Cl, 20.0 °C, total [Se] = 10^{-7} M, total $[Ca^{2+}]$ = 16.5 mM, total $[Mg^{2+}]$ = 6.4 mM. a) Se(VI), b) Se(IV).

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Auto-catalyzed "electroclick" immobilization of a copper complex onto self-assembled monolayers on a gold electrode

A. Gomila[1], N. Le Poul[1], C. Orain[1], N. Cosquer[1], J.-M. Kerbaol[1], I. Jabin[2], O. Reinaud[3], F. Conan[1], Y. Le Mest[1]

1. *Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521, Université Européenne de Bretagne à Brest,, France Email: yves.lemest@univ-brest.fr*
2. *Laboratoire de Chimie Organique, Université Libre de Bruxelles, Brussels, Belgium.*
3. *Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UMR CNRS 8601, Université Paris Descartes, 75006 Paris, France.*

The immobilization of biomimetic redox devices onto solid supports is of particular importance for the development of efficient sensors and catalysts. It also raises the fundamental question of coupled electron transfer to reactivity at a metal center. An appealing strategy to address this issue is to graft a metal center in a well pre-organized and controlled way, such as in self-assembled monolayers (SAMs). Following the recent adaptation of the Cu^{I}-catalyzed azide-alkyne Huisgen 1,3-dipolar cycloaddition (a "click" reaction [1]) to the successful grafting of Fe-Cu models of cytochrome *c* oxidase on gold,[2] we synthesized the biomimetic complex $[Cu^{II}(6\text{-etmpa})(H_2O)]^{2+}$ (6-etmpa = (6-ethynyl-2-pyridylmethyl)bis(2-pyridylmethyl)amine.

This complex can be immobilized onto an azide-undodecanethiol modified gold electrode in water by an "auto-catalyzed" electroclick reaction[3] through the electrochemical reduction of the complex to Cu^{I}. The Cu^{II}/Cu^{I} redox response of the grafted complex in water is fully reversible and the monolayer is stable through potential cycling. It reflects a high stability at both Cu^{II} and Cu^{I} redox states associated to a fast electron transfer. This emphasizes a clean and thorough method for electrode surface modification. The present finding opens the route to an electrochemically addressable molecular platform in which the Cu complex can serve as a mediator for electron transfer to a further-linked reactive site. This platform would then act as an electron outer-sphere donor similar to Type 1 Cu sites found in Nature. Moreover, with regards to recent results on the oxidative properties of several models of copper monooxygenase, this system might as well appear as promising for studying heterogeneous oxidation of hydrogenated substrates in presence of O_2 in water.[4]

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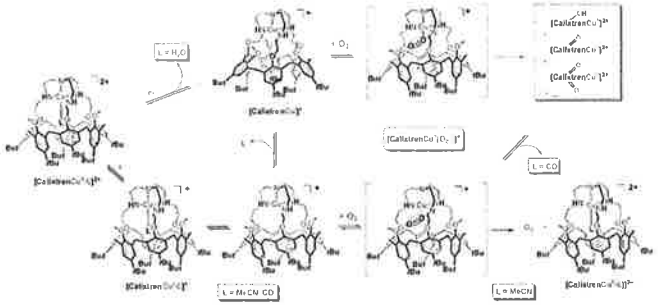
O_2 reactivity at a mononuclear calix[6]-N_4-Cu^I site: electro-catalytic oxidation of amines

B. Douziech[1], L. Billon[1], J. Zeitouny[1], O. Reinaud[2], Y. Le Mest[1]

1. *Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521, Université Européenne de Bretagne à Brest, France. Email: yves.lemest@univ-brest.fr*
2. *Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UMR CNRS 8601, Université Paris-Descartes, 75006 Paris, France.*

Dioxygen activation at a metal center for the functionalization of a C-H bond is a subject of tremendous importance in chemistry. For copper enzymes, the activation process is based on the Cu^{II}/Cu^{I} redox couple, either at a dinuclear or mononuclear center. Copper monooxygenases, namely PHM (Peptidylglycine ő-Hydroxylating Monooxygenase) and Dő H (Dopamine ő-Hydroxylase), involve a common strategy relying on two non-coupled mononuclear copper centers separated by a solvent cleft. Until recently, it was more or less admitted that a two electron reduction of O_2 was necessary to obtain a species reactive enough to break a C-H bond, a Cu^{II}-hydroperoxide {$[Cu^{II}(OOH)]^+$}. A large number of investigations have been devoted to this system and have addressed the capability of such an intermediate to achieve the hydroxylation at aliphatic substrates. However, biochemical, chemical and theoretical evidences suggest that the oxidation mechanism proceeds through the direct attack of the C-H bond by a copper-superoxo $[Cu^{II}(O_2^{\cdot-})]^+$ intermediate.[1-3] Investigations of the oxidative processes induced by mononuclear copper-O_2 adducts are difficult to carry out because model compounds usually either undergo fast dimerization when unhindered or exhibit slow reactivity due to sterical crowding around the Cu center. In a recent paper we described the dioxygen reactivity of a mononuclear Cu^I complex $[Cu^I Calixtren(L)]^+$. With O_2 this monocopper complex undergoes a fast and irreversible redox process, which involved a postulated superoxo-Cu^{II} intermediate.[4] The reaction produced different oxidized species depending on the solvent. In CH_2Cl_2, the calix-ligand itself is oxidized by the $[Cu^{II}(O_2^{\cdot-})]^+$ species. We will present an electrochemical approach of the reactivity of the $[Cu^{II}(O_2^{\cdot-})]^+$ adduct in the presence of easily oxidizable substrates such as primary amines. These substrates are able to coordinate the Cu^{II} center inside the calixarene cavity. After electro-reduction to Cu^I, in presence of O_2 and in non-coordinating solvent, the superoxo $[Cu^{II}(O_2^{\cdot-})]^+$ adduct lead to the substrate oxidation preferably to the calixarene ligand attack. The spectroscopic and electrochemical results of this study will be presented and discussed, as well as the mechanism.



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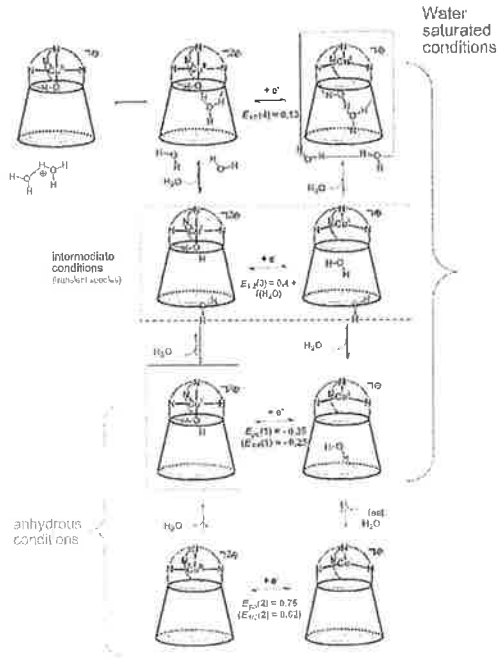
Supramolecular control of the the Cu^{II}/Cu^{I} electron exchange through entrapping of water molecules inside a protein-like pocket of a funnel complex

N. Le Poul[1], B. Douziech[1], G. Thiabaud[2], O. Reinaud[2], Yves Le Mest[1]

1. *Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521, Université Européenne de Bretagne à Brest, France Email: yves.lemest@univ-brest.fr*
2. *Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UMR CNRS 8601, Université Paris Descartes, 75006 Paris, France.*

Water has a determinant effect on the protein structure: stabilization,[1] stiffening,[2] and functionality: folding,[3], electron transfer,[4] proton delivery and catalysis.[5] A recent study has showed for instance that water could inhibit oxygen binding in hemoprotein models.[6] Surprisingly, the influence of water on the redox properties and reactivity of synthetic models of copper proteins has not been yet investigated. Our previous studies on Cu complexes based on a N-functionalized calix[6]arene ligand showed that the specific presence of the calix[6]arene could generate unusual supramolecular effects,[7] and modify the kinetics and thermodynamics of the coupled electron transfer/ligand exchange reaction.[8] In this study, we show the possible. inclusion of water molecules inside the calix[6]arene cone and the resulting modification of the redox properties of the Cu-complex. Particularly, in a H_2O saturated organic medium, the Cu^I complex is able to trap two water molecules in the hydrophobic calix[6]arene pocket. The reversibility and redox potential of electron exchange for the Cu^{II}/Cu^{I} system is thus tunable by variation of H_2O content. This highlights a protein-like behaviour, since water access or gating in the active site pocket of copper monooxygenases may be keys for generating a Cu^I state prone to O_2 activation.



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Ruthenium Nitrosyls Tetraammines as Radical Scavenger

G. Metzker[1], D. R. Cardoso[1], D. W. Franco[1]
1. *University of São Paulo, São Carlos, Brazil.* metzkerg@gmail.com

The reactions of nitrogen oxides (NO_x) with $O_2^{\cdot-}$ and $OH^{\cdot}$ may generate in biological media deleterious and harmful products[1,2]. On this perspective, NO donors or scavengers are required to achieve antioxidant or pro-oxidative biological conditions respectively. Ruthenium tetraammines complexes are good candidates for this goal being already tested *in vitro* and *in vivo* as a trypanomicide and as a vasodilatator agents[3,4]. Encouraged by the possibility of biological applications, the reactions among *trans*-$[Ru(NO)(NH_3)_4(L)]^{n+}$ and [Ru(NO)Hedta] (where L = nitrogen heterocycles ligands like imidazole, substituted pyridines or triethylphosphite) complexes with $OH^{\cdot}$ and $O_2^{\cdot-}$ radicals were investigated in aqueous solution by means of spectroscopic (UV-vis, EPR) and electrochemical (VC, DPV) techniques. The E^0 Ru^{III}/Ru^{II} in the ruthenium nitrosyls were determined as higher than 2.0V *vs.* NHE in acid aqueous solution. The reaction of ruthenium nitrosyls complexes with $OH^{\cdot}$ radical lead to the metal center oxidation (Ru^{II}/Ru^{III} and probably Ru^{III}/Ru^{IV}) as suggested by the spectroscopic techniques. The specific rate constant for the reaction between $OH^{\cdot}$ and *trans*-$[Ru(NO)(NH_3)_4(L)]^{n+}$ in water was close to the diffusion control (~10^9 L mol^{-1} s^{-1}) as probed by a competitive kinetics approach (using EPR spectroscopy and DMPO as a competitor). Although the reaction mechanism is not fully understood yet, a transient paramagnetic species was identified suggesting the formation of the $[Ru^{III}NO^{+}]^{n+}$ fragment. For the reaction of ruthenium nitrosyls with $O_2^{\cdot-}$ the reduction of the coordinate nitrosonium to nitric oxide followed by its aquation and release of NO and *trans*-$[Ru(H_2O)(NH_3)_4(L)]^{n+}$ formation is proposed. Using UV-vis and cytochrome c as a competitor probe for superoxide the specific rate constant for the reaction of $O_2^{\cdot-}$ with *trans*-$[Ru(NO)(NH_3)_4(L)]^{n+}$ was estimated to be in the range of 0.14 to 4.5 x 10^5 L mol^{-1} s^{-1}. All together, under the experimental conditions employed, our results suggest that ruthenium nitrosyls may act as a NO donors and as antioxidant species under physiological conditions and oxidative stress.

Acknowledgements: The authors acknowledge the Brazilian agencies FAPESP (Proc. 05/53266-4 and 06/05877-4), CNPq and CAPES for financial support.

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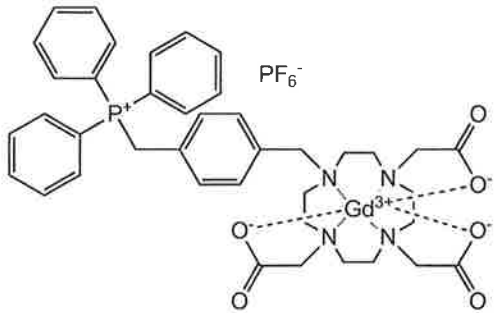
Targeting the mitochondria of cancer cells for gadolinium neutron capture therapy

D. E. Morrison[1], L. M. Rendina[1]
1. *The University of Sydney, Sydney, Australia. Email morris_d@chem.usyd.edu.au*

Arylphosphonium salts, such as tetraphenylphosphonium (TPP) and triphenylmethylphosphonium (TPMP) have shown to selectively accumulate in the mitochondria of cancer cells. With uptake ratios of 40:1 in glioma, these moieties have received much attention for their potential as tumour targeting agents, in particular for boron neutron capture therapy (BNCT). Previous research has provided promising results in BNCT, [1,2] and has led to the investigation of a related application for the related gadolinium neutron capture therapy (GdNCT). This represents a new direction for GdNCT, in which Gd-containing drugs are typically designed to target the nucleus of tumour cells.[3]

1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) and its derivatives are some of the strongest known chelators of Gd^{3+} and other lanthanide ions. Towards this end, the DOTA-like derivative 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A) has been appended to a series of triphenylphosphonium moieties to generate a series of bifunctional chelators for Gd^{3+}. Current progress towards the synthesis, characterisation and evaluation of a series of these compounds will be presented.



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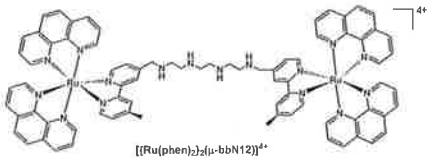
Polyamine- and Polyether-linked Dinuclear Ruthenium(II) Complexes as DNA Binding Agents

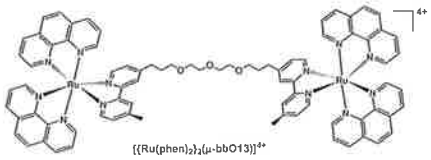
Y. Mulyana[1], D. K. Weber[1], F. R. Keene[1], J. G. Collins[2]

1. *School of Pharmacy & Molecular Sciences, James Cook University, Townsville, Queensland 4811, Australia; yanyan.mulyana@jcu.edu.au*
2. *School of Physical, Environmental and Mathematical Sciences University College, University of New South Wales Australian Defence Force Academy, Canberra, A.C.T., 2600, Australia)*

Previous studies have shown that rigid dinuclear ruthenium(II) complexes bind selectively to the minor groove of duplex DNA. Importantly, these complexes have significantly greater affinity for non-duplex features, such as bulge sites.[1-4] However, due to their rigidity the complexes cannot follow the curvature of the minor groove, so that only one ruthenium centre can associate with the groove with the second metal centre being extra-helical. The introduction of a flexible linker, such as a methylene chain within the bridge overcomes that problem - and enhances the affinity - since the additional flexibility of the aliphatic chain allows the second metal centre to bind (although less strongly) in the duplex region adjacent to the bulge.[5,6] Recent work has demonstrated that the DNA-binding, as well as the cytotoxic properties of the corresponding dinuclear complexes, can be optimised by varying the methylene chain length.[7]

We believed the interaction of the flexibly-linked dinuclear complexes within the minor groove may be enhanced by introducing more polar flexible chains - such as polyamines and polyethers, which would contribute to additional interactions such as hydrogen bonding with specific residues. The synthetic pathways to such species (examples are shown in the figures below), cytotoxicity and the fluorescence studies of the DNA binding of a series of polyamine- and polyether-linked dinuclear ruthenium(II) complexes will be presented.





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Synthesis, Characterization, and in Vitro Evaluation of Potentially Anticancer Ruthenium Complexes

W. Ni, W. L. Man, Y. W. Lam, T. C. Lau
Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong, China
Presenting author's email address: nwenxiu2@student.cityu.edu.hk

It has been well established for several years that Ru(II, III) complexes display interesting anticancer, antimetastatic properties, and some of these compounds are under intensive preclinical and clinical investigation[1-3]. In this report six mononuclear ruthenium complexes with formula $[Ru(cyclen)L_1L_2]^{n+}$ or $[Ru(imcyclen)L_1L_2]^{n+}$ have been synthesized. The ligand cyclen is 1,4,7,10-tetraazacyclododecane and imcyclen is 1,4,7,10-tetraazacyclododeca-1-ene. L_1 and L_2 are both monodentate ligands such as Cl^-, H_2O, DMSO, NO_3^-, pyrazole or imidazole. These compounds have been characterized by elemental analysis, IR spectroscopy, electrospray ionization mass spectrometry, and X-ray crystallography. Moreover, the cytotoxic properties of these compounds have been studied. The toxicity of the water-soluble compound *cis*-$[Ru(cyclen)Cl_2]Cl$ against human cancer cell lines has been investigated. When compared to cisplatin, IC_{50} results show that it had a high toxicity.

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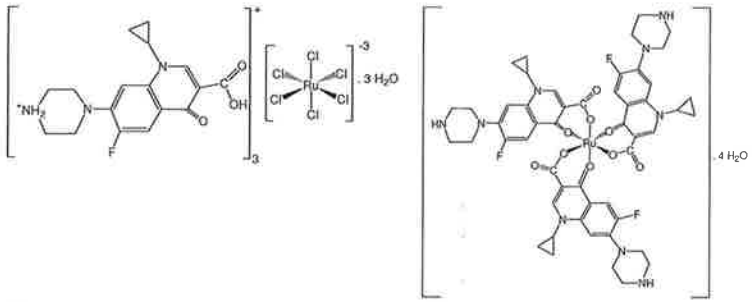
Tuning the reaction products of ruthenium and ciprofloxacin combination for the design of potential metallo-drugs

S. Nikolaou[1], M. K. Tanimoto[1], S. Dovidauskas[2]

1. *Department of Physics and Chemistry, Faculty of Pharmaceutical Sciences of Ribeirão Preto, University of São Paulo, Av. do Café s/n, ZIP CODE 14040-903, Ribeirão Preto, São Paulo, Brazil, Fax: 55 16 36024880*
2. *Institute Adolfo Lutz, R. Minas 877, ZIP CODE 14085-410, Ribeirão Preto, São Paulo, Brazil.*

This work presents the synthesis of two potential new metallo-drugs,[1, 2] the ionic $(C_{17}H_{19}FN_3O_3)_3[RuCl_6].3H_2O$ (**1**) and the coordination $[Ru(C_{17}H_{17}FN_3O_3)_3].4H_2O$ (**2**) compounds, by combining ruthenium (III) and the fluoroquinolone ciprofloxacin in different synthetic conditions (acid media or neutral and reflux conditions, respectively) (Figure 1). The ESI MS (positive mode) spectrum of the ionic compound (**1**) displayed a main peak at *m/z* = 994.6, which was assigned to the gaseous phase adduct $(ciprofloxacin)_3.H^+$, while the coordination compound featured peaks at *m/z* 1093.3 and 547.1 ascribed to the singly and doubly charged ions $(\mathbf{2}).H^+$ and $(\mathbf{2}).2H^+$, respectively. Thermal analysis corroborated the proposed water content for both complexes. The absorption spectra of the compounds in aqueous medium are dominated by the ciprofloxacin transitions in the UV region but two bands were observed at 421nm and 496nm for compound (**1**), assigned to a charge transfer and d-d transitions. In the case of compound (**2**) only a broad shoulder around 450 nm was observed in the visible region, also assigned to a ligand field transition The cyclic voltammograms of complex (**2**) exhibited a quasi-reversible process ascribed to the Ru(II) / (III) redox pair at -0.25 V (*vs* SHE) while compound (**1**) displayed this process at -0.11V, showing that the central ruthenium ion is stabilized in the (III) oxidation state by the coordination to the hard oxygen atoms of the ciprofloxacin ligand. The solubility of compound **1** is pH dependent (as well as free ciprofloxacin) while compound **2** is fully water soluble. Both compounds are stable under physiological, stomachal and intestinal pH over 48 hours. The compounds are also stable under incubation conditions (stomachal pH and 37°C) without significant pH lowering.



(A) (B)

Figure 1. Pictorial view of the proposed structures for compounds (A) $(ciproH_2^+)_3[RuCl_6].3H_2O$ and (B) $[Ru(cipro)_3].4H_2O$

Acknowledgements: FAPESP, CNPq and CAPES.

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Coordination Chemistry for the Development of New Technetium-99m Imaging Agents and Their Rhenium Analogues

A. J. North[1], U. Ackermann[1,2], K. A. Price[3], A. R. White[3], J. M. White[1] & P. S. Donnelly[1*]

1. *School of Chemistry & Bio21 Institute, University of Melbourne, Victoria 3010, Australia, anorth@unimelb.edu.au*
2. *Centre for PET, Austin Hospital, Heidelberg, Victoria 3084, Australia*
3. *Department of Pathology, University of Melbourne, Victoria 3010, Australia*

The radio-imaging properties of technetium-99m are exploited in order to trace areas of hypoxia within the brain both specifically and in a non-invasive manner.

As there are no non-radioactive isotopes of technetium, its congener, rhenium, is used as a surrogate in developmental chemistry. Both the $[M(CO)_3]^+$ and $[M^V{=}O]$ (M = Re, ^{99m}Tc) metal cores are stable platforms ideally suited for radiopharmaceutical application. Consequently, the objective of this project is to develop various stable aromatic-amine containing ligands and thiosemicarbazide-derived ligands which contain a reducible moiety such as a nitro-containing aryl group. Ultimately, a range of pharmacophores can be attached to the ligand framework to facilitate bio-reduction within cells with low oxygen concentrations.

Several potential complexes have been prepared *via* microwave-assisted synthesis and utilise a neutral, bidentate ligand system. These complexes provide interesting preliminary radio-labelling results and also present weak fluorescence, which is used to track uptake in HeLa cancer cells. Moreover, electrochemical studies show that the reduction of the nitro functional group occurs in a region comparable to currently studied hypoxia markers ($E_c \approx -0.60$ V). An ORTEP representation of one of these complexes is displayed below (**Figure 1**).

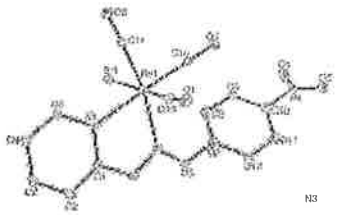

Figure 1. ORTEP representation of $[ReL^1(CO)_3Br]$, where L^1 is the ligand 4-nitrobenzaldehyde 2-(2-pyridinyl)hydrazone

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Zinc(II) Chlorido Complexes of Kinetin and its Derivatives

R. Novotná[1], I. Popa[1], Z. Trávníček[1]

1. *Department of Inorganic Chemistry, Faculty of Science, Palacký University, Tř. 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic*
   zdenek.travnicek@upol.cz

Kinetin (N6-furfuryladenine) was isolated as the first cytokinin, i.e. a plant hormone, in 1955 [1]. Recently, strong anti-ageing effects of kinetin on normal human skin fibroblasts [2] have been reported, which resulted in commercial application of kinetin in cosmetics [3]. Coordination of kinetin as a ligand in zinc(II) complexes may result in a promising mutual synergic effect on a biological activity, e.g. anti-oxidative, which has already been proved in the cases of both the metal and kinetin and its derivatives themselves.

A series of the zinc(II) complexes of the general compositions $[Zn(L^n)_2Cl_2]\cdot x$Solv (**1–5**) [5] and $[Zn(HL^n)Cl_3]\cdot nL^n$ (**6–10**) involving kinetin [L^1, complex **1**; **6**] and its derivatives, i.e. N6-(5-methylfurfuryl)adenine (L^2, **2**; **7**), 2-chloro-N6-furfuryladenine (L^3, **3**; **8**), 2-chloro-N6-(5-methylfurfuryl)adenine (L^4, **4**; **9**) and 2-chloro-N6-furfuryl-9-isopropyladenine (L^5, **5**; **10**), as N-donor ligands, has been synthesized. The complexes have been fully characterized by elemental analyses (C, H, N), FTIR, Raman, ^{1}H and ^{13}C NMR spectroscopy, conductivity measurements, TG/DTA analyses. A single crystal X-ray analysis determined the molecular structures of complexes $[Zn(L^1)_2Cl_2]\cdot CH_3OH$ (**1**) and $[Zn(HL^1)Cl_3]\cdot L^1$ (**6**) (Fig. 1). In both complexes, the Zn(II) atom is tetrahedrally coordinated and the molecules of the L^1 organic compound are bound to the central atom via the N7 atoms. The same conclusions can be also drawn from multinuclear NMR spectroscopic experiments. The cytotoxicity and influence of the presented complexes on the process of mitosis in the plant cell model represented by *Nicotiana tabacum BY-2* cells have been evaluated. The results of the biological activity study will be discussed within the framework of the presentation.

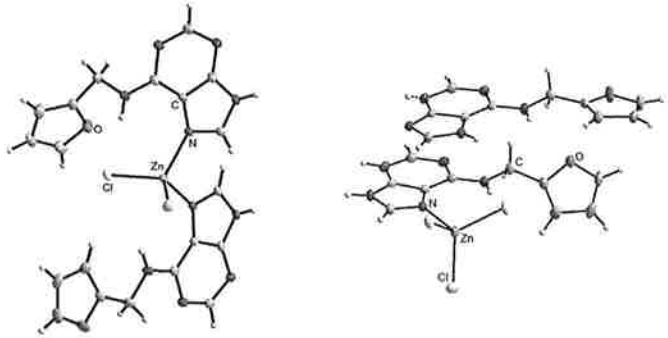

Fig. 1: The molecular structures of complex **1** (left) and complex **6** (right).

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Structural features of Ca^{2+}-carbohydrate solution complexes studied by multinuclear (^{1}H, ^{13}C and ^{43}Ca) NMR spectroscopy

A. Pallagi[1,2], P. Sebők[2], P. Sipos[1], I. Pálinkó[2]

1. *Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary; pallagiattila@chem.u-szeged.hu*
2. *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

Sugar derivatives are known to form weak complexes with Ca^{2+} ion in aqueous solutions of intermediate pH. Their structures in solution have only been studied sporadically. Recently, we have been involved in a comprehensive study concerning the structure and equilibria of Ca^{2+}–gluconate complexes in aqueous solutions, using a broad range of Ca^{2+} and gluconate concentrations and ionic strengths.[1] Structural information was derived from multinuclear NMR measurements and stability constants were quantitatively estimated with the help of the PSEQUAD program.[2]

In order to reveal the fine details of structure-reactivity relationships in these weak metal-carbohydrate complexes, further sugar derivatives were included in the investigations. Results of this experimental work are communicated in this contribution.

A set of sugar derivatives was selected along various lines. One of the selection criteria was the oxidation states of the terminal groups and keeping the chain length of gluconic acid (*i.e.* 6). The group contained D(+)-glucose (partially oxidized at one end), mucic acid (fully oxidized at both ends), D-sorbitol (fully reduced at both ends), L-gulonic acid (fully oxidized at one end and fully reduced at the other). The other was keeping the oxidation states of the terminal group as in L-gulonic acid (or in D-gluconic acid) but increasing (D-heptagluconic acid) or decreasing (arabic acid) the chain length. The acid-base behavior of the relevant compounds (those having carboxylic groups) were investigated first, then, the Ca^{2+} complexation properties were studied both at constant (1.0 M NaCl) ionic strength. The main experimental tool was ^{1}H and ^{13}C NMR spectroscopy, but representative ^{43}Ca NMR spectra were also recorded. The observed variations in the NMR spectra made possible to propose structures for the complexes and from the quantitative analysis of the stability constants factors influencing complex stability were deduced.

Our experiments proved that multinuclear NMR spectroscopy is a useful tool for the determination of the stability constant of these weak complexes. It was found that in these solutions Ca^{2+} complexes with 1:1 composition were mainly formed and their stability constants increased with the increasing oxidation state of the ligand. It also could be observed that the formation of a six- or five-membered chelate ring (where it was possible at all) contributed to the stability increase.

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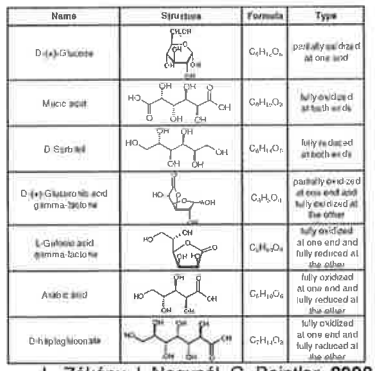
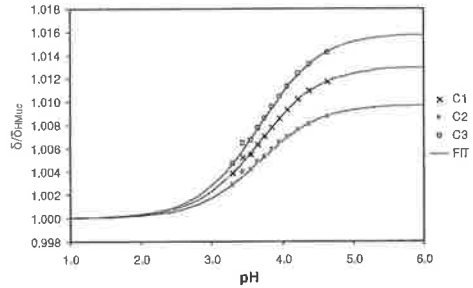


Name	Structure	Formula	Type
D-(+)-Gluconic		$C_6H_{12}O_7$	partially oxidized at one end
Mucic acid		$C_6H_{10}O_8$	fully oxidized at both ends
D-Sorbitol		$C_6H_{14}O_6$	fully reduced at both ends
D-(+)-Glucaro-1,6-acid gamma-lactone		$C_6H_8O_7$	partially oxidized at one end and fully oxidized at the other
L-Galactonic acid gamma-lactone		$C_6H_{10}O_6$	fully oxidized at one end and fully reduced at the other
Arabonic acid		$C_5H_{10}O_6$	fully oxidized at one end and fully reduced at the other
D-Heptagluconate		$C_7H_{13}O_8$	fully oxidized at one end and fully reduced at the other



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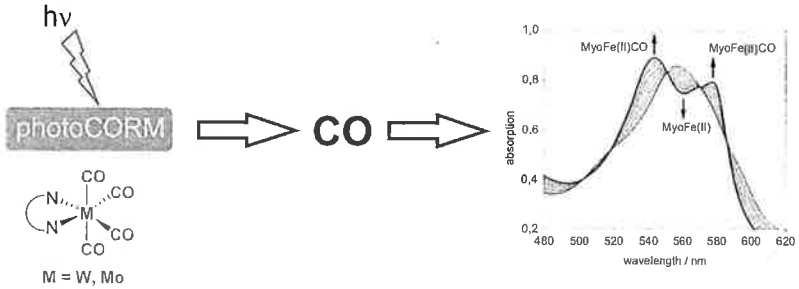
Bioorthogonal coupling strategies in the synthesis of CORM-peptide conjugates

H. Pfeiffer[1], J. Niesel[1], U. Schatzschneider[1]

1. *Ruhr-Universität Bochum, Department of Chemistry and Biochemistry, Universitätsstrasse 150, 44801 Bochum, Germany, hendrik.pfeiffer@rub.de*

In the human body carbon monoxide possesses versatile properties as a signalling mediator and participates in important biological processes. Beside being a potent vasodilator, CO can exert anti-inflammatory, anti-apoptotic, and anti-proliferative effects.[1],[2] Since it is a toxic gas and difficult to handle, there is considerable interest in the development of **CO releasing molecules (CORMs)** as "solid storage forms" for carbon monoxide. Therefore, transition metal carbonyl complexes are highly interesting target structures.[3] Compared to thermally induced liberation of CO, photoactivated CO release will allow for a precise spatial and temporal control of its biological action.[4] We have recently synthesized several tungsten, molybdenum, and manganese complexes with bidentate as well as tridentate nitrogen donor ligands as promising new photoCORMs, which are inert in the dark in aqueous solution, but release CO upon irradiation.[5]

Carrier peptides are important vehicles to achieve accumulation of bioactive cargos in specific biological target sites. Thus, we have explored the functionalization of the parent photoCORMs with model peptides using bioorthogonal coupling strategies, such as oxime ligation, Sonogashira cross-coupling, or the alkyne-azide 1,3-dipolar cycloaddition (click reaction).[6]



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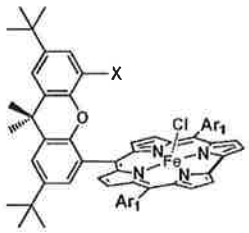
Hangman Iron and Cobalt Corrole-Complexes as Biomimetic Models

M. Schwalbe[1], D. D. Kiper[1], D. G. Nocera[1]

1. *Department of Chemistry, Massachusetts Institute of Technology; 77 Massachusetts Avenue, Cambridge MA 02139, USA, e-mail: matsch@mit.edu*

The activation of oxygen and oxygen-derived species is a major task of natural metallo-enzymes (e.g. heme-oxidase enzymes). A mimic of those natural metallo-enzymes is an obvious starting point, with some precedence, to get more insight into the role that metal ions play in activating oxygen.[1] High valent metal-oxo tetrapyrrolic macrocycles are very likely the key intermediates in the catalytic cycles involved in the activation of oxygen species. We will present the synthesis, as well as, the spectroscopic properties and catalytic activity of new hangman type iron and cobalt corrole compounds. The utilization of corroles as opposed to porphyrins, as is found in nature, is because of the expected greater stability of high oxidation states in those systems. The compounds are prepared to mimic the characteristics of the natural metalloporphyrin oxidants. A detailed characterisation including extensive Mössbauer spectroscopy will be presented.

Special interest will be paid to catalase, an enzyme which is commonly found in living organism to catalyse the decomposition of hydrogen peroxide to water and oxygen, i.e. an O-O bond breaking process. The affect of a supporting ("hanging") group capable of assisting proton-coupled electron transfer (PCET) processes seems to be very important in the hydrogenperoxide dismutation to speed up the reaction,[2] which will be discussed in detail. The results gained in this study also lend insight into the water splitting reaction in photosystem II, as the opposite reaction, i.e. an O-O-bond formation, is found there.[3]



X = Br, COOH **Ar_1 = ^{t}BuPh, Mes, C_6F_5**

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Characterization of One-Electron Oxidized Metal-Salen Type Complexes (Metal = Cu, Ni, Pd, Pt)

Y. Shimazaki
College of Science, Ibaraki University, 2-1-1 Bunkyo,Mito 310-8512, Japan.
e-mail; yshima@mx.ibaraki.ac.jp

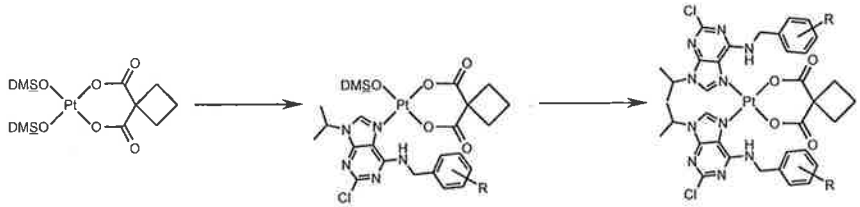
The Cu(II)–phenoxyl radical formed during the catalytic cycle of galactose oxidase (GO) attracted much attention, and the structures and properties of a number of metal–phenoxyl radical complexes have been studied. As a functional model system of GO, Stack et al. reported that the Cu complex of a distorted salen (di(salicylidene)ethylenediamine) derivatives showed the catalytic oxidation of primary alcohols to aldehydes, and formation of the Cu(II)-phenoxyl radical species was revealed in the catalytic cycle.

As an extension of the studies on M(II)–phenoxyl radical species, we synthesized square-planar Cu(II), Ni(II), Pd(II), and Pt(II) complexes of the salen ligands with two bulky substituents on the phenolate moieties and determined the valence state of one-electron oxidized complexes. The electronic structures of one-electron oxidized species depended on the central metal ion and solvents used. Upon one-electron oxidation the Ni(II) complexes were converted to the Ni(II)-phenoxyl radical complexes in CH_2Cl_2 and to the Ni(III)-phenolate species in DMF, and the oxidation state was found to depend on the coordination properties of the solvent molecule. The one-electron oxidized species of the Pd(II) complex was the Pd(II)–phenoxyl radical in the ground state. On the other hand, the one-electron oxidized species of the Pt(II) complex had a large distribution of the radical electron spin at the Pt center, whose oxidation state became slightly higher than +2. On the other hand, the oxidized Cu(II)-salen complexes showed a mainly metal-centered oxidation state except when they were distorted from the square-planar geometry, which is quite different from the observation for the group 10 metal-salen complexes.

Platinum(II) Cyclobutane-1,1-dicarboxylato Complexes Involving N6-benzyl-9-isopropyladenine-based Ligands with Promising *In Vitro* Cytotoxicity

P. Štarha[1], L. Dvořák[1], I. Popa[1], Z. Trávníček[1], Z. Dvořák[2]
1. *Department of Inorganic Chemistry, Faculty of Science, Palacký University, Tř. 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic, zdenek.travnicek@upol.cz*
2. *Department of Cell Biology and Genetics, Faculty of Science, Palacký University, Šlechtitelů 11, CZ-783 71 Olomouc, Czech Republic*

This work presents platinum(II) cyclobutane-1,1'-dicarboxylato (cbdc) complexes of the general composition $[Pt(L)_2(cbdc)]$ (**1–6**), where L stands for 2-chloro-N6-benzyl-9-isopropyladenine derivatives with the substituted benzene ring. The complexes **1–6** were synthesized using $[Pt(DMSO)_2(cbdc)]$ as a key intermediate prepared from $PtCl_2$. This complex was left to react with two molar equivalents of the appropriate L molecule which led to the formation of $[Pt(L)_2(cbdc)]$ complexes, as depicted below in Scheme 1. The obtained products were characterized by means of elemental analysis, FTIR, Raman and multinuclear (^1H, ^{13}C, ^{15}N and ^{195}Pt) and two dimensional (^1H–^1H gs-COSY, ^1H–^{13}C gs-HMQC, ^1H–^{13}C gs-HMBC and ^1H–^{15}N gs-HMBC) NMR spectroscopy and a single crystal X-ray analysis. The complexes **1–6** were tested by an MTT assay for their *in vitro* cytotoxicity against various human cancer cell lines, namely ovarian carcinoma (A2780), cisplatin resistant ovarian carcinoma (A2780cis), malignant melanoma (G361), breast adenocarcinoma (MCF7), lung carcinoma (A549), osteosarcoma (HOS) and cervix epitheloid carcinoma (HeLa). Several representatives of these complexes showed interesting *in vitro* cytotoxic activity. The complex **6** was the most active one, with the IC_{50} values against A2780 and A2780cis equal to 6.4, and 5.6 μM, respectively, which exceeded the results obtained for commercially used platinum-based anticancer drug cisplatin, whose IC_{50} values against mentioned cancer cells were determined to be 11.5, and 30.3 μM, respectively. Moreover, the *in vitro* testing of the prepared platinum(II) cyclobutane-1,1'-dicarboxylato complexes for their toxicity against primary human hepatocytes showed that these substances can be considered as toxicologically safe for human liver cells, since the IC_{50} values were higher than 50.0 μM.



R = 2-F-5Br (complex **1**), 3,4-diCl (**2**), 3-Br (**3**), 2-CF_3 (**4**), 3-CF_3 (**5**), 4-CF_3 (**6**)

(intermediate)

1–6

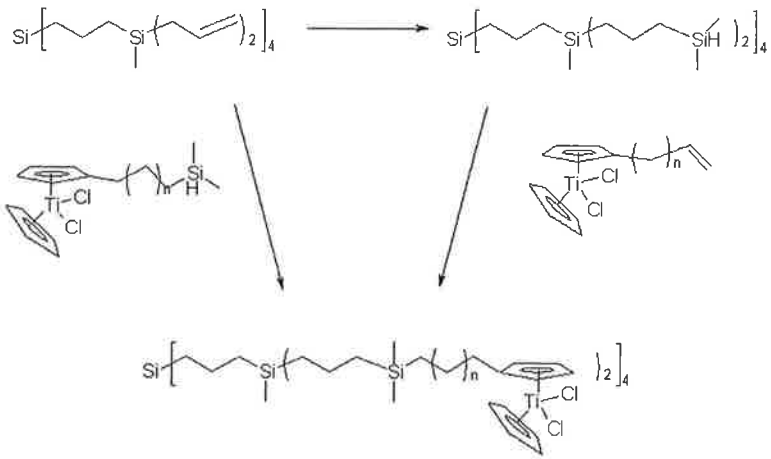
Scheme 1

Acknowledgements: This research was supported by The Ministry of Education, Youth and Sports of the Czech Republic (a Grant No. MSM6198959218).

Carbosilane Dendrimers with Cyclopentadienyl Complexes of Titanium on Periphery

T. Strasak and J. Cermak,
Institute of Chemical Process Fundamentals ASCR, v.v.i., Prague, Czech Republic,
strasak@icpf.cas.cz

Recently, we optimized divergent synthesis of carbosilane dendrimers and analyzed defects in their structure by combination of MALDI-TOF MS and multinuclear NMR [1,2]. We now continue our studies by the functionalization of carbosilane dendrimers with cyclopentadienyl complexes of titanium on periphery. Two synthetic approaches were used both generally include preparation of supporting dendrimer and titanocene dichloride with appropriate anchoring functionalities for selective complex–dendrimer attachment. Carbosilane dendrimers with terminal double bonds on periphery were synthesized. Dendrimers with Si-H functionality necessary for the second strategy were prepared by hydrosilylation of double bonds with chlorodimethylsilane and subsequent reduction by $LiAlH_4$. Another part of our study was focused on the design and synthesis of precursors of cyclopentadienyl ligands for organometallic compounds. These substituted cyclopentadiene precursors must contain a functional group by which they will be connected to the dendrimer. In the first type of ligands alkenyl groups played this role. The second type contained dimethylsilyl group connected to the ring by an aliphatic spacer. Length of this spacer could be changed.
Titanocene dichlorides bearing ligands with complementary functionality to dendrimer peripheral groups were connected to the carbosilane dendrimers by hydrosilylation.



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Gated Electron Transfer Reactions of $[Cu[12]aneS_4]^{2+/+}$ and $[Cu[14]aneS_4]^{2+/+}$ Couples: Re-Examination in Acetonitrile

H. D. Takagi[1], T. Suzuki[2], K. Ishihara[3]
1. *Research Center for Materials Science, Nagoya University, Nagoya, Japan*
2. *Faculty of Science, Okayama University, Okayama, Japan*
3. *Graduate School of Advanced Science and Engineering, Waseda University, Tokyo, Japan*

Outer-sphere gated electron transfer processes are important in biological reactions of some metalloenzymes. In such reaction systems, either the reaction of thermodynamically unfavorable direction is accelerated or the reaction of thermodynamically too favorable direction is slowed down so as to steadily control the concentration of metabolically important chemical species, by means of the conformational changes around the metal centers.

On the other hand, gated reactions have been reported only for the reactions involving Cu(II)/Cu(I) couples. In general, Cu(I) prefers tetrahedral structure while Cu(II) is stabilized in the octahedral/tetragonal or trigonal bipyramidal structure. Currently, two different ideas have been postulated to explain why a certain reaction is gated. One explanation is based on the semi-classical Marcus-Sutin model: (1) since each reactant approaches a common intermediate structure in between the structures of the oxidized and reduced forms within the encounter complex in this model, gated reaction is observed when energies for the structural changes from the oxidized and reduced species to a common intermediate structure are very different. Another explanation is related to the orbital overlap between the reactants: (2) gated reaction is observed only when the electronic coupling between two reactants is very small, and the structural change in one of the reactant induces low-energy CT bands that increase the electronic coupling with the counter reagent. A group of researchers who support explanation (1) examined only Cu-polythioether complexes, while another group of scientists who supports explanation (2) examined only Cu-bidentate polypyridine complexes to date. In this study, we studied the reactions of CuS_4 complexes in acetonitrile, to examine the applicability of explanation (2) to the CuS_4 system.

Figure 1. Ortep (50% probability) of $[Cu[12]aneS_4]^+$ and $[Cu[14]aneS_4]^+$

As the crystal structures have not been reported for some CuS_4 complexes, we synthesized $[Cu[12]aneS_4]^+$ and $[Cu[14]aneS_4]^+$, and obtained the crystal structures. Cross redox reactions of these complexes were also examined in acetonitrile with non-copper counter reagents as well as with other copper complexes. As shown in Fig. 1, $[Cu[12]aneS_4]^+$ and $[Cu[14]aneS_4]^+$ were isolated as a dimer and a ligand-bridged chain, respectively.

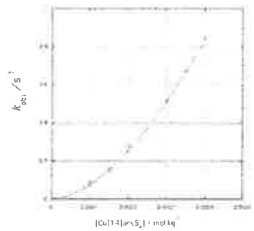

Figure 2. Dependence of the first-order rate constant on $[Cu[14]aneS_4^+]$ for the reaction with $[Ni(tacn)_2]^{2+}$ at 298K. I = 0.1

Kinetic studies revealed that redox reactions involving CuS_4^+ species were not first-order with respect to CuS_4^+. A result with an excess amount of Cu(I) species is shown in Fig. 2. This result indicates that the $[Cu[14]aneS_4]^+$ dimerizes before the electron transfer reaction with Ni(III). Further analyses of this reaction and the reaction with $[Cu[12]aneS_4]^{2+}$ revealed that the electron self-exchange rate constants for the $[Cu[14]aneS_4]^{2+/+}$ couple was estimated to be 2.7 kg mol^{-1} s^{-1} from the cross reactions with Ni(III), while a value of 2.7 x 10^3 kg mol^{-1} s^{-1} was estimated from the cross reaction with $[Cu[12]aneS_4]^{2+}$. Therefore, it seems that the reaction of dimerized $[Cu[14]aneS_4]^+$ with Ni(III) is also gated while the reaction of dimerized $[Cu[14]aneS_4]^+$ with $[Cu[12]aneS_4]^{2+}$ takes place in a concerted manner. These results seems to support the explanation (2) even for the reactions involving $CuS_4^{2+/+}$ couples in acetonitrile.

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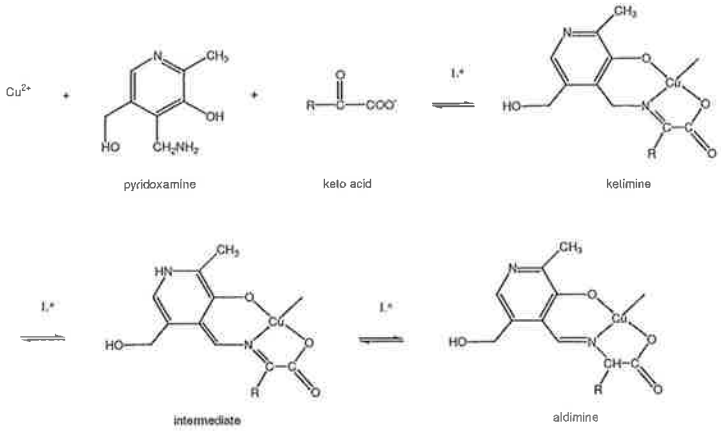
Study on Metal Ion-Mediated Transamination Reactions by the DFT method: Mechanisms and Stereoselectivities

T. Taura, K. Fukami, K. Yamada
Group of Chemistry, Department of Systems Science, University of Aichi Prefecture, Nagakute, Japan, taura@ist.aichi-pu.ac.jp

Transamination reactions are accelerated by the presence of metal ions, e.g. Cu(II), Mn(II), Zn(II) ions, etc. Many studies have been undertaken for clarifying the mechanism of these reactions [1]. Experimental works found that the complex formation of metal ions with vitamin B_6 compounds (pyridoxal, pyridoxamine, and their phosphates), keto acids and amino acids is important. It has been reported that Schiff-base complexes with metal ions play an essential role in these reactions. In a reaction, pyridoxamine, keto acid and a metal ion react to form a Schiff-base complex (ketimine), and then this complex is isomerized to a different type of Schiff base (aldimine) containing an amino-acid part through an intermediate.

However, in spite of a huge number of experimental studies, details of reaction mechanisms including the transition state are still unknown. In this work, we studied transformations of two main Schiff-base metal complexes, i.e. ketimine and aldimine, by the density functional theory (DFT) method. Structures of these Schiff-base complexes having several conformational and rotational isomers were optimized at the B3LYP/6-31G* level. The populations of structures were also estimated from calculated energies for structures.

The DFT computational search of optimum structures indicates that stabilities of Schiff bases depend on orientations of hydroxyl groups and methyl groups of vitamin B_6 parts as well as side chains R of keto-acid or amino-acid parts. Therefore, we picked up several stable structures for vitamin B_6 parts, and then for these structures we optimized structures of conformers about R groups. The calculated energy diagram coincides with the experimental result that ketimine is preferentially transformed to aldimine through an intermediate and the reaction rates depend on the R group [2]. Furthermore, the stereoselective formation of chiral amino acids from keto acids in the Schiff-base complexes was predicted in the presence of optically active ligands L* by DFT calculations using B3LYP/6-31G* level functionals.



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Production, Isolation and Reactivity Studies of Metal(IV)-Oxo Species with Biomimetic Ligands: A Tandem Mass Spectroscopic and Density Functional Theory Study

I. F Taylor[1]; S. J. Blanksby[2]; S. B. Colbran[1]; G. D. Willett[1]
1. *University of New South Wales, Sydney, NSW 2052, Australia, itaylo_au2@hotmail.com*
2. *University of Wollongong, Wollongong, NSW 2522, Australia*

Introduction:
In mononuclear non-heme iron oxidase enzymes, an iron(IV)-oxo intermediate coordinated by the so-called "2 His + 1 Carboxylate" triad is responsible for abstracting hydrogen atoms from the substrate. Metal(IV)-oxo species with two imidazole and a carboxylate ligand cannot be prepared in the solution phase. In this study, tandem mass spectrometry has been used produce such metal(IV)-oxo cations in the gas phase from reactions of methylimidazole-acetato-metal(II) ions with ozone. The reactivity of these metal(IV)-oxo species with saturated and unsaturated hydrocarbons has been probed. Accompanying DFT calculations reveal the structures, energies and spin states of the various ions and provide insights into the interdependencies between these properties and the observed gas phase reactions.

Methods:
Tandem ESI-mass spectrometry experiments were performed on a ThermoFinnigan LTQ linear ion-trap mass spectrometer modified to conduct ion-molecule reactions. Ozone was generated offline and injected via syringe into the helium buffer gas. A second reagent gas was introduced into the ion-trap through a separate syringe pump and the two gases were mixed prior to injection into the buffer gas line. Tandem MS experiments were used to probe the reactivity of the metal(IV)-oxo species towards saturated and unsaturated hydrocarbons. DFT calculations were performed using Gaussian 03.

Preliminary Data:
Key results to be presented will include: (1) ESI-MS spectra of metal(II) acetate and 1-methylimidazole in methanol reveal the imidazole-acetato-metal(II) complex ions, $[M(MeIm)_n(OAc)]^+$ (n = 1, 2, 3). Reactions of these ions with ozone in the ion-trap gave the metal(IV)-oxo complex ions, $[M(=O)(MeIm)_n(OAc)]^+$. The rate of oxygenation of the imidazole-acetato-metal(II) complex ions shows a strong dependence on the metal centre, coordination environment, spin and effective nuclear charge.[1] (2) All metal(IV)-oxo complex ions catalyse the epoxidation of olefins in the gas-phase. The epoxidation of cyclooctene out competes the oxygenation of the metal(II)-imidazole-acetate complex ions at small to immediate timescales (reaction delay 10-1000 ms). The epoxidation reaction rates depend on metal centre and coordination environment. (3) DFT calculations were performed to reveal the structures, relative energies and spin states for the first-row transition metal(IV)-oxo species. For the late first-row transition metal (Fe–Cu) complexes, significant spin density on the oxo ligand correlates with a lower activation barrier for hydrogen atom abstraction. (4) The isolation of saturated fatty acid-substituted metal(IV)-oxo ions, $[M(=O)(MeIm)_n(O_2CR)]^+$ (RCO_2H = a saturated fatty acid). The fatty acid chain is catabolised by the metal(IV)-oxo centre in the presence of ozone. (5) Formation of epoxide adducts of unsaturated fatty acid-substituted metal(IV)-oxo ions, $[M(=O)(MeIm)_n(O_2CR)]^+$ (RCO_2H = a unsaturated fatty acid). When mono-unsaturated fatty acid-substituted metal(IV)-oxo ions were isolated in the presence of ozone, an additional oxygen adduct formed compared to that observed for the analogous unsubstituted metal-imidazole-acetate. This suggests an intra-molecular epoxidation process. These intra-molecular reactions depend on the relative positioning of the metal(IV)-oxo centre and the unsaturated bond(s) in the fatty acid.

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Antitumoral action of tetraethylorthosylicate nanoparticles loaded with ruthenium nitrosyl complexes on human neoplasic cell

E. Tfouni[1], E. M. Espreáfico[2], A. J. Gomes[3]

1. *Departamento de Química da Faculdade de Filosofia Ciências e Letras de Ribeirão Preto – Universidade de São Paulo (FFCLRP – USP) / e-mail eltfouni@usp.br*
2. *Departamento de Biologia Celular e Molecular e Bioagentes Patogênicos da Faculdade de Medicina de Ribeirão Preto (FMRP – USP).*
3. *Faculdade de Ceilândia – Universidade de Brasília (UnB-FCE).*

Nitric oxide (NO) is an important signaling molecule that plays key roles in several biological processes. NO induces apoptosis in cancer cells at high concentrations, and has also been implicated in limiting tumor metastasis, being possibly a potent anticancer agent[1]. Ruthenium nitrosyl complexes are able to release NO, chemically and/or photochemically. This release can be tuned by the adequate choice of ligands[2], making them potentially useful for several clinical applications. In order to expand these possibilities, ruthenium nitrosyls have recently been successfully incorporated into different materials, such as PLGA microparticles, xerogels, silica and dendrímer[2,4]. This work reports the encapsulation of the ruthenium nitrosyl complexes *trans*-$[Ru(NO)(NH_3)_4(py)](BF_3)_4$ (py-NO); *trans*-$[RuCl(NO)(cyclam)](PF_6)_2$ (cyclam-NO); and [Ru(NO)(Hedta)] (Hedta-NO) in tetraethylorthosylicate (TEOS) nanoparticles and its evaluation in relation to its morphological, chemical and spectroscopic properties in solution and in a cellular environment, using dynamic light scattering (DLS), scanning electron microscopy (SEM), atomic force microscopy (AFM), Energy dispersive spectroscopic (EDS), and other techniques. The ruthenium nitrosyl complexes (py-NO, cyclam-NO and Hedta-NO) were loaded into TEOS nanoparticles using the sol-gel method[5], with an entrapment efficiency of 96%. According to SEM (Figure 1), AFM and DLS, the particles are spherical, with diameters in the 180-260 nm range, and show low tendency to aggregate, as confirmed by the zeta potential (+16.7 mV). The EDS of the entrapped nitrosyl complex shows the Ru signal at 2.55 KeV. The MTT assay showed that in the absence of light irradiation, the nitrosyl complex in solution has a reduced toxicity at concentrations $<1x10^{-4}$ M, and the complexes entrapped in TEOS nanoparticle are non toxic for WM1552-C cells. Upon light irradiation, the encapsulated complexes release NO that can diffuse out of the matrix, reaching the adjacent cell membranes, and promoting the tumor cell death of 58.1% for py-NO; 43.2% for cyclam-NO and 7.6% for Hedta-NO in relation to the control. This result can be associated to a higher entrapment efficiency compared to py-NO complex entrapped in PLGA microparticles that lead to 12% of cell death (B16-F10)[3]. The phototoxicity strongly suggests that cell death is due to NO released from the complex entrapped in the TEOS nanoparticles, which can release NO locally at the surface of the tumor cell by irradiation with light only. The results indicated that the TEOS nanoparticles could be used as a NO-releasing system inhibiting the growth of melanoma cells after irradiation. We believe that ruthenium nitrosyl complexes are an emerging family of metallodrugs that may find application as agents for the treatment of cancer.

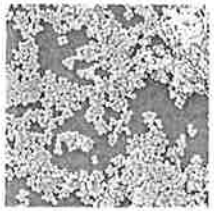

Figure 1 – Surface morphology of TEOS nanoparticles (Magnification 50.000X

Acknowledgements: FAPESP, FAP-DF, CNPq and CAPES.

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Effect of Single Nucleotide Polymorphisms on the Drug Metabolizing Properties of Human Cytochrome P450 1A2

T. Uno[1], S. Morita[1], A. Tsujimoto[1], S. Murata[2], M. Egawa[2], T. Yamashita[1], and H. Aoyama[1]

1. *Graduate School of Pharmaceutical Sciences, Osaka University, Japan. unot@phs.osaka-u.ac.jp*
2. *Graduate School of Pharmaceutical Sciences, Kumamoto University, Japan.*

Cytochrome P450s (CYPs) are membrane-associated heme proteins and metabolize clinically, physiologically, and toxicologically important compounds in many species. Mammalian CYPs recognize and metabolize various xenobiotic substances such as some drugs and environmental chemicals. Five human CYPs, CYP1A2, CYP2C9, CYP2C19, CYP2D6, and CYP3A4, are the major drug-metabolizing isoforms, and contribute to the oxidative metabolism of more than 90% of the drugs in current clinical use. Recently, it is reported that CYP genes show some Single Nucleotide Polymorphisms (SNPs) that originate reduction of metabolizing activity, posing very important problems to the clinical use of drugs. Correlation between the metabolizing activity and SNPs has not been explained fully at molecular level. Therefore, we focused on CYP1A2 (Fig. 1) and investigated drug binding affinities and metabolizing activities of WT and SNP variants.

CYP1A2 is mainly a hepatic enzyme which metabolizes aromatic amines and polycyclic aromatic hydrocarbons (PAHs) as substrates. This isoform is reported to metabolize 4% of the drugs in current clinical use and is responsible for metabolic activation of carcinogens. It has been reported that there are 18 SNPs (CYP1A2*2, CYP1A2*3 and so on) on CYP1A2 gene, and we focused on some of them, which were cloned and expressed successfully.

We first measured metabolizing activities of SNP variants using caffeine, phenacetin, propranolol, amitriptyline, and imipramine as substrates. Although the activity of D348N variant was similar to that of WT, G299S variant showed larger K_m value than WT whereas V_{max} of the two variants were nearly the same as that of WT. We determined drug dissociation constants (K_d) of WT and SNP variants in order to clarify the effect of the drug binding on metabolizing activity. The K_d values of G299S were larger than those of WT. Crystal structure of CYP1A2 is reported[1], and Gly299 residue is shown to locate at an access channel for substrates. These results suggested that Gly299 is involved in the binding of drugs, greatly affecting the metabolizing activity. On the other hand, Asp348 mutation was less effective in the metabolizing activities. We also measured resonance Raman spectra in order to reveal the heme environment in CYP1A2. The observed Raman frequencies indicated that the heme iron in CYP1A2 is penta-coordinated and that the heme environment is highly hydrophobic. This coordination structure is strongly suggested to be connected to the relatively high activity of CYP1A2 and the drug specificity. We will also report the effects of other SNP mutations on the drug binding and metabolizing properties of CYP1A2.

Fig. 1 Crystal Structure of CYP1A2 (1HI4.pdb)

Acknowledgements: This work was supported by Grant-in-aid for Scientific Research (20390011 to T. U.) from JSPS, Japan.

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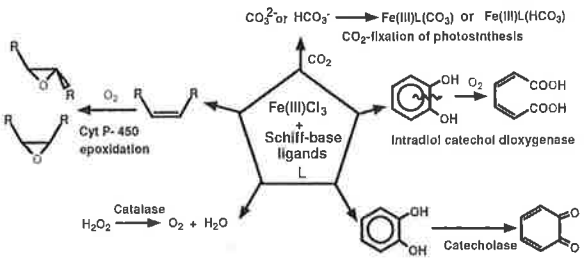
Studies of multi-biological function of model iron(III) complexes with Schiff-base ligands

J. W. Lu, C. Y. Chen ,Y. J. Chen, Y. H. Liang, S. C. Tzeng and H. H. Wei
Department of Chemistry, Tamkang University, Tamsui, 25137, Taiwan

A series of iron(III) complexes with Schiff-base ligands have been prepared and structures characterized. The catalytic activity of the following five biological reactions with the prepared mononuclear iron(III) complexes have been monitored by means of spectroscopy.



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Chiral interactions in metal complexes for optical resolutions of amino acids

T. Yajima[1], M. Kimura[1], A. Uno[1], N. Ishida[1], S. Ito[1], T. Shiraiwa[1]
Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan.

A number of bio-active compounds have chirality, and their stereoisomers exhibit various activities in biological systems and play key roles in sustaining life. Especially, optically active amino acids have been used in foods, medicines, pesticides, cosmetics, and even as chiral reagents for asymmetric syntheses. Enantiomeric compounds have been obtained by refining natural products, asymmetric syntheses, optical resolution from racemates, and so on. Optical resolution of racemic amino acids (AAs) is a suitable method to obtain a large amount of non-natural amino acids and is achieved by various procedures to give their enantiomers. However, the procedures are limited to resolution of certain AAs, and there is a strong demand for the method of general applicability. Transition metal ions can bind two or more ligands, so that a metal complex containing a chiral AA may coordinate the second ligand (AA') enantioselectively for steric or other reasons, enabling separation of the racemic mixture of this ligand by differences in solubility or reactivity. We first studied selective incorporation of an enantiomer of a racemic AA' into Cu(II) complexes with an active AA, Cu(AA)(AA').

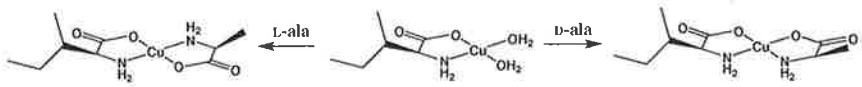
The ternary Cu(II) complex containing L-isoleucine (ile) and D-alanine (ala), [Cu(L-ile)(D-ala)], is less soluble than [Cu(L-ile)(L-ala)], because of the difference in configuration: [Cu(L-ile)(D-ala)] has a *cis*-configuration, whereas [Cu(L-ile)(L-ala)] has a *trans*-configuration.[1] Cis-trans isomerism may have an influence on the properties of ternary Cu(II) complexes; for complexes containing D/L-aminobutanoic acid (abu) instead of D/L-ala, [Cu(L-ile)(L-abu)] is over 10 times more soluble than [Cu(L-ile)(D-abu)]. Such a wide difference in solubility may arise from the stability difference between the diastereoisomers of the ternary complexes (Table 1).

Table 1. Configuration, solubility, and stability constants of [Cu(A)(B)]

A	B	Configuration	Solubility[a)]	log b_{1110}[b)]
L-ile	D-ala	*cis*	0.145	15.499(5)
	L-ala	*trans*	0.578	15.344(7)
	D-abu	*cis*	0.049	15.692(9)
	L-abu	*trans*	0.847	15.166(25)
D-aile	D-ala	*cis*	3.208	15.777(29)
	L-ala	*cis*	2.071	15.293(38)

a) g/100 cm³ of water, 20 °C. b) Parentheses are denoted standard deviations.

On the other hand, two ternary complexes containing L-alloisoleucine (aile) and D/L-ala, [Cu(L-aile)(D/L-ala)], exhibit the same *cis*-configuration and similar higher solubilities than the complexes containing L-ile.



[Cu(L-ile)(L-ala)] [Cu(L-ile)(H_2O)$_2$] [Cu(L-ile)(D-ala)]

In order to attain efficient separation of racemic AAs, we studied potentiometrically the M–L–AA ternary systems, where M refers to Zn^{2+}, Cu^{2+}, and Ni^{2+} and L to tris(2-pyridylmethyl)-amine (TPA). Potentiometric titrations of the M–TPA–AA systems revealed that stable ternary complexes, [M(TPA)(L-AA)], are formed for M = Ni^{2+}, while ternary complexes with M = Zn^{2+} or Cu^{2+} are not formed or less stable. The stability constants of [Ni(TPA)(AA)] for AA = chiral amino acids are slightly smaller than the value of [Ni(TPA)(gly)], suggesting that the side chain of AA may give rise to steric hindrance with the pyridine ring of TPA and that it may be possible to resolve efficiently a number of amino acids by a chiral TPA-type ligand. We now study intramolecular chiral interaction of complexes containing *N,N*-bis(2-pyridylmethyl)-1-(2-pyridyl)ethylamine (MeTPA),[2] which has one chiral center, and amino acids

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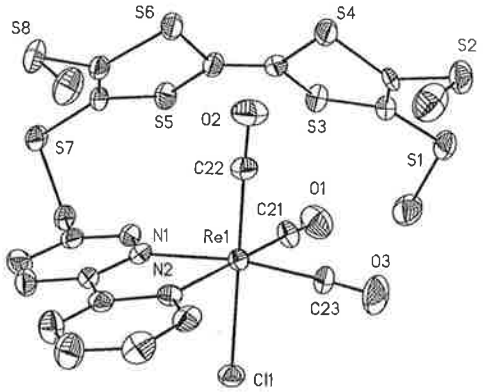
Rhenium(I) tricarbonyl complexes with bispyridine ligandsattached to tetrathiafulvalene syntheses, structures and properties

T. Jin [1], G. N. Li [1], X. S. Wang [2], J. L. Zuo [1,*], X. Z. You [1]

1. *Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,Nanjing University, Nanjing 210093, PR China*
2. *National Laboratory of Solid State Microstructure, Nanjing University, Nanjing 210093, PR China*

A new tetrathiafulvalene-substituted 2,2-bipyridine ligand, 2,3,6-trimethylthio-7-(2,2'-bipyridin-5-ylmethylthio) tetrathiafulvalene (TMT-bipy-TTF) has been prepared and characterized. And the new ligand has been used to prepare a Rhenium(I) tricarbonyl complex([Re(CO)$_3$ (TMT-bipy-TTF)(CHCl$_3$)] Cl), which was determined using X-ray single crystal diffraction.
The absorption spectra, redox behavior, and luminescence properties of the complex ([Re(CO)$_3$ (TMT-bipy -TTF)(CHCl$_3$)] Cl) and the free TMT-bipy -TTF ligand, have been studied. The UV–vis spectra show that there exists intramolecular charge transfer (CT) and MLCT transitions. Remarkably, the complex exhibits luminescence from the Re$^+$→L metal-to-ligand charge-transfer (MLCT) state. Electrochemical measurements were performed on the complex ([Re(CO)$_3$ (TMT-bipy -TTF)(CHCl$_3$)] Cl) and the Re(I)/Re(II) and TTF/TTF+•/TTF2+ redox processes were observed. A single-crystal X-ray analysis was performed on [Re(CO)$_3$ (TMT-bipy -TTF)(CHCl$_3$)] Cl , showing a distorted octahedral geometry around the Re (I) centre.



Acknowledgements: This work was supported by the Major State Basic Research Development Program (Grants 2006CB806104 and 2007CB925103), the National Science Fund for Distinguished Young Scholars of China (Grant 20725104), and the National Natural Science Foundation of China (Grant 20721002).

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Solvent-Dependent Coordination Structures of Dinuclear Lanthanide Complexes with TCNQ Radicals.

C. Kachi-Terajima[1,2], Y. Kuboki[1], N. Kimura[1], C. Kanadani[2], T. Saito[2,3], T. Kitazawa[1,2]

1. *Department of Chemistry, Faculty of Science, Toho University, Chiba, Japa*
   e-mail: chihiro.kachi@chem.sci.toho-u.ac.jp
2. *Research Center for Materials with Integrated Properties, Toho University*
3. *Department of Physics, Faculty of Science, Toho University*

The large magnetic moment and magnetic anisotropy of lanthanide ions make particularly attractive for magnetic materials. The design and synthesis of lanthanide complexes are of growing interest in the field of molecule-based magnets, because of their unique magnetic properties found in single-molecule magnets or single-chain magnets. An attempt was made to develop new magnetic systems with lanthanide complexes as anisotropic building blocks and paramagnetic TCNQ anions.

Two types of dinuclear lanthanide complexes (Ln = Gd^{3+}, Tb^{3+}, Dy^{3+}) with 7,7,8,8-Tetracyanoquinodimethane (TCNQ) radicals have been selectively synthesized by varying the reaction solvents: (type-I) $[Ln_2(dap(BH)_2)_2(TCNQ)_4(MeOH)_2](TCNQ)_2{\cdot}2MeOH$ (dap(BH)$_2$ = 2,6-diacetylpyridine-bis(benzoylhydrazone) (Fig. 1),[1] Ln = Gd(**1**), Tb(**2**), Dy(**3**)) (Fig. 2), (type-II) $[Ln_2(dap(BH)_2)_2(TCNQ)_4(EtOH)_2](TCNQ)_2{\cdot}4EtOH$ (Ln = Gd(**4**), Tb(**5**), Dy(**6**)) (Fig. 3). Their coordination modes and packing arrangements are completely different. Strong intermolecular dimerization of the TCNQ molecules is found in compound **1-3** obtained from MeOH solvent. The magnetic susceptibility of these complexes indicates the paramagnetic behaviour of lanthanide ions without TCNQ spins, which implying diamagnetic TCNQ dimers; $(TCNQ)_2$.

By contrast, compounds **4-6** crystallized in EtOH possess three different π–π stacking modes between TCNQ molecules, and one of these forms one-dimensional chain. Despite the different coordination and packing modes, magnetic measurements of **4-6** also show the presence of only the lanthanide ions due to the diamagnetic nature of dimerized TCNQ molecules.

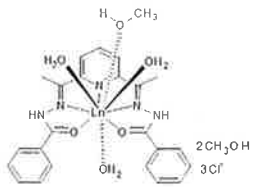

Fig. 1 Structure of $[Ln(dap(BH)_2)(MeOH)_2(H_2O)_3]Cl_3{\cdot}2MeOH$.

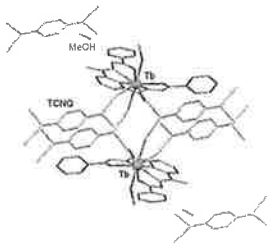

Fig. 2 Molecular structure of complex **2** (type-I).

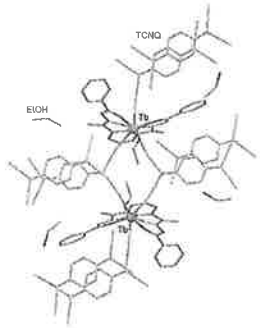

Fig. 3 Molecular structure of complex **5** (type-II).

Acknowledgements: This work was financially supported by the "High-Tech Research Centre" Project 2005-2009 and a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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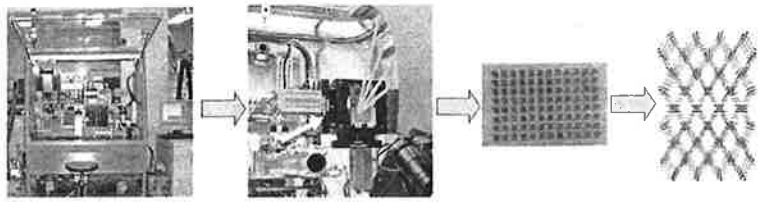
Development of High-throughput Techniques for the Synthesis and Screening of Novel Metal Organic Frameworks for MRI

D. F. Kennedy,[1*] M. R. Hill,[2] P. P. Wyss,[1] B. W. Muir,[1] D. G. Hay,[2] C. J. Drummond[1,2]
1. *CSIRO Molecular and Health Technologies, Bag 10, Clayton MDC, Victoria, Australia, 3169.*
2. *CSIRO Materials Science and Engineering, Bag 33, Clayton MDC, Victoria, Australia, 3169.*
**Danielle.Kennedy@csiro.au*

Metal-organic frameworks (MOFs) are porous hybrid materials consisting of metal clusters bridged by rigid organic linkers.[1] MOFs have attracted a great deal of research interest in recent years as they have found application in many different areas including gas storage, gas separation and catalysis. There are several factors crucial to the performance of MOFs in all applications; their crystallinity, their porosity and their water stability. The use of MOFs is not limited to gas storage devices. Recently, preliminary work showed that MOFs had potential as gadolinium (Gd) based MRI contrast agents.[2] The framework structure sequesters the otherwise toxic Gd ion. Another benefit of the MOFs for this application is the fact that the microporous networks generated allow the direct interaction of water with the metal centres which is crucial for an effective MRI contrast agent.

The synthesis of MOFs remains poorly understood. The reaction conditions required for the successful preparation of a crystalline MOF vary wildly according to the specific system. Understanding the conditions required for the preparation of these materials will only be achieved by screening the material composition space available in these complex systems. Here we present a high throughput platform for the preparation, identification and characterisation of metal-organic framework materials and a series of novel of MOFs which have been identified through high-throughput synthesis and screening. The high-throughput screening undertaken involved three phases, screening for crystallinity, screening for porosity and screening for water stability. A high-throughput powder X-ray diffraction (PXRD) was developed and used at the Australian Synchrotron to identify the materials which were crystalline and porous. Colorimetric assays were then applied for the screening of the generated MOFs for high porosity and water stability.



High throughput platform; from robotic synthesis through synchrotron and colorimetric screening to MOF identification and characterisation.

Acknowledgements: Portions of this work was undertaken at the Powder diffraction beam line of the Australian synchrotron and we acknowledge their support.

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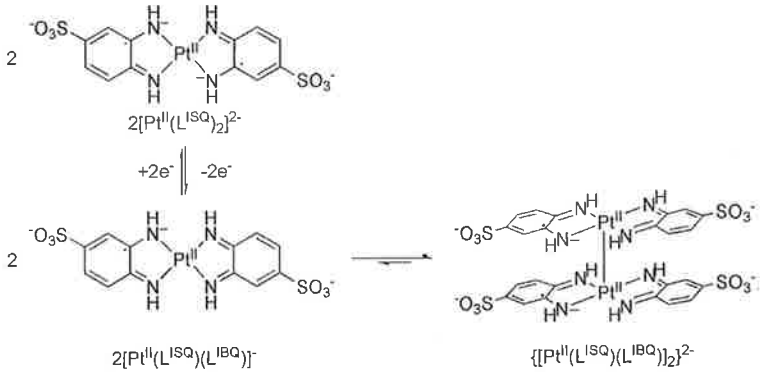
pH-Responsive Switching of Near-Infrared Absorption of Water-Soluble Bis(*o*-diiminobenzosemiquinonato)platinum(II) Complex

A. Masuya[1], N. Iki[1], C. Kabuto[2], Y. Ohba[3], S. Yamauchi[3], H. Hoshino[1]
1. *Graduate School of Environmental Studies, Tohoku University, Sendai, Japan, E-mail masuya@analchem.che.tohoku.ac.jp*
2. *School of Engineering, Tohoku University, Sendai, Japan*
3. *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan*

Near infrared (NIR; 700-1200 nm) light effectively penetrates into biological tissues, hence *in vivo* imaging technique based on NIR absorption has been received much attention. In this technique, NIR-absorbing dyes play an important role as the contrast agent. We previously found that complexes of Pt(II) with *o*-phenylenediamine derivative displayed NIR absorption in hydrophobic media, but did not in aqueous solution.[1] The complex could be applied to an NIR-absorbing contrast agent to stain hydrophobic microenvironment of liposome bilayer. However, the response of the complex to hydrophobicity posed a question whether the Pt(II) complex exhibits NIR absorption in hydrophilic media. In this work, we prepared a water-soluble Pt(II) complex with an *o*-phenylenediamine derivative and revealed NIR absorption property in aqueous solution.

The water-soluble Pt(II) complex with 3,4-diaminobenzenesulphonate (H_2L^{PDI-}) was prepared to show intense NIR absorption ($\varepsilon = 1.1 \times 10^5\ M^{-1}\ cm^{-1}$) at 705 nm in basic aqueous solutions. The NIR absorption decreased at pH < 4.0 to display pH-responsive switching of NIR absorption. The electronic structure of the NIR absorbing complex in the alkaline solution was determined to be singlet diradical $[Pt^{II}(L^{ISQ})_2]^{2-}$ ($(L^{ISQ})^{\cdot 2-}$ = *o*-diiminosulfobenzosemiquinonate radical) with X-ray diffraction and ^{1}H NMR. Cyclic voltammetry (CV) showed oxidation of $[Pt^{II}(L^{ISQ})_2]^{2-}$ to $[Pt^{II}(L^{ISQ})(L^{IBQ})]^-$ ($E_{1/2} = -0.26$ V vs. Fc^+/Fc) ($(L^{IBQ})^-$ = *o*-diiminosulfobenzoquinonate). Splitting of the reduction wave of $[Pt^{II}(L^{ISQ})(L^{IBQ})]^-$ in CV and the weak EPR signal suggested the formation of the dimer $\{[Pt^{II}(L^{ISQ})(L^{IBQ})]_2\}^{2-}$ (Scheme). Because the rest potential of the solution exceeded E_{pa} at pH < 4.0, the decrease of NIR absorption at pH < 4.0 was caused by the oxidation of $[Pt^{II}(L^{ISQ})_2]^{2-}$ to $[Pt^{II}(L^{ISQ})(L^{IBQ})]^-$ followed by dimerization to $\{[Pt^{II}(L^{ISQ})(L^{IBQ})]_2\}^{2-}$.



Scheme. Oxidation of $[Pt^{II}(L^{ISQ})_2]^{2-}$ to $[Pt^{II}(L^{ISQ})(L^{IBQ})]^-$ followed by dimerization to $\{[Pt^{II}(L^{ISQ})(L^{IBQ})]_2\}^{2-}$ at pH < 4.0 in aqueous solution.

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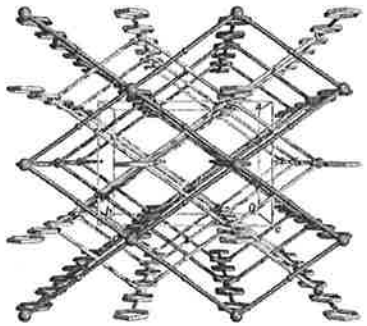
Multifunctional Materials: Combining Spin Crossover, Colossal Uniaxial Negative Thermal Expansion and Nanoporosity

B. R. Mullaney[1], D. J. Price[1], C. J. Kepert[1]
1. *School of Chemistry, University of Sydney*

The ability to design molecular materials for specific applications is a major goal in modern chemistry.[1] Most current research focuses on the study of materials with a single functional behaviour. However, combining different functionalities in the same material can lead to greater versatility, and unforeseen applications.

A novel nanoporous coordination framework was recently discovered that displays 'colossal' uniaxial negative thermal expansion, in addition to undergoing spin crossover. The framework is also robustly porous, and the two behaviours show significant guest-dependence. This material is a three-dimensional interpenetrated Hofmann-like framework of formula $Fe(bpethy)(Au(CN)_2)_2$ (bpethy = 1,2-bis(4'-pyridyl)ethyne), with each (4,4)-net comprised of a two-dimensional sheet of Fe(II) centres linked by $Au(CN)_2$, which are pillared by the bpethy ligand (see graphic). Aurophilic interactions between Au atoms in adjacent nets are the dominant packing influence that determines the relative positions of the nets.

The coordination environment around the Fe(II) is well-known to produce the intermediate ligand field strength required to allow spin crossover to occur[2] and, similar to the pyrazine Hofmann-type spin crossover framework $Fe(pyrazine)M(CN)_4$,[3] the behaviour of the spin transition depends strongly on the guest species within the pores. The negative thermal expansion is observed along the *a* axis, parallel with the metal cyanide grids, at temperatures below the spin transition, and is accompanied by a similarly large positive thermal expansion along *b*. When solvated with ethanol, the thermal expansion coefficients lie in the range $-101 \times 10^{-6} > \alpha_a > -258 \times 10^{-6}$ K^{-1} and $81 \times 10^{-6} < \alpha_b < 169 \times 10^{-6}$ K^{-1} respectively, within the temperature range $218 > T > 150$ K. This thermal expansion behaviour is similar to that observed by Goodwin et al. in $Ag_3[Co(CN)_6]$,[4] and arises from a 'scissor-like' motion of the $Fe(Au(CN)_2)_2$ layer, as the grid is distorted at higher temperatures, but is driven to adopt a configuration that is closer to orthogonal at lower temperatures.



Acknowledgements: The Australian Synchrotron

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Synthesis and characterisation of a new series of bistable iron(II) spin crossover metal-organic frameworks

M. C. Muñoz,[1] J. A. Real,[2] V. Martínez,[2] F. J Muñoz-Lara,[2] A. B. Gaspar[2], G. V. Bukin,[3] G. Levchenko[3]
1. *Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, C/ Catedrático José Beltrán Martínez 2, 46980 Paterna (Valencia), Spain.*
2. *Departamento de Física Aplicada, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain.*
3. *Donetsk Physico-Thechnical Institute, NAS of Ukraine, R. Luxemburg 72, 83114 Donetsk, Ukraine.*

In this contribution we will present the synthesis, structural, magnetic and calorimetric studies of a series of coordination polymers with formula $\{Fe(3\text{-}Xpy)_2[M^{II}(CN)_4]\}$ (M^{II} = Ni, Pd, Pt; X = F, Cl, Br, I). The fluoro and iodo compounds as well as the chloro-derivative with M^{II} = Pt crystallise in the monoclinic C2/m space group while the rest of chloro and all bromo derivatives crystallise in the orthorhombic Pnc2 space group. In all cases, the iron(II) atom resides in a pseudo-octahedral $[FeN_6]$ coordination core with similar bond lengths and angles. The major difference between both kinds of structures arises from the stacking of consecutive two-dimensional $\{Fe(3\text{-}Xpy)_2[M^{II}(CN)_4]\}_\infty$ layers, which allow different disposition of the X atoms. The fluoro and chloro derivatives undergo cooperative spin crossover (SCO) with significant hysteretic behaviour while the rest are paramagnetic. The thermal hysteresis, for X = F, shifts toward room temperature without changing cooperativity as pressure increases in the pressure interval 10^5 Pa - 0.5 GPa. At ambient pressure, the SCO phenomenon has been structurally characterised at different significant temperatures and the corresponding thermodynamic parameters were obtained from DSC calorimetric measurements. Compound $\{Fe(3\text{-}Clpy)_2[Pd(CN)_4]\}$ represents a new example of "re-entrant" two-step spin transition showing the Pnma space group in the IP phase while in the LS and HS phases the space group is Pnc2.[1]

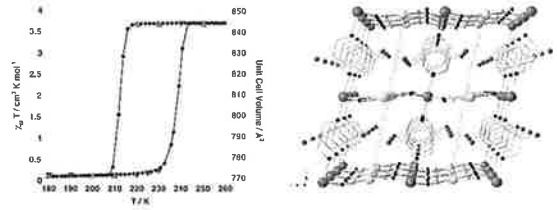

Figure 1. Thermal variation of the magnetic properties and unit cell volume (left) and structure of $\{Fe(3Fpy)_2[Pt(CN)_4]\}$ (right).

Acknowledgements: This work was supported by the Spanish Ministerio de Ciencia e Innovación (MICINN)/FEDER (CTQ2007-64727) and the Generalitat Valenciana (ACOMP/2009/326).

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Incorporation of O_2-binding metalloligands into metal-organic framework materials for application in selective gas separation

M. Murphy[1], T. D. Keene, C. J. Kepert
1. *University of Sydney m_murphy@chem.usyd.edu.au*

The gas sorption properties of metal-organic frameworks have shown remarkable gas sorption through their potential for high surface areas, porosity and bare metal sites[1]. Ongoing investigations into their application to reversible oxygen binding, through coordinatively unsaturated metal sites, are examined.

The reversible oxygen binding capabilities of the $[Co(CN)_5]^{3-}$ anion and related species allow for the synthesis of a rare type of coordination framework material incorporating coordinatively unsaturated Co^{II} metal centres. The oxygen binding properties of Co^{II} compounds have been well documented;[2,3,4] however, the incorporation of a pentacyanocobaltate building block into a Hofmann like structure has not previously been accomplished. The addition of bridging ligands will potentially allow for the selective solid state adsorption of oxygen. Through tailoring the pore size and distribution of Co^{II} bare metal sites it is hoped that reversible oxygen binding can be achieved within readily accessible temperature ranges.

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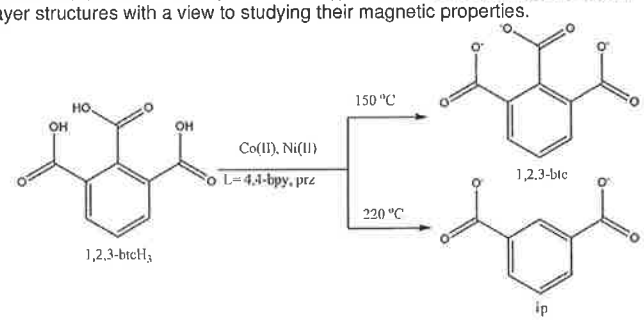
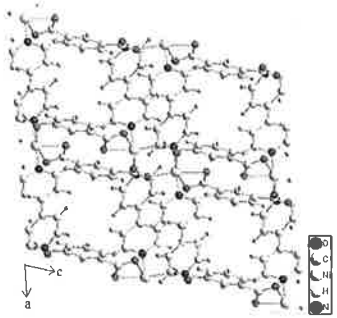
Temperature dependent synthesis of metal-organic frameworks via in situ ligand transformation reactions

M. A. Nadeem[1], J. A. Stride[1,2]
1. *School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia.*
2. *Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia.*

Metal–organic hybrid materials are currently of great interest due to their fascinating structural diversities and potential applications as functional materials. Formation of these frameworks is influenced by many factors, such as the nature of ligands, the coordination geometry of metal ions, the ratio between the metal salt and ligand, and the reaction conditions. However, there has been less attention given to how these affect the reaction pathways that then lead to differing products. In recent years, interest in hydro- and solvo-thermal reactions with *in situ* ligand synthesis has grown, which is highly dependent on reaction conditions. We present herein a systematic study of the hydrothermal reactions of 1,2,3-benzene tricarboxylic acid (1,2,3-btcH_3) and linear bridging ligands 4,4-dipyridyl (bpy) and pyrazine (pyz) with metal salts (Co, Ni, Cu), under various reaction conditions. The aim of this work is to both directly study the affect of temperature on in situ ligand transformation, in this case decarboxylation of 1,2,3-btcH_3 into isophthalic acid (ip = 1,3 benzene dicarboxylic acid), and to arrive at pillared-layer structures with a view to studying their magnetic properties.





Acknowledgments:
Dr. Mohan Bhadbhade (Analytical centre, university of new south wales)

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Preparation of Novel Mixed-valent Multilayer Film Composed of Dinuclear Ru Complexes on Surface

T. Nakabayashi, K. Kanaizuka, M. Haga
Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University
E-mail : mhaga@kc.chuo-u.ac.jp

Mixed-valent metal complexes play an important role in many areas of inorganic chemistry. Changing the bridging ligand enables us to afford different charge localization in the mixed-valent complexes. We have studied the redox-active Ru-Ru dinuclear complex (1) bearing bridged bis(terpyridyl)benzene and tetrapod phosphonate anchors in Fig 1, in which one-step two-electron oxidation process was observed. [1] In this presentation, we synthesized new rod-shaped dinuclear complex (2), [(L)Ru(tppz)Ru(L)], having tetra(2-pyridyl)pyrazine (tppz) as a bridging ligand and auxiliary tridentate bis(benzimidazolyl)pyridine ligand with four phosphonate anchors (L). Cyclic voltammetry (CV) in acetonitrile showed two well-separated one-electron oxidations at +0.87 V and +1.08 V vs Fc+/Fc, and the potential separation between 1st and 2nd oxidations was 220 mV. The simple immersion of an ITO electrode into the [(L)Ru(tppz)Ru(L)] solution, the complex was immobilized on the ITO electrode, which showed two successive oxidative CV waves (Fig 1b). AFM measurement of the monolayer film with low coverage on sapphire surface revealed pinnacle-like morphology with average height of ~ 2 nm, which is consistent with that expected from the molecular model with vertical molecular orientation. Multilayer films were constructed by layer-by-layer method with Zr(IV) ion as a chemical glue. Multilayer formation on the ITO substrate was monitored by UV-vis spectra and CV measurement. CV of multilayer films also showed two successive oxidation waves, keeping their shape and also oxidation potentials, while the peak current linearly increased with increasing the number of layers. These results indicate that the quantitative complexation took place on the surface, however the interaction between the layered molecular units is relatively weak.

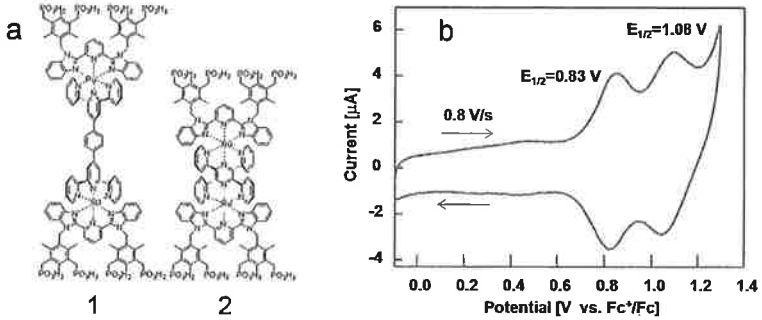

Fig 1. Structures of Ru dinuclear complexes (a) and cyclic voltammogram of 2 immobilized on the ITO in 0.1 M CH3CN/TBAP (b).

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Synthesis and optical properties of HDA capped metal sulphide nanoparticles

A. O. Nejo[1], A. A. Nejo[1], V. S. R. Pullabhotla[1], N. Revaprasadu[1]
Department of Chemistry, University of Zululand, Kwadlangezwa, South Africa

Colloidal semiconductor nanocrystals have been subject of intensive research in the last years. This is mainly due to the size dependent new properties of these materials. The photo-emission and absorption of semiconductor nanocrystals is tuneable by the size as a result of quantum confinement effects. As part of our continuing effort to synthesize monodisperse nanoparticles, we report here the synthesis of semiconductor sulphide nanocrystals of lead and zinc through a facile and reproducible synthetic route. The synthetic approach involves the reduction of sulphur powder in water to produce sulphide ions which act as sulphur source followed by addition of different metal salts which acts as the metals precursor. The metal nanocrystals were grow and capped via thermolysis in hot hexadecylamine (HDA) solution. The obtained particles were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), absorption spectroscopy and photoluminescence spectroscopy. TEM images show well dispersed particles.

Keywords: CdS; nanoparticles; thermolysis; HDA

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Synthesis and Photophysical properties of Ruthenium(II) Isocyanide Complexes containing 8-Quinolinato Ligands

S. M. Ng,[1] C. F. Leung,[1] J. Xiang,[1] W. Y. Wong,[2] C. C. Ko,*[,1] and T. C. Lau*[,1]

1. *Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong, stellang@student.cityu.edu.hk*
2. *Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon, Hong Kong.*

A series of ruthenium(II) *bis*(8-quinolinolato) complexes bearing isocyanide ligands (RNC) have been synthesized by the reaction of $[RuQ_3]$ (Q = 8-quinolinolato) with RNC in the presence of Zn/Hg. These complexes have the general formula $[RuQ_2(RNC)_2]$ (**1**, R = *t*-butyl; **2**, R = 4-MeO-Ph; **3**, R = 4-Cl-Ph; **4**, R = 2,4,6-Br_3-Ph). Both the yellow *cis,cis,trans*- (**a**) and orange-red *trans,trans,trans*- (**b**) isomers have been isolated for complexes **1-4**. *Trans,trans,trans*-$[Ru(Tol\text{-}Q)_2(^tBuNC)_2]$ (**6**, HTol-Q = 8-hydroxyl-5-tolylquinoline) has also been prepared from $[Ru(PPh_3)_2Cl_2]$. The structures of **2a**, **3a** and **4b** have been determined by X-ray crystallography. These complexes exhibit an intense absorption band in the UV region (λ_{max} = 320-390 nm) with molar extinction coefficients (ε) in the order of 10^4 dm^3 mol^{-1} cm^{-1}, and a moderately intense absorption with ε in the order of 10^3 dm^3 mol^{-1} cm^{-1} at 400-492 nm. The intense absorption at 320-390 nm is assigned to the ligand-centered $\pi \rightarrow \pi^*$ transitions of the quinolinolate ligands, probably mixed with the $\pi \rightarrow \pi^*$ transitions of the isocyanide ligands. The lower energy absorptions at 400-492 nm are assigned to $Ru(d\pi) \rightarrow \pi^*(Q)$ metal-to-ligand charge transfer (MLCT) transitions. Upon excitation at λ > 350 nm at room temperature in dichloromethane solution, **1a-3a** exhibit orange-red luminescence (645-680 nm). In 77K EtOH/MeOH glass, complexes **1-4** and **6** give intense structured emission spectra (593-638 nm) These emissions are tentatively assigned to be derived from the MLCT $[d\pi(Ru) \rightarrow \pi^*(Q)]$ excited state. The cyclic voltammograms (CV) of **1a-4a** generally exhibit an irreversible or quasi-reversible $Ru^{III/II}$ couple at the potential range of 0.02 – 0.38 V *vs* Fc^+/Fc; except in the case of **1a**, where a reversible $Ru^{III/II}$ and a quasi-reversible $Ru^{IV/III}$ (0.68V *vs* Fc^+/Fc) couple are observed. The potential for the $Ru^{III/II}$ couple increases with the π-accepting ability of the isocyanide ligands. In the CV of **1b-4b**, a reversible $Ru^{III/II}$ (-0.16 - 0.065V) and quasi-reversible $Ru^{IV/III}$ (0.52 - 0.70V) couple are observed.

Acknowledgments

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A New Take on Metal-Organic Frameworks: Nets Based Upon Flexible Ligands Coordination Chemistry for the 21st Century

M. Ng[1], M. A. Nadeem[1], J. A. Stride[1,2]

1. *School of Chemistry, University of New South Wales, Sydney 2052, Australia.*
2. *Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia.*

Maggie.ng@student.unsw.edu.au; z3238479@student.unsw.edu.au; j.stride@unsw.edu.au

Four iso-structural metal-organic frameworks have been synthesised based upon the flexible sub-units of 1,4-phenylene dicarboxylic acid and 1,2-di-(4-pyridyl)-ethane as ligands with managenese, cobalt, copper and nickel centers. The resulting hydrothermal reactions produced an isostructural series of 3D networks consisting of 1D chains of metal ions bridged by 1,2-di-(4-pyridyl)-ethane, bonded to three equivalent neighbouring chains via the 1,4-phenylene dicarboxylic units. The structure displays some degree of porosity and is free of host solvent molecules, highlighting the potential of such materials for gas storage applications.

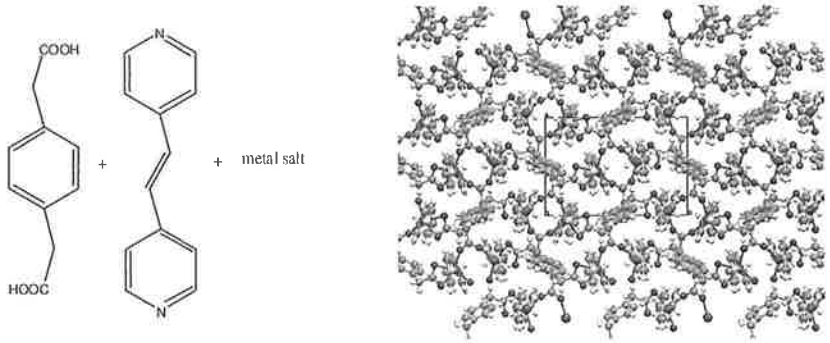

Figure 1. *Left:* Solvothermal reaction between 1,4-phenylene dicarboxylic acid, 1,2-di-(4-pyridyl)-ethane and metal salt. *Right*: Structure of iso-structural MOFs with oxygen (red), Nitrogen (blue) and Mn(II), Ni(II), Cu(II) or Co(II) (olive green) as the metal center as viewed along the *c*-axis. The open, solvent-free, internal surfaces can be clearly seen.

Acknowledgements: This work was supported by the Australian research council (DP880199). We thank Dr. Mohan Bhadbhade for carrying out the x-ray experiments.

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Vanadium(III) and Vanadium(IV) Complexes with O,O Bidentate Ligands.

C. Pretorius[1], A. Roodt, J. A. Venter.
Department of Chemistry, University of the Free State, Nelson Mandela Avenue, Bloemfontein 9300, South Africa, E-mail:2005071853@student.ufs4life.co.za

Vanadium chemistry has long been regarded as a rich and varied research field with formal oxidation states ranging from -3 to +5,[1] and the coordination number of vanadium compounds varies between four and eight with typically distorted geometries.[2] The vanadyl ion, VO^{2+}, has dominated much of the research done on vanadium due to its unique stability, and it has earned the title of the most stable diatomic ion known by retaining its identity in a wide variety of reactions and complexes.[1] In addition, vanadium betadiketonato complexes has been proposed and evaluated as insulin mimicking agents.[3],[4]

$[V^{IV}O(acac)_2]$ (acac = acetylacetonate) complexes have already been synthesised and reported on during the past millenium. The vanadyl interaction in the five-coordinated species is axial, exhibiting partial triple-bond character. Equatorial bonding primarily involves sigma interaction between the lone pairs on the oxygen of the acetylacetonate ligands and the Vanadium $3d_{xy}$ orbital. [5],[6]

On the other hand, the vanadium(III) species, *i.e.*, tris(acac)vanadium(III) was also reported, and the first structural determination of $[V^{III}(acac)_3]$ by Morosin *et al.*[7] identified two different crystal packings namely α-$[V^{III}(acac)_3]$ and β-$[V^{III}(acac)_3]$. The two structures are only differentiated by their crystal packing and space groups.[8] $[V^{III}(acac)_3]$ is unique amongst V^{3+} complexes with regard to its stability in air.

The current study focuses thus on two types of complexes by introducing a variation of substituents of the O,O donor ligands, but maintaining the diketonate [both alpha and beta] unit, including derivatives such as thenoyltrifluoroacetone and tropolone in the vanadium(III) and vanadium(IV) complexes. It underlines the influence of derivatives of these monocharged bidentate ligands (O,O-Bid) and analogues on the properties and packing modes of the $[V^{III}(O,O\text{-}Bid)_3]$ complexes.

Furthermore, the $[V^{IV}O(O,O\text{-}Bid)_2]$ type complexes are also reported for a range of bidentate ligands, and in addition, a sixth ligand [pyridine and picoline derivatives; piperidine and lutidines] was coordinated to the V(IV) centre to incorporate a variation of nitrogen bonding modes trans to the oxo ligand in an octahedral geometry.

Structural data of the above mentioned complexes, as well as some aspects of the solution behaviour, reactivity and formation, as obtained from kinetic data, will be presented and discussed.

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Application of Novel Schiff Bases and their Complexes as Corrosion Inhibitors for Mild Steel in 1 M Hydrochloric Acid

N. Ramlee[1], S.N.A. Bakar, H. Bahron, K. Kassim, M.K. Harun, M.Z.A. Yahya and S.K. Yong
Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia.
laila_meng@yahoo.com

The work herein describes the performance of three novel Schiff bases derived from *o*-vanilin with *m*-phenylenediamine, its CH_3– and Cl– derivatives; namely L1, L2, L3 and their respective Co(II) and Zn(II) complexes. The ligands and complexes are characterized using various physicochemical and spectral methods, then investigated for their corrosion inhibition performance for mild steel in 1 M HCl by means of the weight loss (WL), linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) methods. All measurements revealed that the compounds under study exhibit good corrosion inhibition efficiency, E_i, for mild steel where the values and trends obtained from the various methods employed are in good agreement. L1 shows the highest E_i, indicating that the introduction of electron donating groups –CH_3– into the structure increases E_i, whereas the unsubstituted L3 exhibits the lowest E_i. It is intriguing to note that L2 which contains an electron withdrawing substituent –Cl–, had a lower E_i value than L1, but higher than L3. Scanning electron microscopy (SEM) is utilised to identify the surface morphology of the mild steel both in the absence and presence of the inhibitors.

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Polyoxometalates as Ligands for Polynuclear Lanthanoid Complexes

C. Ritchie[1], E. G. Moore[1], R. W. Gable, M. Speldrich[2], P. Kögerler[2], C. Boskovic[1]
1. *School of Chemistry, University of Melbourne, Victoria, 3010, Australia; critchie@unimelb.edu.au*
2. *Institute of Inorganic Chemistry, RWTH Aachen University, D-52074 Aachen, Germany*

The investigation of polyoxometalates (POMs) continues to provide interesting new molecules with properties relevant to a wide variety of applications. Of particular interest to us is the ability of lacunary POMs to act as ligands to other metals, affording complexes with novel electronic and/or magnetic behaviour. Lacunary POMs offer useful features as ligands, including their size, solubility, diamagnetic nature, arrangement of coordination sites, flexibility of coordination modes and ability to rearrange. Oxophilic trivalent lanthanoid metal centres are particularly well-suited for binding to lacunary POMs and examples of POM-ligated lanthanoid complexes with one or more lanthanoid metals are known.

We have recently utilized the lacunary POM $[As_2W_{19}O_{67}(H_2O)]^{14-}$ as a precursor for new POM-ligated lanthanoid complexes.[1,2] The $\{WO(H_2O)\}$ linker between the two $[B\text{-}\alpha\text{-}AsW_9O_{33}]^{9-}$ subunits is critical to the reactivity of this precursor, serving as a starting point for apparent free rotation and/or disassociation of the $\{AsW_9\}$ groups. This facilitates the generation of a number of POM-based building blocks in solution. Combining this property with the stereodirecting influence of the lone pair on the As^{III} heteroatom has enabled the stabilization of rare POM architectures and the inclusion of unprecedented structural features.

Using this approach we have obtained a number of extended and molecular POM-ligated lanthanoid complexes, including examples of purely inorganic and inorganic-organic hybrid materials. These include the first luminescent Tb complex with POM and organic ligands and new Dy-based single-molecule magnets.

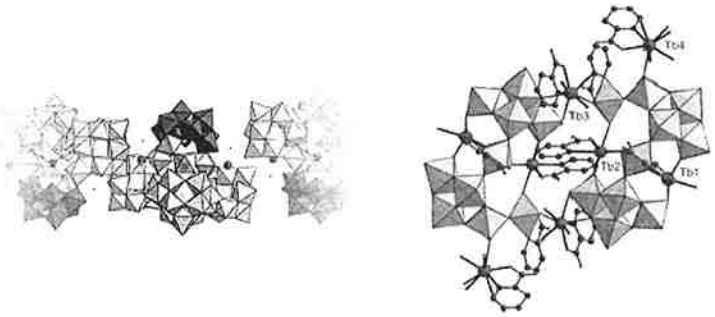

Figure 1. Graphical representation of $[Nd_3As_4W_{41}O_{141}OH(H_2O)_{10}]$ and $[Tb_2(pic)(H_2O)_2(B\text{-}\beta\text{-}AsW_8O_{30})_2(WO_2(pic))_3]$.

Acknowledgements: We thank the Australian Research Council and University of Melbourne for funding.

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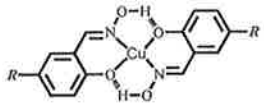
From Artifacts to Facts: Novel Trinuclear Copper Complexes

B. D. Roach[1], P. A. Tasker[1], K. Mason[1], E. K. Brechin[1], F. J. White[1], P. G. Plieger[2] and R. S. Forgan[1]
1. *School of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ, UK. Ben.roach@ed.ac.uk*
2. *Institute of Fundamental Science, Massey University, 4442 Palmerston North, NZ.*

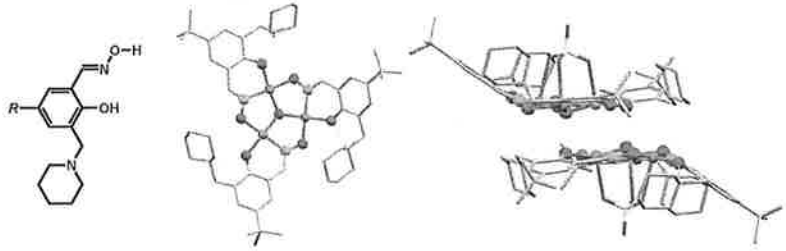
Approximately a quarter of the world's copper is produced by solvent extraction using simple phenolic oxime ligands,[1] which selectively remove Cu^{2+} from feeds containing Fe^{3+} and other metal ions.



$[Cu(L)_2]$

Electrospray mass spectrometry showed that the complex, $[Cu(L)_2]$, predominates in a *two* phase system, but in a *single* phase when the copper concentration ≥ ligand concentration, polynuclear complexes can form. Polynuclear complexes using phenolic oxime ligands have been previously reported with trivalent transition metals Mn,[2] Co,[2] and Fe,[2] and the first hexanuclear salicylaldoximato-bridged Cu^{II} complex was reported last year.[3]

In this paper we report how trinuclear complexes, first detected in the mass spectra, were characterized in solution and isolated as crystalline materials. The magnetism, electrochemistry and possible future applications as novel materials will be discussed.



(a) **LH** (b) **$[Cu_3L_3\mu_3\text{-}OH]^{2+}$** (c) **$[(Cu_3L_3\mu_3\text{-}OH)(ClO_4)]_2[ClO_4]_2$**

Acknowledgements: We acknowledge the EPSRC and Cytec Industries for financial support.

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Synthesis of Novel Silicon Ligands and Metal-Organic Frameworks

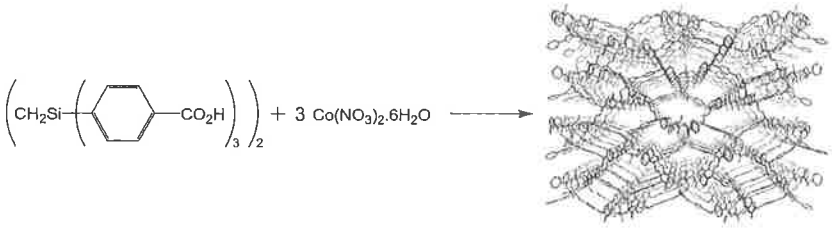
K. A. Robertson[1], R. P. Davies[1], P. D. Lickiss[1]

1. *Imperial College London, Chemistry Department, South Kensington Campus, London, SW7 2AZ, United Kingdom. kr07@imperial.ac.uk*

The emerging field of metal-organic frameworks (MOFs) is ever expanding as new applications for these versatile materials are discovered. A MOF is a porous coordination network consisting of metal ions or metal centres linked together by organic-based multidentate ligands. It is the permanent porosity of MOFs and the potential functionalisation of the pores that gives them such versatility. The nature of these pores is largely dependant on the nature of the ligands and metal centres.

We have previously reported three MOFs using bi-, tri- and tetra-dentate silicon ligands[1].We now describe the synthesis of new Si-based carboxylate ligands and their use in the construction of new MOFs. Using chlorosilane and ethoxysilane precursors a series of carboxyphenylsilanes which can act as hexa-, tetra-, tri- and bi-dentate ligands have been prepared. These new ligands have then been used to synthesise MOFs of novel topology. The ligands were synthesised by lithiation of dibromobenzene which reacts with a chlorosilane or ethoxysilane to give a bromophenylsilane intermediate. This is then lithiated and carboxylated to give the final ligand. The precursors can be varied to introduce functional groups and to alter the distances between the coordinating carboxylate groups.

For example, the MOF (displayed below) was synthesised from the solvothermal reaction of bis(triscarboxyphenylsilyl)ethane and $Co(NO_3)_2.6H_2O$ in 1:1 dimethylacetamide(DMA):H_2O. It is a 3D porous structure with a previously unreported topology represented by the Schläfli notation $(4^3.6^3)_2(4^6.6^7.8^2)$ for the Si nodes and metal nodes respectively. There are channels of c.a. 6x8Å in the 100 plane (shown in the diagram below). These channels contain solvent molecules which can be removed under vacuum giving access to the channels. In addition to the uncoordinated solvent within the channels this MOF has water molecules coordinated to the metal centres which can potentially be removed under vacuum. This would result in unsaturated metal centres which can increase the functionality of the resultant MOF. For gas storage this has the potential to increase the binding energy to the guest molecules [2] and so increasing the storage capacity of the MOF at ambient temperature and pressure.



Acknowledgements: We would like to thank Dr Andrew White for the X-ray crystallographic studies and the EPSRC for funding.

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A New Simple Preparation Method of Pd/C via Self-Redox of Tetraoxalato Complex of Pd(II) and Its Catalytic Property

T. Akiyama[1], A. Mashiko[1], M. Kusaka[1], T. Tsurui[2], M. Kurihara[1], M. Sakamoto[1]

1. *Faculty of Science, Yamagata University, Yamagata, Japan sakamoto@sci.kj.yamagata-u.ac.jp*
2. *Center for Integrated Nanotechnology Support, Tohoku University, Sendai, Japan*

A new simple preparation method of palladium metal nanoparticles supported on activated carbon (Pd/C) has been developed, in which the activated carbon was impregnated with an aqueous solution of $(NH_4)_2[Pd(C_2O_4)_2]\cdot 2H_2O$, followed only by the heat-treatment at 473 K. In this method, the usual reduction process in a hydrogen gas flow at 473-623 K or with reducing agents such as $NaBH_4$, KBH_4 and formaldehyde is not required, because the Pd metal is easily formed even in an air atmosphere by the self-redox reaction of $(NH_4)_2[Pd(C_2O_4)_2]\cdot 2H_2O$ at 473 K. TEM observation showed that the metallic Pd nanoparticles with an average size of 2 nm in diameter were uniformly distributed on the activated carbon. Catalytic activity of 5wt%-Pd/C for the hydrogenation of phenol was investigated in hexane at 393 K under an initial H_2 pressure of 0.7 MPa in a closed reactor (amount of Pd/C: 0.02 g, hexane solution of phenol: 0.32 M, 10 mL). Overall conversion of phenol was increased with the reaction time, and was ca. 100 % after 12 h. After 9 h, the overall conversion was ca. 90 %, and respective conversion to cyclohexanone and cyclohexanol were ca. 83 and ca. 7 %. Catalytic activity of the Pd/C prepared in this work was not significantly changed for its repeated use, while that of a commercially available Pd/C was remarkably lowered. This difference was reflected in the Pd metal size after the use as catalyst: TEM image revealed that the initial size (2 nm) of Pd metal was maintained in our Pd/C, whereas the particle growth proceeded in the commercial Pd/C to afford many large Pd metal particles with 10 – 20 nm.

A New stable Copper (III) tetraphenylporphyrin complex

M. Saphier*[1,2], T. Yifrah[3], I. Zilbermann[1,3], O. Saphier[2], D. Meyerstein[3,5] and D. M. Guldi[4]

1. *Nuclear.Research.Centre.Negev, Beer-Sheva, Israel.*
2. *Sami Shamoon College of Engineering of the Negev –Israel*
3. *Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva –Israel*
4. *Chemistry Department, Friedrich-Alexander-Universitat Erlangen-Nuernberg -Germany*
5. *Biological Chemistry Department, Ariel University Center, Ariel, Israel.*

Abstract:

The dissolution of $CuCl_2$ in a deaerated polar dry organic solvent(dichloromethane, dichloroethane) in the presence of the tetraphenylporphyrin free base surprisingly results in the formation of copper (III) tetraphenylporphyrin and $Cu(I)_{solv.}$ via a disproportionation reaction. The copper (III) tetraphenylporphyrin is characterized by XPS, UV-vis and electrochemical techniques. The new, Cu(III)porphyrin exhibits different UV-vis absorption, epr, and fluorescence patterns then the well known Cu(II)(TPP), Cu(II)($TPP^{+\cdot}$) and Cu(II)($TPP^{+2\cdot}$). Furthermore the new, Cu(III)porphyrin in the presence of molecular oxygen and Cu(I)($CH_3CN)_4^+$ forms a new species which exhibits blue shift UV-vis absorption compared to Cu(III)porphyrin, presumably [Cu(II)TPP-O_2]

The following mechanism is proposed:

1. $Cu^{+2} + H_2TPP \rightleftharpoons Cu(II)TPP + 2H^+$
2. $2Cu^{+2} + H_2TPP \rightleftharpoons Cu(III)TPP^+ + Cu^+ + 2H^+$
3. $Cu^+ + 4CH_3CN \rightleftharpoons Cu(I)(CH_3CN)_4^+$
4. $Cu(I)(CH_3CN)_4^+ + O_2 \longrightarrow Cu^{2+} + O_2^{\cdot-}$
5. $Cu(III)TPP^+ + O_2^{\cdot-} \rightleftharpoons [Cu(II)TPP\ O_2]^+$

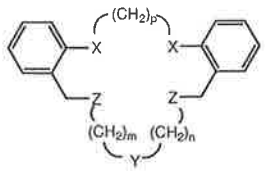
$2Cu(III)TPP^+ + H_2O \longrightarrow 2Cu(II)TPP + 2H^+ + H_2O_2$

New Potentially Pentadentate Schiff-base Macrocyclic Ligands Incorporating Non-Symmetrically Arranged N_3OS-, N_3S_2- and N_3O_2-Donor sets.

I. M. Vasilescu[1], J. K. Clegg[2], L. Feng[2], L. F. Lindoy[2] and G. V. Meehan[1]

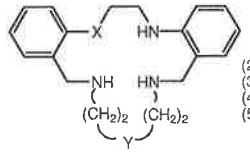
1. *School of Pharmacy and Molecular Sciences, James Cook University, Townsville, Qld. 4811, Australia.*
2. *Centre for Heavy Metals Research, School of Chemistry, University of Sydney, N. S. W. 2006, Australia.*

The design and synthesis of macrocyclic ligands for metal ion recognition and/or discrimination has been a topic of considerable interest over the years.[1-3] Particular attention has been given in our previous studies to the synthesis of an extended series of related mixed-donor, dibenzo-substituted macrocyclic rings of type (1) (Z = NH) required for systematic investigation of metal ion discrimination.[1] Related systems of type (1) (Z = S) have been employed by other workers in extensive structural studies.[4]



X, Y = NH, O and/or S
Z = NH or S
m = 2, 3, or 4
n = 2 or 3
p = 1, 2, 3 or 4

(1)



(2) X = S, Y = S
(3) X = S, Y = O
(4) X = O, Y = S,
(5) X = O, Y = O

Remarkable structural diversity and substantial metal-ion discrimination can be attained from the use of macrocyclic ligands of this type containing different donor atom combinations with different metal ion affinities.[1,5] However, these studies have previously involved ligands which have a symmetrical arrangement of their donor atoms; very few rings of this type where the donor atoms have an unsymmetrical arrangement have previously been reported. In part, this is due to the more challenging nature of their preparation.

We now present the synthesis of a further four members of the above series. The new ligands (2) – (5), which incorporate a *non-symmetrical* arrangement of their donor atoms, serve to complete the 'matrix' of 17-membered macrocyclic ligands of this type showing donor set variation. These ligands can address deficiencies in current knowledge with respect to the effect which the *sequence* of the donor atoms in the macrocyclic ring has on the stability of resulting metal complexes.

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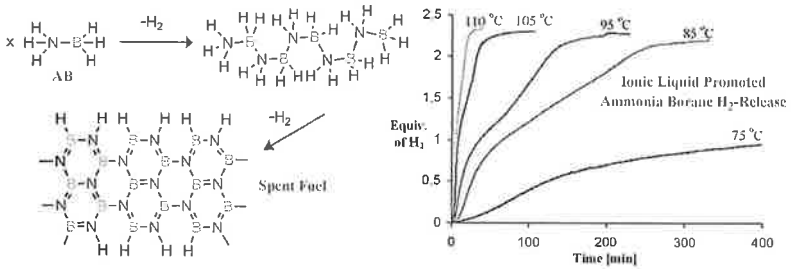
Amine Borane Based Chemical Hydrogen Storage

L. G. Sneddon[1,*], D. W. Himmelberger[1], M. E. Bluhm[1], L. R. Alden[1], E. Berkeley[1], W. R. H. Wright[2], G. P. Rachiero[2] and R. T. Baker[2,*]

1. *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323 USA lsneddon@sas.upenn.edu*
2. *Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, 30 Marie Curie, Ottawa, ON K1N 6N5 Canada*

The development of efficient methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. Although many molecular hydrides have certain features that might be attractive for chemical hydrogen storage, the high hydrogen capacities needed for transportation applications exclude most compounds. The realization that amine boranes, such as ammonia borane, BH_3NH_3 (19.6 wt% hydrogen) and ammonia triborane (17.8 wt%), are unique in their potential ability to store and deliver large amounts of hydrogen through dehydrogenation and/or hydrolysis reactions has stimulated new interest in their syntheses, structures and chemical properties.[1] We report here our studies demonstrating that the rate and extent of hydrogen release from amine boranes can be significantly increased through the use of ionic liquids, metal catalysts and/or chemical additives. Studies that have elucidated the H_2-release pathways will also be presented.[2]



Acknowledgements: We thank the US Department of Energy for grants from the Center of Excellence for Chemical Hydrogen Storage and the Division of Basic Energy Sciences for the support of this research.

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Formation kinetics of mixed halido and N-O-donor multidentate ligand complexes of Zirconium.

M. Steyn[1], H.G. Visser[1] and A. Roodt[1]

Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa, E-mail: steynm@ufs.ac.za

Zirconium and hafnium show extremely similar chemical properties and occur together in nature. Zirconium ore (a.k.a. Zircon – $ZrSiO_4$) is found to always contain hafnium as an impurity (1-5%), and separation of these two metals is very difficult due to their near identical chemical properties. The aim of this project was to find significant chemical differences between the N- and O-donating multidentate ligand complexes of zirconium and hafnium which would allow the separation and purification of these metals.

In the present investigation of these complexes, structural characterisation by means of single crystal X-ray diffraction, NMR spectroscopy and UV/Vis spectrophotometry will be discussed. Optimal reaction conditions have been found for different substituted L,L'-bidentate halido-zirconium complexes[1]. The crystallographic characterisation of the tetrakis(quinolinolato-κ^2-N,O)zirconium(IV) complex (See Figure) is presented and compared with literature. Advances toward tri- and tetra dentate ligand coordination experiments are also included, discussing observed trends with regard to steric bulk as well as rigidity and flexibility of multi-dentate ligands.

A discussion of the principles of the kinetic approach employed is also included as well as experimental results. Conclusions regarding the coordination mechanism by which this reaction proceeds were obtained from observations made during the synthesis, characterisation and preliminary kinetic studies. The initial coordination mechanism is postulated for the four observed steps of zirconium chelating reactions individually identified and analysed with bidentate ligands. A step-wise substitution mechanism is proposed and discussed for this formation reaction of the $[Zr(ox)_4]$ complex as studied by time resolved stopped-flow and slower UV/Vis spectroscopy.

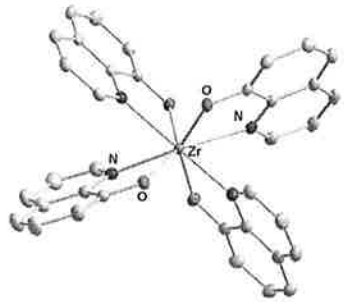

Figure. Representation of the $[Zr(ox)_4]$ complex, showing the displacement ellipsoids (50% probability). Hydrogen atoms are omitted for clarity.

Acknowledgements:
Financial assistance from the Advanced Metals Initiative (AMI), the Department of Science and Technology (DST) of South Africa, The New Metals Development Network (NMDN) and the South African Nuclear Energy Corporation Limited (Necsa) is gratefully acknowledged.

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DPK Complexes of Cu(I) and Cu(II) containing iodide and thiocyanate ligands. An unusual case of pseudo-aldol condensation.

K. B. Szpakolski,[1] K. Latham,[1*] C. J. Rix,[1] J. M. White [2]
School of Applied Sciences, Applied Chemistry, RMIT University, Melbourne, VIC 3001.
Fax: +61 3 9925 3747; Tel: +61 3 9925 2635; E-mail: kay.latham@rmit.edu.au
School of Chemistry, University of Melbourne, Melbourne, VIC 3011

Copper(I) complexes which contain N-heterocyclic ligands are important due to their properties and potential applications.[1, 2] Polydentate heterocyclic ligands such as di-2-pyridyl ketone (*dpk*) are versatile and easily accessible.[3-5] Three novel dimeric and polymeric copper(I) and copper(II) complexes which contain *dpk* as a bi- (N,N) and tri- (N,N,O) dentate have been synthesised, and characterised by spectral and structural studies. **(1)** and **(2)** are polymorphs of a polymeric copper(I) complex, $[Cu(dpk)(NCS)]_n$ containing *dpk* with thiocyanate anions which bridge to form a one-dimensional polymeric network. Whilst the dinuclear copper(II) complex **(3)**, $[Cu_2(dpk.acetone)_2(NCS)_2]$, was formed when products **(1)** and **(2)** were allowed to re-dissolve in the supernatant. In this instance it appears that a transition-metal promoted aldol condensation has occurred between the acetone solvent and the keto-carbonyl of *dpk* to produce the novel ligand, *dpk.acetone*. Product **(3)** contains two six coordinate copper(II) ions, both with octahedral coordination, containing a copper-copper direct bond and further bridged through deprotonated hydroxyl groups on each *dpk.acetone*. A mechanism for the formation of **(3)** is proposed. A dinuclear copper(I) complex, **(4)** $[Cu_2(dpk)_2I_2]$ is also reported. **(4)** contains two four-coordinate copper(I) ions, that are bridged together through iodide ions.

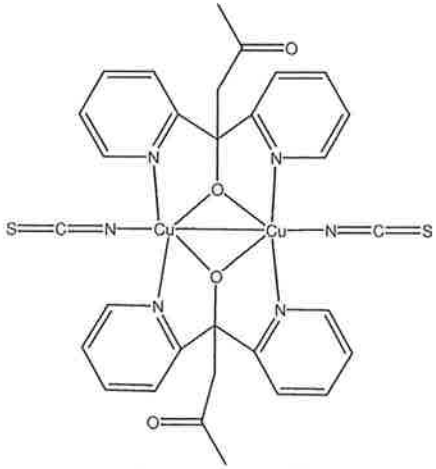

Figure 8 Complex (3)

Reference

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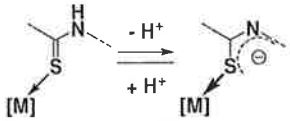
Tuning of Electrochemical Properties of Ruthenium Pincer Complexes Containing of the (S,C,S)- and (S,N,S)-Ligands.

T. Teratani[1], T. Koizumi[1], T. Yamamoto[1], T. Kanbara[2].
1. *Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Yokohama, Kanagawa 226-8503, Japan*
2. *Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Science, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8573, Japan*
E-mail: tteratani@macromol.res.titech.ac.jp

Secondary thioamides are in equilibrium between amino-thione and imino-thiol tautomers, and their deprotonated form has several resonance structures. The N-H proton of secondary thioamides exhibits stronger acidity than those of the corresponding amides. Therefore, secondary thioamides coordinated to transition metals are easily deprotonated to give their anionic forms, which enhances the donor ability of the sulfur atom *via* the N-to-S backbone (Scheme 1).[1] Previously, we reported transition metal-pincer complexes containing two thioamide groups in the pincer ligand. Pincer complexes are of interest for their potential use as homogeneous catalysts and functional materials. Typical pincer ligand is derived from 1,3-disubstituted benzenes, and the centered coordination site of the tridentate ligand is usually constructed by the benzene ring. Since the M-C(phenyl) σ-bond of the pincer ligand serves as a strong electron donor, it affects redox behavior of the metal center. In this study, we prepared new ruthenium complexes containing benzene and pyrrole centered pincer ligands (Figure 1) with two secondary thioamide wings. Tuning of electrochemical properties of the complexes by addition of acid and base is reported.



Scheme 1.

The ruthenium complexes **1** and **2** were prepared by the reaction of $[RuCl_3(tpy)]$ with the corresponding pincer ligands. The obtained complexes were stable in air, and the chemical structures of the complexes were confirmed by NMR, ESI-MS spectroscopy and elemental analysis.

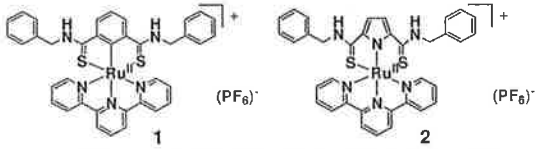


Figure 1. Structures of ruthenium complexes **1** and **2**.

Figure 2 shows the cyclic voltammograms of **1**, **1** with 2 mol equiv of triethylamine (NEt_3) and **1** with 2 mol equiv of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU). Upon addition of 2 mol equiv of NEt_3, the metal-centered Ru(III)/Ru(II) redox couple of **1** was negatively shifted. When 2 mol equiv of DBU was used, further negative shift of the metal-centered redox couple of **1** was observed. The newly appeared redox couples under the NEt_3-added and DBU-added conditions are considered to be based on the mono-deprotonated and di-deprotonated form of **1**, respectively. Similar electrochemical behavior was observed in **2**. The redox potential of both complexes returned to the original one by the addition of methanesulfonic acid (MSA). These results indicate that the redox potential of complexes **1** and **2** can be regulated by the reversible deprotonation-protonation of N-H proton(s) using base and acid.

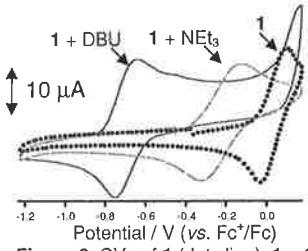


Figure 2. CVs of **1** (dots line), **1** + 2 mol equiv of NEt_3 (dash line) and **1** + 2 mol equiv of DBU (solid line).

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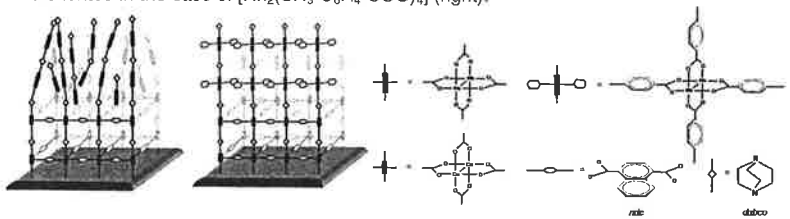
Heteroepitaxial Layer-by-Layer Growth of Hybrid MOFs Thin Films

O. V. Vreshch, K. Yusenko, R. A. Fischer
Chair of Inorganic Chemistry II, Ruhr-University Bochum, Universitaetsstr. 150, D-44801 Bochum, Germany, email: roland.fischer@rub.de

The synthesis of metal-organic frameworks (MOFs) as both the bulk compounds and thin films is a matter of high concern.[1] The large number of existing organic linkers and the unique physical features of inorganic units lead to a modulation of the pores shape and the properties of the final materials. MOFs based on dirhodium- or diruthenium-carboxylates are particularly interesting for us to investigate since they hold the perspective to possess redox- or/and catalytic activities. In fact, the preparation of rhodium and ruthenium analogues of known MOFs of Cu(II) and Zn(II) carboxylates appeared to be a notoriously difficult task, and almost no cases are reported to date. In meanwhile, crystalline phases of such copper systems can be grown in stepwise layer-by-layer mode on different surfaces as well.[2] The usage of these copper MOFs on the surface as frame templates may afford the heteroepitaxial[3] implementation of dirhodium or diruthenium units into 3D structure and therefore the growing some films containing Rh or Ru-based MOFs with desired or probably new properties. Our first attempts are focussed on the fabrication of rhodium-containing films using $[Rh_2(CH_3COO)_4]$ or $[Rh_2(CH_3\text{-}C_6H_4\text{-}COO)_4]$ and $[Cu_2(ndc)_2(dabco)]_n$ framework grown on pyridine terminated gold surface (Fig). It can be realized by means of growing several layers composed of rhodium units bind with *dabco* (the same interplanar linker as for copper) on top on 25-30 layers of $[Cu_2(ndc)_2(dabco)]_n$, and then capping again with 25-30 layers of the same copper system. The growing process we monitor by quartz crystal microbalance and base on X-ray diffraction data to make conclusion about crystallinity and up to some point composition of the films. We believe that using of more sterically bulk in comparison with $[Rh_2(CH_3COO)_4]$ blocks (like $[Rh_2(CH_3\text{-}C_6H_4\text{-}COO)_4]$), which can be connected by weak interactions (for instance, π-π staking or H-bonds) in the structure of final MOFs, to a greater extent could lead to ordering films. Figure schematically represents our considerations concerning the growth of rhodium units on the copper framework: chaotic in the case of $[Rh_2(CH_3COO)_4]$ (left) and more oriented in the case of $[Rh_2(CH_3\text{-}C_6H_4\text{-}COO)_4]$ (right).



Acknowledgements: Financial support from Research School at Ruhr-University Bochum is gratefully acknowledged.

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Di-cobalt Oxo-Bridged Cluster as Building Blocks for Mono and Heterometallic Clusters

P. Wang[1,2] and T.S. A. Hor[1,2,*]
1. *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543*
2. *NUS Graduate School for Integrative Sciences and Engineering (NGS), Center for Life Sciences (CeLS), #05-01, 28 Medical Drive Singapore 117456*

Binuclear metal bridged clusters have been widely explored and shown prominent properties in molecular magnetism and metal catalysis.[1],[2],[3] We have serendipitously synthesized the tetra-nuclear cobalt cubane cluster and dicubane cluster, which exemplify the importance of binuclear cobalt oxo-bridged cluster as building blocks for more complicated mono and heterometallic clusters. This discovery has led to the incorporation of alkali metals, alkaline-earth metals and the rare-earth metals into the dicobalt cluster to yield intermetallic polynuclear structures. The magnetic properties of these clusters are being explored. In this presentation, we shall outline the strategy and some resent findings in the cluster designs.

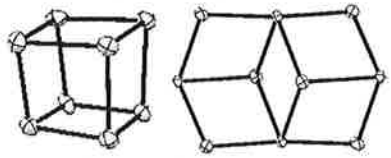

Figure 1. Schematic diagram of cubane (left) and dicubane (right)

Acknowledgement: We acknowledge NUS, MOE and A*Star for financial support. Pei Wang acknowledges NGS for a graduate scholarship.

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Elucidating Negative Thermal Expansion in Metal-Organic Frameworks Through Structural, Vibrational and Computational Investigation

Y. Wu[1], A. Kobayashi,[2] G. J. Halder,[3] V. K. Peterson,[4] G. J. Kearley,[4] K. W. Chapman,[5] N. Lock,[6] P. D. Southon,[1] A. J. Ramirez-Cuesta,[7] E. Kemner,[8] C. J. Kepert[1]

1. *School of Chemistry, The University of Sydney, wu@chem.usyd.edu.au*
2. *Division of Chemistry, Hokkaido University (Japan)*
3. *Materials Science Division, Argonne National Laboratory (USA)*
4. *Bragg Institute, Australian Nuclear Science & Technology Organisation*
5. *X-ray Science Division, Argonne National Laboratory (USA)*
6. *Department of Chemistry, University of Aarhus (Denmark)*
7. *ISIS, Rutherford Appleton Laboratory, Oxfordshire (UK)*
8. *BENSC, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin (Germany)*

Negative thermal expansion (NTE) is a rare materials property, with heretofore notable research in this area focusing primarily on simple metal oxide and cyanide framework materials. We have performed the first comprehensive characterisation of the mechanism of NTE in a metal-organic framework (MOF), 'HKUST-1' - Cu_3(1,3,5-benzenetricarboxylate)$_2$ - using a three-pronged approach.[1,2] MOF materials have been a focus of recent research due to their exceptional properties including permanent porosity, high surface area, reversible guest sorption and chemical functionisability. However, the anomalous thermal expansion of MOFs is an unusual property that to date has not been extensively characterised. Due to the structural versatility of MOF chemistry, this research points to the development of materials with tailored thermal expansion properties, which may find application in a wide range of technological applications where high precision over a large temperature range is required.

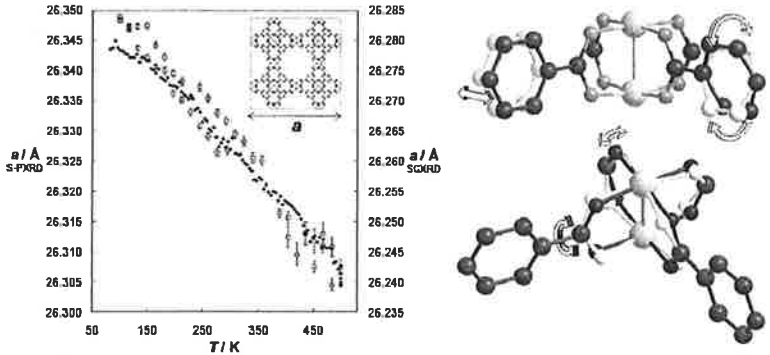

Figure 1: (L) Quantification of NTE in HKUST-1 using single crystal and synchrotron powder X-ray diffraction. (R) Schematic of aspects of the vibrational mechanism

This work has show that the mechanism of thermal expansion in this material stems from several aspects of the HKUST-1 structure, which is more complex than previous NTE materials (most notably, metal oxide and cyanide frameworks). In particular, the inherent strain of forcing the 3-connecting linker into a non-ideal conformation and the flexibility of the dimetal-carboxylate 'paddlewheel' structure result in a material that exhibits local vibrational modes of the paddlewheel uncoupled with whole-lattice vibrations. This is a newly discovered attribute for framework materials which we believe encourages negative thermal expansion, a hypothesis that is supported by our preliminary research on a number of MOFs featuring flexible metal-oxygen cluster motifs.

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Tuning of Orbital Energies in Bis-tridentate Ru Complexes by Introducing Cyclometalated Ligand

S. Yoshikawa[1], K. Kanaizuka[1], M. Haga[1]

1. *Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, Japan*

Tuning of redox potential and photophysical properties in metal complexes is important to implement molecular functions for the practical applications such as dye-sensitized solar cell and redox catalyst. As for Ru complexes, these properties can be tuned by changing tridentate ligand from N^N^N to cyclometalated one such as N^C^N or C^N^N, because the rise cyclometalation induces the energy of frontier orbitals by strong σ donation[1]. In the present study, we synthesized a series of novel Ru complexes bearing the unique N-heteroaromatic ligands such as nitrogen atoms (N^N^N Ru complex) , or bis(benzimidazolyl)benzene with N^C^N coordination mode (N^C^N Ru complex), shown in Figure 1 , and examined the effects of the coordination environment on electrochemical and photophisical properties. Ru complexes having proton dissociable benzimidazole moiety showed a pH dependent electrochemical behavior and examined the effects on the introduction of Ru-C bond. The UV-vis absorption spectral and electrochemical data are summarized in Table 1. Cyclometalation resulted in the red shift in metal-to-ligand charge-transfer(MLCT) band on UV-vis absorption spectra, and the negative shift of 0.6V for the metal-based oxidation (Ru(III/II)) on cyclic voltammogram. These shifts reflect on the decrease of HOMO-LUMO energy gap and the increase of HOMO energy level. Strong σ donor property by cyclometalation led to the increases of the electron density on metal center, and therefore the rise of HOMO energy level. At the same time, the LUMO energy level increased with increasing the back-donation by electron rich metal center, but this change was smaller than that for the HOMO level. In Ru complexes having proton dissociable moieties, the first pK_a value was shifted from pK_{a11} = 6.3 to 10.8 by substitution from pyridine group to phenyl one. This alteration is due to the increase of electron density on the benzimidazolyl ring by introducing the Ru-C bond in the complex.

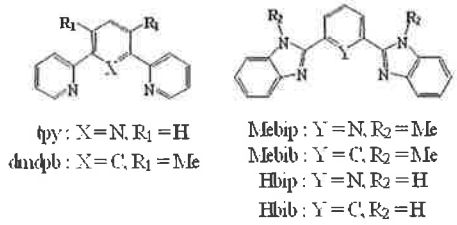

Fig.1 Series of ligands used in this study

Table 1 UV-vis spectral and electrochemical data of complexes

	Complex	λ_{max} / nm(ε /10^3M^{-1}cm^{-1})	$E_{1/2}$V / vs Fc^+/Fc (ΔE_p / mV)		
		MLCT band	Ru(Ⅲ/Ⅱ)	L/L$^{\cdot-}$	L'/L'$^{\cdot-}$
N^N^N Ru complexes	[Ru(tpy)(Mebip)] $^{2+}$	480 (14.4)	0.64(66)	-1.68(59)	-1.96(72)
	[Ru(Mebip)$_2$] $^{2+}$ a)	490(7.9)	0.30(61)	-1.80(62)	-2.12(80)
N^C^N Ru complexes	[Ru(tpy)(Mebib)]$^+$	501(11.7)	0.02(73)	-2.00(71)	
	[Ru(dmdpb)(Mebip)]$^+$	515(19.1)	-0.04(60)	-1.99(52)	
	[Ru(Mebib)(Mebip)]$^+$	512(12.1)	-0.16(61)	-2.02(55)	

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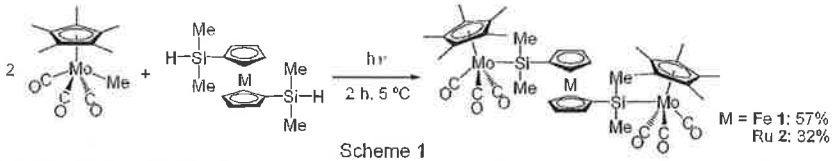
Synthesis and electrochemical property of dinuclear molybdenum complexes connected by 1,1'-bis(silyl)metallocene spacer

M. Itazaki, A. Ichimura, Hiroshi Nakazawa*
Department of Chemistry, Graduate School of Science, Osaka City University mitazaki@sci.osaka-cu.ac.jp

Polysilylferrocenes have been under investigation for their attractive conductivity and magnetic property.[1,2] However, a limited number of silyl-ferrocenes and ruthenocenes have been reported where the silyl group is bonded to transition-metal(s).[3] We herein report the synthesis of Mo–Si complexes containing a metallocene in the reactions of (dimethylsilyl)ferrocene and 1,1'-bis(dimethylsilyl)metallocene with the molybdenum methyl complex.

Photoreaction of $Cp^*(CO)_3Mo(Me)$ with (dimethylsilyl)ferrocene at 5 °C afforded the molybdenum-silyl complex having the ferrocenyl moiety, $Cp^*(CO)_3Mo–SiMe_2(C_5H_4)Fe(C_5H_5)$. On the other hand, reactions of 1,1'-bis(dimethylsilyl)metallocene $[(HMe_2SiC_5H_4)_2M]$ (M = Fe, Ru) with a 2-fold molar excess of $Cp^*(CO)_3Mo(Me)$ afforded the desired tri-nuclear complexes $[(Cp^*(CO)_3MoSiMe_2C_5H_4)_2M]$ (M = Fe: **1**, Ru: **2**) having two terminal Mo–Si bonds (Scheme 1).



Scheme 1

The molecular structures of **1** and **2** were determined using single crystal X-ray diffraction. The ORTEP drawing of **2** is shown in Fig. 1. The two molybdenum units, $Cp^*(CO)_3Mo$, are connected by the $(–(Me_2SiC_5H_4)Ru(C_5H_4SiMe_2)–)$ spacer. Complexes **1** and **2** are the first examples of methallocenes having two terminal Mo–Si moieties.

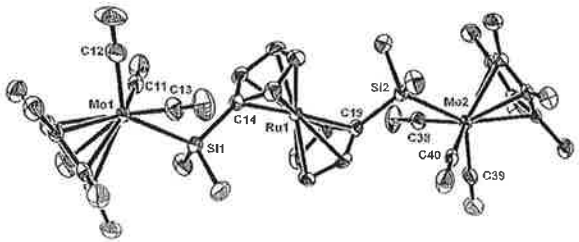


Fig. 1. ORTEP drawing of **2**.

The electrochemical properties of these complexes and reactions of 1,1'-bis(dimethylsilyl) metallocene with other methyl complexes will be discussed.

Acknowledgements: This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 20750049) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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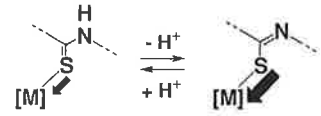
Synthesis, structures and electrochemical properties of Rh(III) complexes bearing a secondary thioamide ligand

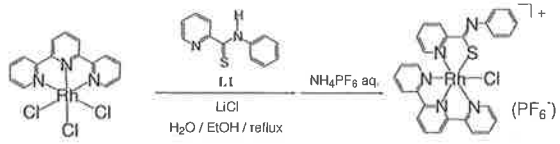
T. Koizumi, M. Kawase, T. Teratani
Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503 Japan e-mail: tkoizumi@res.titech.ac.jp

Rh complexes have two coordination structures, a square-planar structure for Rh(I) and a octahedral structure for Rh(III). There have been a lot of reports about their structures, chemical properties, and reactivities up to now. However, researches on the electrochemistry of Rh complexes are very limited. We have been researching the synthesis and electrochemical properties of transition metal complexes containing a secondary thioamide as a ligand.[1] Secondary thioamides have an N-H proton, therefore the ligand can control the redox potential of the central metal by pH (Scheme 1).[2] In this study, we prepared new Rh(III) complexes having a secondary thioamide-derived ligand, and clarified their chemical and electrochemical properties. Electrochemical reduction of carbon dioxide using these complexes as a catalyst was also investigated.



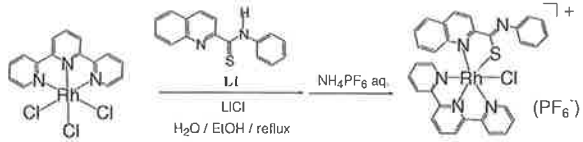
Scheme 1.

Rh(III)-thioamide complexes $[1](PF_6)$ and $[2](PF_6)$ were prepared by the reaction of $RhCl_3(tpy)$ (tpy = 2,2':6',2"-terpyridyl) and corresponding thioamides **L1** and **L2**, respectively, as shown in eqs. 1 and 2.



(1)

$[1](PF_6)$ (57%)



(2)

$[2](PF_6)$ (55%)

Molecular structures of $[1](PF_6)$ and $[2](PF_6)$ were determined by X-ray crystallography. Figure 1 depicts the ORTEP drawing of $[1]^+$. From the result, the thioamide ligand is deprotonated, and it coordinates to Rh as a thioamidate fashion. The S atom in the thioamidate ligand and the Cl atom are situated at mutually *trans* position. The electrochemical properties of the complexes were measured by cyclic voltammetry. Complex $[1]^+$ exhibited two-step pseudo-reversible reduction peaks at $E_{1/2}$ = -1.233 and –1.387 V (*vs.* Fc^+/Fc). They may be assigned to the Rh(III)/Rh(I) redox couple. On the other hand, $[2]^+$ showed the Rh(III)/Rh(I) redox couple at $E_{1/2}$ = -1.072 V (*vs.* Fc^+/Fc) as one-step reduction wave.

In a CO_2-saturated DMF solution, large catalytic currents at *ca.* -1.5 V for $[1]^+$ and ca. -1.6 V for $[2]^+$ were observed, respectively. These results strongly suggest that both $[1]^+$ and $[2]^+$ have an ability to reduce CO_2.

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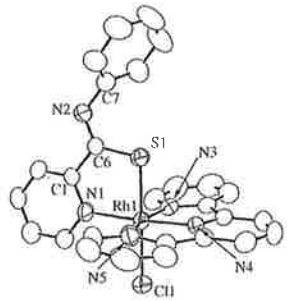

Figure 1. ORTEP drawing of $[1]^+$ with 50% thermalellipsoids. Hydrogen atoms are omitted for simplicity.

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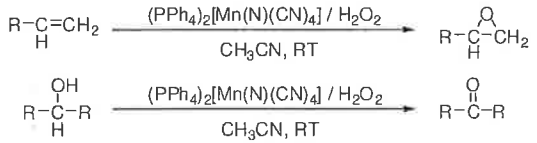
Catalytic Oxidation of Alkenes and Alcohols by $(PPh_4)_2[Mn(N)(CN)_4]$ Using Hydrogen Peroxide as Terminal Oxidant

H. K. Kwong, W. L. Man, T. C. Lau
Department of Biology and Chemistry, City University of Hong Kong, Kowloon Tong, Hong Kong, China. Email:bhtclau@cityu.edu.hk

Hydrocarbons are the major components in petroleum. Therefore the conversion of them into useful materials is an important process in chemistry. Nowadays the issue of green chemistry has received much attention. Much effort has been made on developing industrial processes that involve the use of less hazardous reagents and generate less toxic wastes. Hydrogen peroxide is an attractive oxidant since it generates H_2O as the only by-product. In this project, the catalytic oxidation of hydrocarbons by $(PPh_4)_2[Mn(N)(CN)_4]$ using hydrogen peroxide as terminal oxidant has been investigated. Alkenes and alcohols were oxidized to epoxides and ketones with moderate to high yields under ambient condition. Mechanistic studies of this reaction have also been carried out.



Acknowledgements: This work was supported by the Research Grants Council of Hong Kong (CityU 101607).

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Fe(II) pyrazolyl N,N and P,N metal complexes as catalysts for organic transformations

T. O. Nguyen[1], B. A. Messerle[1]
The University of New South Wales, New South Wales, Australia. thi.oanh.nguyen@gmail.com

The catalysed synthesis of amines and alcohols can be achieved through the mild reduction of imines and ketones, respectively, using transition metal catalysis. In particular, complexes of Group VIII metals are known to be effective catalysts for the hydrosilation of carbonyl compounds and imines.[1] Of the Group VIII transition metal series, Fe is an attractive option because it is an abundant and cheap element and as a first row transition metal, it is highly reactive. Furthermore, Fe(II) complexes have been shown to catalyse a wide variety of organic transformations such as allylic amination and Micheal Addition reactions.[2]

Our studies have been focusing on the synthesis of group VIII transition metal complexes containing pyrazolyl derived N,N and P,N ligands and their application as catalysts for organic transformations.[3] As a result a variety of Ru and Os metal complexes containing the 1-[2-diphenylphoshpino)ethyl]pyrazole (Pyp) ligand and its dimethyl derivative 3,5-dimethyl[1-((-2-diphenylphoshpino)ethyl)]pyrazole (Me_2Pyp) were synthesised.[4]

The goal of this work is to synthesise analogous [Fe(II)(N,N)] and [Fe(II)(P,N)] complexes and explore their activity as catalysts for the reduction of imines and ketones. The synthesis of this new series of Fe(II) complexes, such as those in Figure 1, is presented herein along with temperature dependant studies on the structure of the metal complexes.

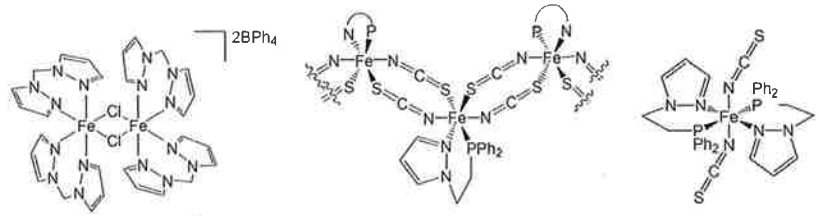

Figure 1: Example of several novel [Fe(II)(N,N)] and [Fe(II)(N,P)] complexes.

Acknowledgements: The University of New South Wales and the Australian Postgraduate Award.

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Close Approaches of C-H Bond Hydrogens to Transition Metals: New Types of Interactions with agostic-like characteristics

A.J. Nielson[1], J. A. Harrison[1], M. Lein[1]
Chemistry, Institute of Natural Sciences, Massey University at Albany, Private bag 102 904, North Shore Mail Centre, Auckland, New Zealand.
e-mail: a.j.nielson@massey.ac.nz

We have identified new types of agostic interactions in transition metal complexes where the central metal is either electron poor or electron rich. These interactions are represented in the complexes by the trityl C-H bond of the tris(hydroxyphenyl)methane ligand, $[CH(ArOH)_3]$, (Fig.1). This close approach of a C-H bond hydrogen was first found in the anion $[\{CH(ArO)_3\}TaCl_3]^-$ where the hydrogen atom approaches the metal in a linear fashion.[1] A close linear approach of this H atom is also revealed by the X-ray structure of $[\{CH(ArO)_3\}Ti(NEt_2)]$.[2] The bonding situation in this complex was identified by theoretical studies. In particular the Quantum Theory of Atoms in Molecules (QTAIM)[3] was used as it allows a quantitative comparison of topological properties of electron density. AIM analysis shows that a bond path exists for the H atom and the metal and that the magnitude of the electron density, Laplacian of the electron density at the H···Ti bond critical point as well as the energy and charge of the H atom basin are consistent with an agostic interaction. This feature is supported by calculated Wiberg bond indices, and an NBO analysis shows a significant interaction of the C-Hσ NBO orbital with an NBO hybrid Ti d orbital in a unique 'over the top' of the hydrogen atom manner. The calculated C-H coupling constant compares well with the experimental value and an increase in the IR C-H stretching frequency value compared with the free ligand is explained by a cage effect. In the nickel dianion $[\{CH(ArO)_3\}Ni(OPh)]^{2-}$, the AIM analysis shows a distinct bond critical point and other features characteristic of an agostic interaction. NBO analysis indicates this agostic interaction involves a C-Hσ NBO orbital interacting with a low-lying NBO hybrid Ti s orbital. However there is also now a back-donation effect where an occupied NBO metal hybrid d orbital donates to the NBO C-Hσ* orbital. Overall the situation in both complexes is that of C-H bond electron density interacting with a positively charged metal center but in the electron-rich metal center there is a back-donation effect.

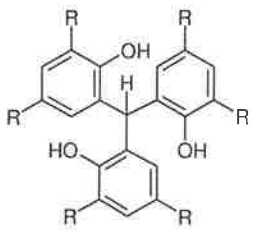

Figure 1. R = H, Me, CMe_3

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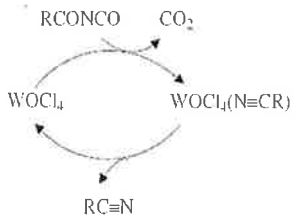
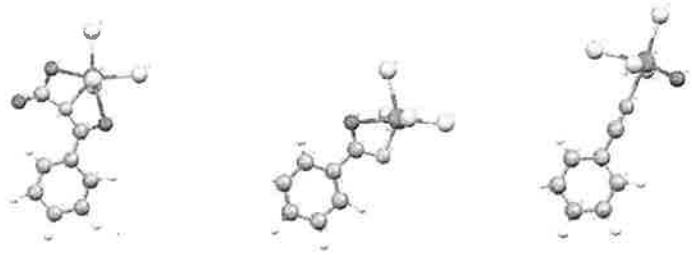
Stoichiometric and Catalytic Aryl Nitrile Formation from Amides and Aroyl Isocyanates using High-Valent Early Transition Metal Complexes.

A.J. Nielson[1], P. D. W. Boyd[2], M. A. Glenny[2]

1. *Chemistry, Institute of Natural Sciences, Massey University at Albany, Private bag 102904, North Shore Mail Centre, Auckland, New Zealand. e-mail: a.j.nielson@massey.ac.nz*
2. *Department of Chemistry, The University of Auckland, Private bag 92019. Auckland, New Zealand.*

Reaction of $PhCONH_2$ with $[WCl_6]$ under reflux in benzene gives a near quantitative yield of $[WOCl_4(NCPh)]$ **1** which can be prepared directly by the reaction of PhCN with $[WOCl_4]$. An X-ray crystal structure of **1** shows *cis*-chloro ligands and the PhCN nitrogen lying *trans* to a terminal oxo ligand. $PhCONH_2$ reacts with $[WOCl_4]$ under reflux in benzene to give $[WO_2Cl_2(NCPh)]$ **2** and with $[NbCl_5]$ under similar conditions to give $[NbOCl_3(NCPh)]$ **3**. $PhCONH_2$ and $TiCl_4$ give $[TiCl_4(NH_2COPh)_2]$ **4**. Reaction of the aroyl isocyanate PhCONCO with $[WOCl_4]$ gives $[WOCl_4(NCPh)]$ **1** and 4-Me_3CPhCONCO and $[WOCl_4]$ gives $[WOCl_4(NCPhCMe_3\text{-}4)]$ **5**. PhCONCO reacts catalytically with $[WOCl_4]$ or $[WOCl_4(NCPh)]$ to give quantitative yields of PhCN. Similarly, 4-Me_3CPhCONCO and 2-ClPhCONCO react catalytically with $[WOCl_4]$ to give complete conversion to 4-Me_3CPhCN and 2-ClPhCN. DFT calculations on the catalytic mechanism for the reaction between $[WOCl_4]$ and PhCONCO show an initial near barrierless process in which a chlorine atom of $[WOCl_4]$ moves from a *cis* to a *trans* position with respect to the oxo group as the isocyanate group nitrogen approaches the tungsten atom and the carbon atom approaches the oxo group oxygen. A metallocycle complex then forms from which there is a rotation around the C-CO bond which allows the aroyl group oxygen to coordinate to the metal (structure **a**). CO_2 is then eliminated from this complex to give a metallocycle containing a bidentate PhCON ligand (structure **b**).This ligand then undergoes a concerted rearrangement to give *cis*-$[WOCl_4(PhCN)]$ (structure **c**) which is less stable than *trans*-$[WOCl_4(PhCN)]$ and this complex is more stable than the dissociated complex $[WOCl_4]$ and PhCN.





(a) (b) (c)

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Synthesis, characterisation and solution behaviour of phosphoryl complexes of tin tetrafluoride

M. A. Sanhoury, M. T. B. Dhia and M. R. Khaddar
Laboratory of Coordination Chemistry, Department of Chemistry, Faculty of Sciences of Tunis,University of Tunis El Manar, 2092 Tunis, Tunisia. E-Mail : senhourry@yahoo.com

The synthesis, characterisation and solution behaviour of a series of octahedral complexes $SnF_4.2L$ (L = $R_2NP(O)F_2$; R = Me (1); Et (2), L = $(R_2N)_2P(O)F$; R = Me (3); Et (4) or L = $(Me_2N)_3P(O)$ (5)) are described. The adducts have been fully characterised by multinuclear (^1H, ^{31}P, ^{19}F and ^{119}Sn) NMR, IR spectroscopy and elemental analysis. In dichloromethane solution, the NMR data particularly the ^{19}F NMR spectra showed the presence of a mixture of *cis* and *trans* isomers. Interestingly, the solution structure of the complexes studied by variable temperature NMR in the presence of excess ligand indicated that, unlike in the $SnCl_4$ analogues [1,2], the ligand exchange on the *cis* isomer is only observed when L = $R_2NP(O)F_2$. The metal-ligand exchange barriers in $SnF_4.2L$ and $SnCl_4.2L$ systems were estimated and compared. The results show that both the difference in the Lewis acidity between SnF_4 and $SnCl_4$ and the nature of the substituents on the phosphorus atom of the ligand could be responsible for the lability of the complex formed.

Acknowledgement:
We are grateful to the Tunisian Ministry of High Education and Scientific Research and Technology for financial support (LR99ES14) of this research.

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Heterobimetallic Complexes of Rhodium and Iridium Stabilized by *Bis*(dicyclohexylphosphino)methane and Comparison to their *Bis*(diphenylphosphino)methane Analogs

K. Searles, S. Schreiner
Department of Chemistry, Randolph-Macon College, Ashland, VA 23005, USA (keithsearles@rmc.edu)

Although the reaction chemistry of low valent rhodium and iridium homonuclear complexes stabilized by diphosphine ligands has been studied[1],[2], relatively little focus has been placed on the investigation of heterobinuclear rhodium and iridium complexes. One of the few heterobinuclear rhodium and iridium systems that have been studied is the *bis*(diphenylphosphino) methane (dppm) system, which has shown to be a bimetallic catalyst[3],[4]. Thus far, no complexes have been reported in literature using the much bulkier ligand, *bis*(dicyclohexylphosphino)methane (dcpm), to stabilize heterobinuclear complexes of rhodium and iridium. We wish to report on the synthesis and characterization of several heterobinuclear rhodium-iridium-dcpm complexes and compare their reactivity to the analogous rhodium-iridium-dppm complexes[5].

The synthesis of heterobinuclear rhodium- iridium-dcpm complexes requires the use of $[Rh(CO)(dcpm)_2]Cl$ (**1**) and $[Ir(CO)(dcpm)_2]Cl$ (**2**) as starting materials. These complexes were prepared in about 90 % yield from $[(M)(Cl)(CO)(PPh_3)_2]$ (M = Rh, Ir) with 2 molar equivalents of dcpm. Their trigonal bypyramidal structure was determined by IR and multinuclear NMR spectroscopy.

Synthesis of the heterobinuclear ionic complex, $[RhIr(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dcpm)_2]^+[RhCl_2(CO)_2]^-$ (**3**), is achieved by reacting (**2**) with $[Rh(Cl)(CO)_2]_2$ (**4**) under N_2 in appropriate mole ratios.

The covalent heterobinuclear rhodium- iridium-dcpm complex, $[RhIr(Cl)_2(CO)_2(\mu\text{-}dcpm)_2]$ (**5**) is obtained by a slight modification of the synthesis for the ionic complex (**3**). Complex (**5**) can be reduced with sodium borohydride under a CO atmosphere to yield a complex tentatively formulated as $[RhIr(\mu\text{-}CO)(CO)_2(\mu\text{-}dcpm)_2]$ (**6**). The reactivity of (**6**) towards small molecules such us O_2, H_2, CO_2, and HCl will be discussed.

Acknowledgements: This work is supported by National Science Foundation, W. M. Keck Foundation, and the Jackson Endowment.

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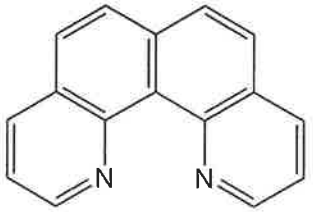
Towards Selective Small Cation Chelation

K. J. Shaffer[1] P. G. Plieger,[1]
1. *Institute of Fundamental Sciences, Massey University, Palmerston North, New Zealand*

The synthesis of quino[7,8-h]quinoline (of basic type **L**) was first published in 1987 and subsequently utilised as a proton sponge.[1] Twenty one years later and little has been explored in regards to the coordination chemistry of ligands of this type with just a handful of complexes currently published.[2] It strikes us that this small ligand with its tight binding pocket might be a useful binder of smaller cations such as boron and beryllium and may even impart selectivity of these smaller cations over less favourable larger ones. Our current progress will be outlined.



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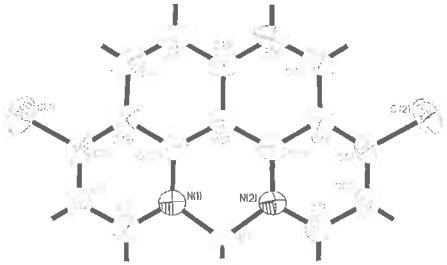

Acknowledgements: KJS would like to thank the NZ government for a Top Achievers Doctoral Scholarship.

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Bimetallic Catalyst System for Tandem Reactions

M. G. Timerbulatova, B. A. Messerle, J. H. H. Ho
School of Chemistry, University of New South Wales, Sydney, NSW 2052,
timerbulatova2007@yahoo.com

Polycyclic heteroatom containing molecules are attractive synthetic targets as they are often biologically active. However, traditional organic routes for the synthesis of such molecules commonly involves a number of steps resulting in low yields and high costs. An area of increasing interest is the simplification of synthetic processes, particularly the application of "one-pot" reactions to multiple step synthesis. Processes which involve multiple catalytic transformations in "one-pot" followed by a single work-up can lead to reduction in costs and production time.[1]

The goal of this work is to synthesise a multimetallic catalytic system which promotes two processes as a tandem reaction in "one-pot". A series of Ir and Rh bimetallic complexes containing bidentate N-donor ligands (Figure 1) have been synthesised and shown to be active for the dihydroalkoxylation reaction (Scheme 1).[2] Our studies have focused on a comparison of the catalytic activity of these bimetallic complexes with the activity of their monometallic analogues. We are using kinetic studies to establish the nature of the cooperativity between the two metal centers of the bimetallic complexes. We are also developing new bimetallic system for promoting hydroarylation and hydroamination reactions simultaneously.

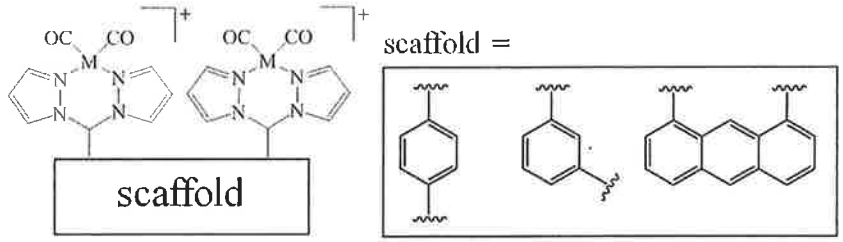
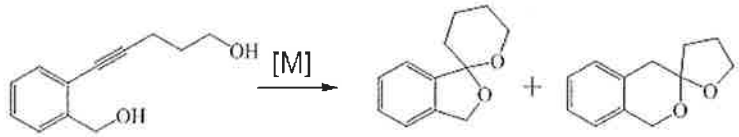


Figure 1. Schematic structure of Ir and Rh bimetallic complexes containing bidentate N-donor ligand



Scheme 1. Model catalytic reaction of dihydroalkoxylation

Acknowledgements: University of New South Wales for UIPA. Special thanks to all BAM group members of UNSW School of Chemistry.

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Pyrazol-1-yl- and Imidazolyl-Copper and Zinc Complexes as Initiators for the ROP of Lactide and ε-Caprolactone

J. L. van Wyk[1] J. Darkwa[1] D. Appavoo[1] M. Yankey[1] A. Bhaw-Luximon[2] and I. A. Guzei[3]

1. *Department of Chemistry, University of Johannesburg, Auckland Park Kingsway Campus, Auckland Park 2006, Johannesburg, South Africa*
2. *Department of Chemistry, University of Mauritius, Réduit, Mauritius*
3. *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706 , USA*

In recent years polyesters such as polylactide and polycaprolactone has received considerable interest due to the biodegradability and biocompatible properties of these polymers.[1,2] The most efficient method of producing these polyesters is by the ring opening polymerization (ROP) of cyclic esters using metal complexes or organocatalytic initiators.[3,4] A wide variety of initiating systems are known for the preparation of polyesters from lactides and lactones. However this area continues to generate interest due to the desire to develop initiating systems which allows control over the polymerization process in order to produce polymers with predictable physical properties. It has also been shown that the physical properties of a homopolymer may be altered by copolymerization with other cyclic ester monomers.[5] Thus initiators which show good activity over a wide monomer scope is of interest since this allow finetuning of the properties of the polymer.

Considerable research efforts have focused particularly on developing metal complexes containing biocompatible metals since complete removal of the initiator from the polymer is not possible.[6,7] In this paper the general coordination chemistry of zinc(II) and copper(II) metal complexes derived from pyrazol-1-yl and imidazolyl ligands, such as the complex shown in figure 1, will be discussed as well as the activity of these complexes in the ROP of D,L-lactide and ε-caprolactone.

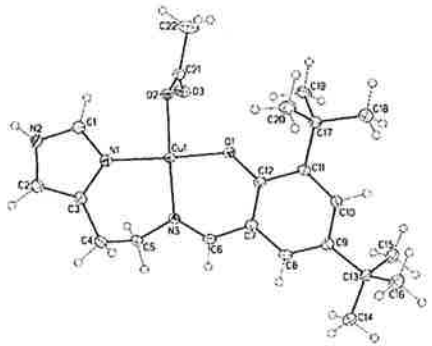

Figure 1: Copper(II) imidazolyl salicylaldimine complex.

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Polymer-Supported Vanadium Catalysts for Oxidation Reactions

R. S. Walmsley[1], Z. R. Tshentu[1]

1. *Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa, email: ryanwalmsley@gmail.com*

Vanadium-dependant haloperoxidases (VHPO's) are enzymes capable of catalyzing the oxidation of halides, leading to the formation of halogenated organic molecules. The active site of all VHPO's depicts vanadate coordinated to an imidazole nitrogen of a histidine amino acid.[1]

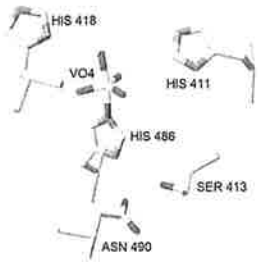

Figure 1. Active site of the vanadium dependant haloperoxidase *A. nodosum*, showing coordination of histidine 486 to vanadate.[2]

The oxidative capability of these enzymes has led to the development synthetic vanadium compounds which have proven successful not only in oxidative halogenation reactions, but also the oxidation of several other substrates.[3] The active site of the VHPO's has inspired us to immobilize imidazole-based ligands onto a polymeric support resulting in a ligand bound polymer which was subsequently reacted with vanadyl sulfate.

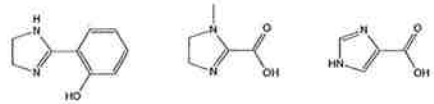

Figure 2. The ligands above have been anchored to a polymeric support. From left to right; 2-(2'hydroxyphenyl)imidazoline, 1-methylimidazole-2-carboxylic acid and imidazole-4-carboxylic acid

The resultant polymer-bound catalysts show promising catalytic activity for the oxidation of sulfides and alkenes as well as oxidative bromination reactions using hydrogen peroxide as the oxidant. The catalysts exhibited excellent recyclability with only very minor loss in activity after three consecutive catalytic experiments.

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Bipyridine type Ligand Bridged Complexes of Palladium(II) and Gold(III) as Carbon-Carbon Bond Formation Catalysts.

C. Young[1], B. C. B. Bezuidenhoudt and A. Roodt

1. *Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa*
   Email: technetium3006@hotmail.com

The processes used in the production of industrial and fine chemicals place an enormous burden on the environment, and it has become imperative to develop ways in which to conserve energy and minimize the adverse effects of these processes. One way in which this can be achieved is through the development of more efficient and effective catalysts.

Although a wide variety of metals are used in catalysis today, the platinum group metals still show the many promising catalytic properties [1]. Of all the transition metal catalysts, palladium displays the most versatility when applied to carbon-carbon bond formation reactions. In recent times, gold, a relatively noble metal in terms of catalysis, has also proved to be an excellent oxidation catalyst. Gold nanoparticles, in particular, show good activity in this regard[2]. Although these metals are relatively expensive, the proper exploitation of their catalytic potential can be profitable.

In this presentation, the catalytic properties of several bridged palladium(II) and gold complexes are explored with regards to the Wacker oxidation and Heck coupling. The square planar nature of the bipyridine based bridging ligands (Figure 1) can be used to promote optimum dispersion when these complexes are deposited onto supports. Crystal engineering techniques and substituent-support interactions are also exploited for the deposition process. The synthesized complexes are characterized by means nuclear magnetic resonance and single crystal X-ray diffraction.

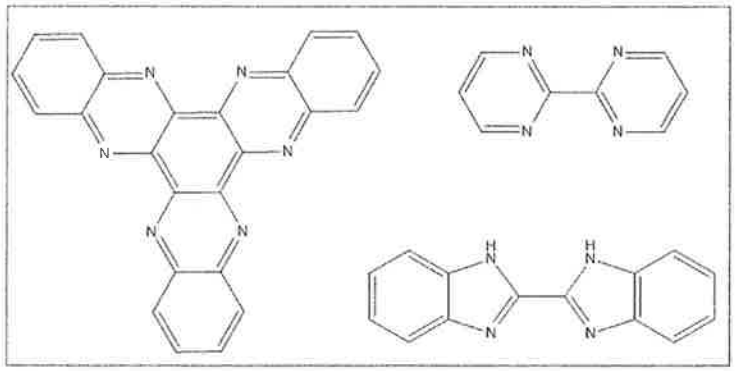

Figure 1: Square planar bipyridine bridging ligands.

Acknowledgements: University of the Free State and Sasol.

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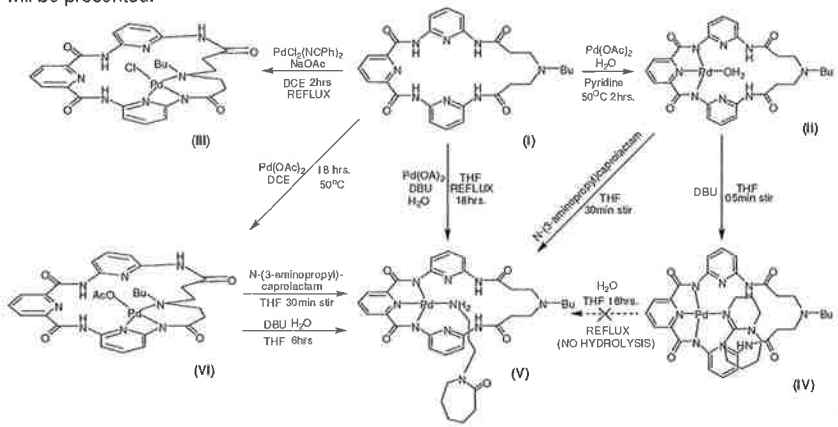
Synthesis and Characterization of Palladium complexes of a large macrocyclic ligand

M. N. Zafar, M.G. Burgess, L.J. Wright

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

mzaf001@ec.auckland.ac.nz

Macrocyclic ligands that are capable of coordinating a metal ion in such a way that bound substrate molecules can be activated both through interactions with the metal centre and strategically placed functional groups on the ligand backbone are an attractive synthetic target. Metal complexes of this type are expected to display new and unusual catalytic activity for reactions involving industrially important compounds.[1][2] The new amide- and pyridine-containing macrocyclic ligand H_4L_{nBu} (**I**) that contains two potential coordination pockets has been synthesized. Palladium coordinates to the head or tail region of **I** to give the complexes **II**, **III** or **VI** depending on the conditions employed. Water can be displaced from **II** by DBU or N-(3-aminopropyl)caprolactam to form **IV** or **V** (Scheme A). Alternately **V** (which has palladium coordinated in the head region) can be made directly from **VI** by treatment with DBU in THF for 6 hours. Further information about these complexes and the reactions they undergo will be presented.



Scheme A: Reactions of macrocycle (**I**) and its palladium complexes (**II-VI**)

Acknowledgements: Higher Education Commision Of Pakistan (HEC)

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Removal of Fluoride Ion by New Carbonaceous Materials in Aqueous Phase

N. Kawasaki[1], F. Ogata[1], H. Tominaga[1], S. Burapadaja[2], C. Loetkham[2]
1. *Faculty of Pharmacy, Kinki University, kawasaki@phar.kindai.ac.jp*
2. *Faculty of Pharmacy, ChiangMai University*

To maintain the safety and the reliability of drinking water, it must be treated with various technologies, including adsorption and decomposition. The quality of drinking water is very important for public safety and quality of life. Toxic cations, for example heavy metals, have been a serious problem, while anions, for example nitric ion and nitrous ion, can cause methemoglobinemia.[1] Moreover, the fluoride ion must be removed from tap and ground waters, because it causes teeth to become mottled. Fluoride derives from geological features and it is widely distributed in the natural world. Fluorine is contained in coal; when it burns, the fluorine spreads in atmosphere and then dissolves in water. Somebody who drinks drinking water containing the fluoride ion may suffer from mottled teeth and bone abortion. In this study, the adsorption characteristics of the fluoride ion onto various porous carbonaceous materials such as activated carbons, charcoal, carbon black and bone char are investigated. The effects of temperature, pH, and the presence of another anion were determined.[2]

The carbonaceous materials we used included 6 kinds of activated carbons (ACs), carbon black (CB), 4 kinds of charcoals (CCs), and bone char (BC). Activated carbons 1 and 3 (AC1 and AC3) were produced from coal; AC2, AC4, and AC5 were produced from wood; and AC6 was produced from petroleum coke. The charcoals were produced from *C. obtusa* (CC1), *Q. phillyraeoides* (CC2), *Q. mongolica* (CC3) and *Q. pubescens* (CC4). All carbonaceous materials are commercial. The iodine adsorption capacities are correlated to the specific surface area. The iodine adsorption capacities of ACs are larger than those of CCs and BC because AC1, AC2, AC3, AC4 and AC5 are activated by steam and AC6 by potassium hydroxide. The base and acid consumptions were the greatest in AC6 and BC, respectively. The base consumption of the carbonaceous materials indicated the number of carboxyl and phenolic hydroxide groups on the carbonaceous materials' surface. In other words, the number of these groups on AC6 was the greatest.

To estimate the adsobability of fluoride ion onto porous carbonaceous materials, the percentage of fluoride ion removal by each of them was measured. Two hundred mg of each carbonaceous material was added to 20 ml of fluoride ion solution at the concentration of 20 mg/L and was shaken for 3 h. The removal percentage of fluoride ion by BC was greater than that by ACs, CCs and CB. That of fluoride ion by CCs was the smallest. The removal percentage of fluoride ion by the carbonaceous materials, except for BC, increased with iodine adsorption capacity. This means that the adsorbability of the fluoride ion onto carbonaceous materials depends upon the specific surface area. Generally speaking, the amount of adsorbates adsorbed onto carbonaceous materials depends upon pore size distribution because adsorption occurs in pores. Generally speaking, the adsorption of organic compounds onto carbonaceous materials is based on exothermic adsorption. The adsorption isotherm of the fluoride ion onto BC was measured at different temperatures. The amount of fluoride ion that was adsorbed increased at higher temperatures. This result indicated the adsorption mechanism of fluoride ion onto bone char is an endothermic reaction, that is, the phosphate in BC consumes heat in exchanging with a fluoride ion.

In conclusion, (1) the adsorption ability of the fluoride ion on BC is the greatest of all carbonaceous materials, (2) the amount of fluoride ion adsorbed onto AC increased with the specific surface area of AC, (3) the adsorption mechanism of the fluoride ion onto BC is the reaction between calcium phosphate and fluorine, (4) the chemical adsorption of the fluoride ion onto BC is endothermic, (5) the amount of fluoride ion adsorbed increased with decreasing pH, and (6) the adsorption of the fluoride ion onto BC in a sodium chloride solution increased due to "salting out".

Acknowledgements: This study was financially supported by the Ministry of Education, Culture, Sports, Science and Technology under the "Antiaging Center Project" of Private Universities, 2008–2012.

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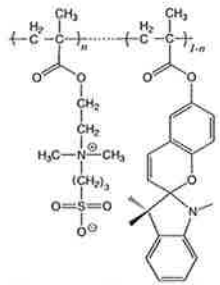
Photo-reversible and Cu^{2+}-selective Complexation of Sulfobetaine Copolymer Ligand in Aqueous Solution

T. Suzuki[1], Y. Hirahara[1], K. Bunya[1]
1. *Department of Green & Sustainable Chemistry, Faculty of Engineering, Tokyo Denki University, 2-2 Nishiki-cho Kanda, Chiyoda-ku, Tokyo, Japan, E-mail: suzutaka@cck.dendai.ac.jp*

Upon irradiation with UV or visible light, spiropyrans isomerizes between open and closed forms, respectively. Metal ions can influence this isomerization by association with the open form through electron-rich oxygen atoms. In contrast, visible light produces high concentrations of the closed form, and thus hinders metal binding. Spiropyrans, therefore, have potential for providing photo-reversible metal complexation. However, some problems of spiropyrans remain as a material for repeated-use metal ion sensing, *i.e.* "real-time" monitoring of metal ions, for biological and environmental applications: (a) high sensitivity to a target metal ion, and (b) photo-reversible function in an aqueous environment with no organic solvent. However, no accounts of spiropyrans showing specific binding to a target metal ion in a purely aqueous environment have been reported because of the difficulty of satisfying the requirements for (a) and (b) with one molecule. The molecular structure of the spiropyrans, especially modification of the pyran ring, is likely to influence the isomerization characteristics of the closed and open forms and their metal complexation characteristics. The application of spiropyran-carrying copolymers has been reported for use in aqueous solution.[1, 2]
A sulfobetaine copolymer (**1** shown in Chatpter 1) carrying a photochromic spiropyran residue was synthesized, which reversibly isomerized between the closed and open forms in pure water and in saline by irradiation with visible light. The thermodynamic stability of the open form of the spiropyran methacrylate (SPMA) units of compound **1** was reduced upon increasing NaCl concentration. In addition, photo-reversible and selective Cu^{2+} complexation in saline solution ([NaCl] = 1.0 wt%) was achieved using compound **1** with metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, or Co^{2+}). Covalently cross-linked compound **1** showed selective Cu^{2+} adsorption in pure water. In contrast, the other metal ions were increasingly adsorbed as NaCl concentration increased, resulting in lower selectivity of Cu^{2+} ion adsorption with **1**, *e.g.*, the ratios of adsorption of Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} with **1** in 10 wt% saline were 73, 20, 10, and 3%, respectively, while only Cu^{2+} adsorption was observed in a solution of 1.0 wt% NaCl. Because the stability of the open form of the SPMA units and the metal complexation of **1** were influenced by NaCl concentration, the electrostatically cross-linked networks of the zwitterionic sulfobetaine units of **1** may be loosened by NaCl addition, resulting in easy entry of metal ions into the network. The order of metal complexation among the four metals corresponded to the Irving–Williams series. Hydrogen-bonded networks of water molecules also may contribute to the relatively ineffective selective adsorption of Cu^{2+} ions by **1** compared to the electrically neutral spiropyran-carrying copolymer of *N*-isopropylacrylamide.



Chapter 1 Structure of **1**

Acknowledgements: We thank the Research Institute for Technology (No. Q09M-02) of Tokyo Denki University, Japan.

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Comparative study on the electrochemical behavior of Cobalt-, Nickel- and Iron complexes with various salen ligands

D. Komatsu[1], T. Ueda[1], A. Onda[2], A. M. Bond[3]

1. *Department of Applied Science, Faculty of Science, Kochi University, Kochi 780-8520, Japan; chuji@kochi-u.ac.jp*
2. *Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, 780-8073, Kochi, Japan*
3. *School of Chemistry, Monash University, Clayton, Vic. 3800, Australia*

Metal Complexes with salen-ligands are important in catalysis and as model compounds for metalloenzymes and metalloproteins. It is well known that electrogenerated cobalt(I) and nickel(I) complexes with salen ligands catalyze de-halogenation reactions for halogenated organic compounds. We have now studied complexes with similar catalytic behavior to cobalt(II)- and nickel(II)-salen complexes. Electrogenerated Fe(I)Cl-salen complexes also catalyze de-halogenation reactions in acetonitrile. In this study, we have examined in detail the catalytic behavior of cobalt, nickel and iron complexes with different kinds of salen-ligands in a range of solvents both in the absence and presence of halogenated organic compounds (Fig. 1). In addition, the effect of cations on the voltammetric behavior was investigated and digital simulations were performed to explore the redox mechanism.

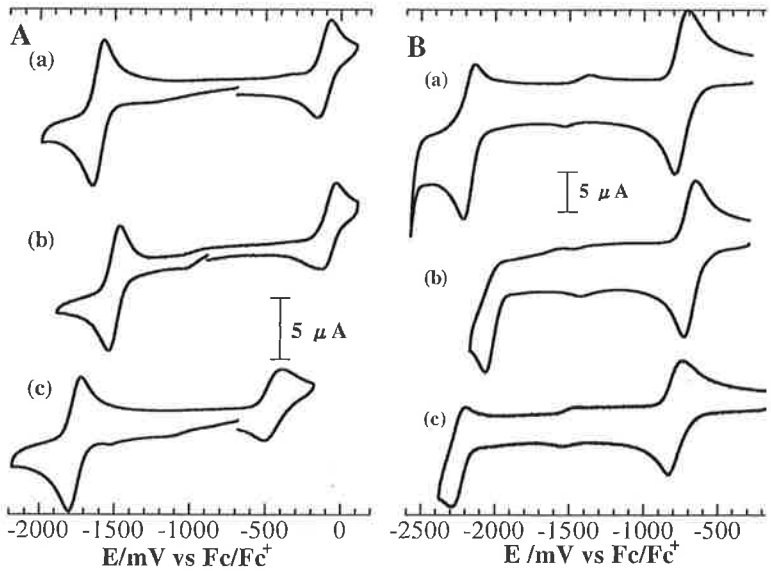

Fig. 1 Cyclic voltammograms of (A) 0.25 mM cobalt and (B) 0.5 mM iron complexes with (a) salen, (b) salophen, and (c) cyclohexane-salen as a ligand, respectively, in CH_3CN containing 0.1 M n-Bu_4NPF_6. Scan rate: 0.1V/s.

Synthesis and Characterization of Novel Vanadium(V)-substituted Wells-Dawson Type Tungstosulfates

M. Ohnishi[1], S. Yokoyama[1], T. Ueda[1], D. Kaneno[1], J. F. Boas[2], A. M. Bond[3]

1. *Department of Applied Science, Faculty of Science, Kochi University, Kochi 780-8520, Japan; gomasesami@yahoo.co.jp*
2. *School of Physics, Monash University, Clayton, Vic. 3800, Australia*
3. *School of Chemistry, Monash University, Clayton, Vic. 3800, Australia*

Polyoxometalates (POM) are inorganic clusters that consist of addenda ions such as molybdate and tungstate and hetero ions such as phosphate and silicate. Although POMs have been studied for 200 years, many aspects of their formation mechanism and redox behavior remain ambiguous even though they have been widely applied in fields such as biochemistry, materials science and catalysis. Recently POM research has been focused on development of environmentally friendly acid and oxidation catalysts. It is also known that the redox potentials of vanadium-substituted POMs are more positive than non-substituted ones, indicating that substituted ones will be stronger oxidants than non-substituted ones. In this study, we have isolated new Wells-Dawson type vanadium(V)-substituted tungstosulfate complexes (Fig. 1). Although non vanadium-substituted tungstosulfate, $[S_2W_{18}O_{62}]^{4-}$ has been isolated and characterized,[1-4] there are few reports on vanadium-substituted ones.

n-Bu_4N^+ salts of $[S_2VW_{17}O_{62}]^{5-}$ have been prepared and isolated from a W(VI)-V(V)-H_2SO_4-CH_3CN system in two isomeric forms 1-$[S_2VW_{17}O_{62}]^{5-}$ and 4-$[S_2VW_{17}O_{62}]^{5-}$, that have different vanadium-substitution positions. 1-$[S_2VW_{17}O_{62}]^{5-}$ and 4-$[S_2VW_{17}O_{62}]^{5-}$ were prepared and isolated by altering the order of adding V(V) to the reaction mixture. These POMs were characterized by IR (Fig. 2), Raman and NMR spectroscopy. In addition, detailed electrochemical analysis of the $V^{V/IV}$ couple and its dependence on acidity was undertaken in CH_3CN (100 mM n-Bu_4NPF_6) with the aid of NMR and ESR measurements.

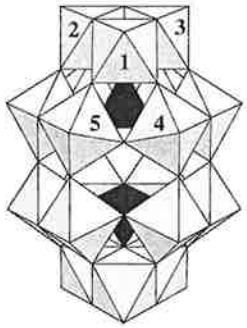

Fig. 1 Strucrure of Wells-Dawson type POM

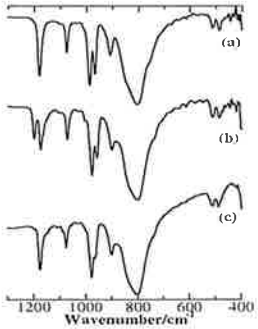

Fig. 2 IR spectra of n-Bu_4N salt of (a) $S_2W_{18}O_{62}^{4-}$, (b) 1-$S_2VW_{17}O_{62}^{5-}$, and (c) 4- $S_2VW_{17}O_{62}^{5-}$ in the KBr pellets.

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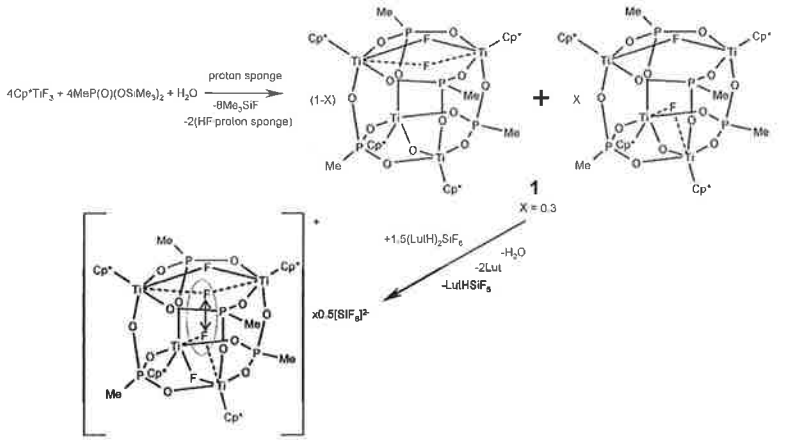
The Titanophosphonate Cage Compounds with a Rattling Fluoride Ion

A. Pevec[1], F. Perdih[1], J. Pinkas[2], J. Košmrlj[1], G. Mali[3], A. Levstik[4], C. Filipič[4], A. Demšar[1]
1. *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Sloven*
andrej.pevec@fkkt.uni-lj.si
2. *Department of Chemistry, Masaryk University Brno, Czech Republic*
3. *National Institute of Chemistry, Ljubljana, Slovenia*
4. *Jozef Stefan Institute, Ljubljana, Slovenia*

The fluoride anion is frequently found in small cages of microporous materials prepared from fluoride-containing mixtures. The cages that contain fluoride are cubes $M_4P_4O_{12}$[1], bicapped cube $V_4P_4O_{14}$[2] and silica cages[3]. The fluoride anion is either in the centre of the cage or bonded off-centre to one, two or three silicon or metal atoms.
We report herein the syntheses and characterization of titanophosphonate cage compounds $[(Cp^*TiO_3PMe)_4(\mu\text{-}F)_2(\mu\text{-}O)]$ (**1**) and $[(Cp^*TiO_3PMe)_4(\mu\text{-}F)_3]_2SiF_6$ (**2**) with the fluorine atom within the cage. The synthesis of **1** was achived by the reaction of Cp^*TiF_3, $MeP(O)(OSiMe_3)_2$ stoichiometric amount of water and 1,8-bis(dimethylamino)naphthalene (proton sponge). The treatment of **1** with $(LutH)_2SiF_6$ (Lut = 2,6-dimethylpyridine) in toluene solution gave ionic compound **2** with the SiF_6^{2-} as a charge-compensating anion (Scheme 1). The X-ray structures of both compounds are best described as $Ti_4P_4O_{12}$ cubes bicapped with the oxygen and the fluorine atom (**1**) or with two fluorine atoms (**2**). The interior of the titanophosphonate cage in both compounds shows two electron density maxima that can be refined as a single disordered fluorine atom. The combined results of the X-ray structure and the solid-state ^{19}F and ^{31}P NMR spectra of **1** and **2** suggest that in the case of compound **1** two isomeric molecules exist in the solid state. Contrary, the fast dynamic between two positions of the inside fluorine atom of compound **2** can be found even in the solid state by solid-state NMR.
The new compounds **1** and **2** were characterized by elemental analysis, IR spectroscopy, ^1H, ^{19}F, ^{31}P VT NMR spectroscopy, ^{19}F, ^{31}P solid-state NMR spectroscopy, ESI-MS spectroscopy, dielectric spectroscopy, DSC measurements and single-crystal X-ray diffraction. The dynamics of cage fluorine was calculated for isolated model compounds by quantum mechanical calculations.



Scheme 1

Acknowledgements: This work was supported by the grant P1-0175 from the Ministry of Higher Education, Science and Technology, Republic of Slovenia.

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Activation and Cleavage of the N-N Bond in Side-On Bound $[L_2M\text{-}NN\text{-}ML_2]$ (L = NH_2, NMe_2, N^iPr_2, C_5H_5, C_5Me_4H) Transition Metal Complexes of Dinitrogen

R. Stranger,[1] G. Cavigliasso,[1] B. F. Yates[2]
1. *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, (rob.stranger@anu.edu.au)*
2. *School of Chemistry, University of Tasmania, Hobart, TAS 7001, Australia*

The activation and cleavage of the N-N bond in side-on bound $[L_2M\text{-}NN\text{-}ML_2]$ (L = NH_2, NMe_2, N^iPr_2, C_5H_5, C_5Me_4H) dinitrogen complexes of transition metals in groups 4 through to 9 have been investigated using density functional theory. Calculations on these species have shown that when the terminal $[ML_2]$ fragments adopt a perpendicular orientation with respect to the central [N-N] unit, a considerably higher degree of N-N activation is predicted relative to that observed in the experimentally characterized cyclopentadienyl analogues of group 4 metals (Ti, Zr, Hf) and in related systems involving end-on dinitrogen coordination. An examination of the orbital interactions between the metal-based fragments and the dinitrogen unit shows that both δ and δ bonding are important in the side-on binding mode, in contrast to the end-on mode, where metal-nitrogen δ interactions are dominant. A significant result obtained for the amide complexes containing metals from groups 5 (V, Nb, Ta), 6 (Cr, Mo, W), and 7 (Mn, Tc, Re), is the presence of metal-metal bonding in configurations that are considerably distorted from planarity. As a consequence, these complexes exhibit strongly enhanced stability relative to species where metal-metal bonding is absent. In contrast, the d^2 metal-based configurations in the group 4 complexes of Ti, Zr, and Hf are unable to provide the six electrons required for complete reductive cleavage of the dinitrogen unit which is necessary in order for the metal centres to approach one another sufficiently for metal-metal bond formation.

Metal-Dinitrogen Bonding Orbitals in $[(NH_2)_2Zr\text{-}(\Delta_2,\Delta^2,\Delta^2\text{-}N_2)\text{-}Zr(NH_2)_2]$

Metal-Metal Bonding Orbitals in $[(NH_2)_2Re\text{-}(\Delta_2,\Delta^2,\Delta^2\text{-}N_2)\text{-}Re(NH_2)_2]$

Acknowledgements:
The authors gratefully acknowledge the Australian Research Council for financial support and the Australian National University for access to the supercomputer facilities of the NCI (National Computational Infrastructure).

Synthesis and Characterization of novel Polyoxometalates with Inverted-Keggin Structure

T. Ueda[1], K. Machida[1], M. Shiro[2], T. Yonemura[1], D. Kaneno[1]

1. *Department of Applied Science, Faculty of Science, Kochi University, Kochi 780-8520, Japan; chuji@kochi-u.ac.jp*
2. *X-ray Research Laboratory, Rigaku Corporation, Akishima, Tokyo 196-8666, Japan*

Polyoxometalates (POMs) have a variety of structure such as, so-called, Keggin, Wells-Dawson, Andersson. Recently, there have been a lot of reports on the synthesis of huge POMs with different valence of molybdate(VI/V) and tungstate(VI/V), and functionalized POMs. The structure of POMs mainly depends on that of hetero ions. The POMs with tetrahedral hetero ions such as SiO_4^{4-}, PO_4^{3-}, and SO_4^{2-} lead to Keggin- and Wells-Dawson-type structure. Additionally, Lacunary species and sandwich-type POMs with tetrahedral hetero ions have been derived by removal of a few of molybdate and tungstate units of Keggin and Wells-Dawson. Based on this idea, novel POMs could be prepared if other types of hetero ions except for tetrahedral hetero ions were used. We have tried to prepare and characterize novel POMs containing $P_2O_7^{4-}$, PHO_3^{2-}, SeO_3^{2-}, and TeO_3^{2-}.[1-3] Recently, other POMs containing methylphospate or ethylphosphate as hetero ions could be prepared in aqueous-organic mixed media. X-ray analysis indicated both of them had Inverted-Keggin structure (Fig. 1).[4] It was the first time to prepare Inverted-Keggin type POMs containing organophosphate, although POMs containing arsenate and organoarsenates with Inverted-Keggin structure had been already reported. In this study, we have tried to prepare other POMs containing various organophosphates. Some of them have been found to have Inverted-Keggin structure by X-ray analysis. They were characterized with IR, Raman, UV-Vis, NMR, and X-ray analysis to be compared to one another (Fig. 2).

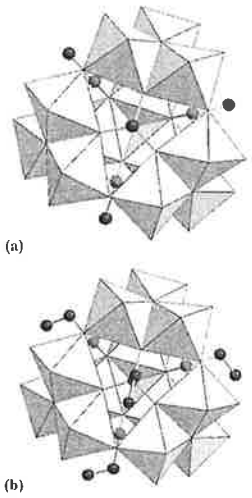

Fig. 1 Strucrure of (a) Molybdo-methylphosphate and (b)–ethylphosphate.

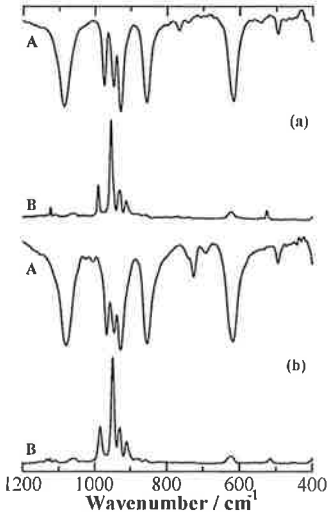

Fig. 2 IR (A) and Raman (B) spectra of (a) Molybdo-methylphosphate and (b)–ethylphosphate.

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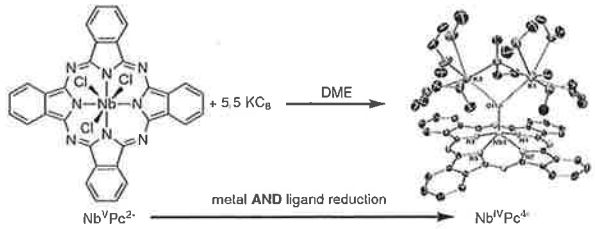
Structure and Electronic Properties of a Niobium(IV)-oxo Complex Incorporating a Redox-active Phthalocyanine Ligand

E. W. Y. Wong[1], C. J. Walsby[1], T. Storr[1], D. B. Leznoff[1]

1. *Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6*

Reports of transition metal complexes with redox-active ligands are becoming increasingly more common. Redox-active ligands have been shown to augment the reactivity of a complex and this new reactivity has been exploited for the design of new catalysts.[1,2] The redox-active nature of phthalocyanines (Pc) is well-known, but their use as redox-active ligands is relatively unexplored. Our initial studies have been focused on the reactivity of reduced niobium phthalocyanine complexes.

The reduction of $PcNbCl_3$ with 5.5 equivalents of potassium graphite in 1,2-dimethoxyethane (DME) resulted in the isolation of $K_2PcNbO{\cdot}5DME$ (**1a**). Addition of 18-crown-6 to **1a** gave $[K(18\text{-crown-}6)]_2(\mu\text{-DME})PcNbO$ (**1b**). Both **1a** and **1b** were structurally characterized by single crystal X-ray diffraction analysis.[3] Details of the spectroscopic techniques and density functional theory (DFT) calculations used to establish the electronic structure of **1a** will be discussed. These results illustrate the value of Pc as a chemically inert, redox-active ligand for stabilizing reactive metal centres. In addition, recent advances in exploring the reactivity of the Nb=O bond of **1a** and the synthesis of substituted-phthalocyanine niobium complexes will be presented.



Acknowledgements: We thank the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University for financial support and WestGrid for computational resources.

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Molecular Alloys - Concentration Gradients in $K_3[M^{(III)}_xM^{(III)}_{1-x}(C_2O_4)_3]$ Crystals

J. Bouzaid[1], J. McMurtrie[1], T. Nguyen[1], T. Bostrom[1], L. Rintoul[1],
1. *Chemistry, Queensland University of Technology, j.bouzaid@qut.edu.au*

Since its conception, supramolecular chemistry has evolved rapidly and diverged into many specialised areas. A common objective across all of these areas is the desire to manipulate the molecular components and reaction conditions to engineer supramolecular materials to exact specifications.
In this project Raman spectroscopy together with X-ray crystallography (single crystal and powder) and scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) were used to characterise single crystals of the generic formula $K_3[M^{(III)}_xM^{(III)}_{1-x}(C_2O_4)_3]$; where $M^{(III)}$ is a trivalent metal ion such as $Cr^{(III)}$ and $Fe^{(III)}$. The crystals were formed by co-crystallisation from solutions containing two different $K_3[M^{(III)}(C_2O_4)_3]$ complexes in varying ratios to yield single "co-crystals" containing both metal complex species.
Research into the growth of crystals from solutions containing two or more different metal complexes has been reported,[1-5] however the outcomes of this project are to our knowledge novel and undocumented. We report the formation of single co-crystals that exhibit directional intracrystal concentration gradients (figure 1). $[M^{(III)}(C_2O_4)_3]^{3-}$ complexes are known to possess interesting magnetic properties depending on the coordinating metal ion, for example substituting $Fe^{(III)}$ for $Cr^{(III)}$ introduces competing ferri- and ferromagnetic interactions.[6,7] The presence of a concentration gradient presents the potential for a single crystal to display a continuously varying degree of magnetism (and/or other physical property) between two extremes.

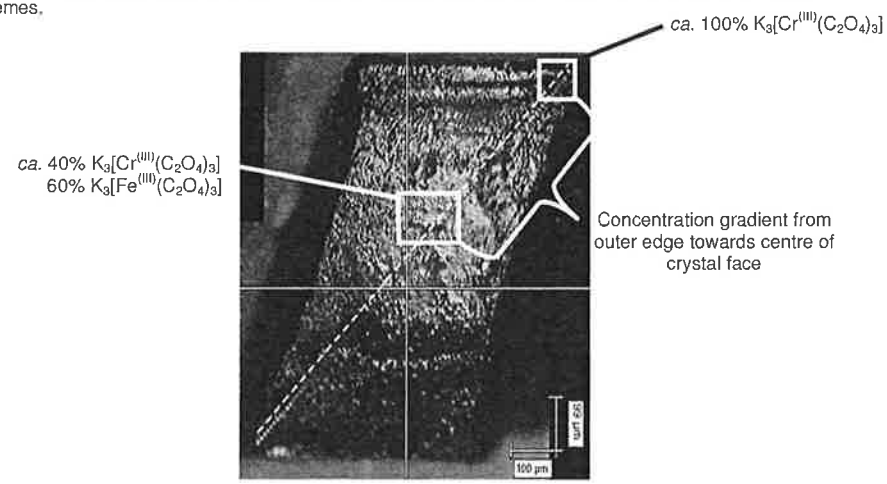

Figure 1. Image of a single co-crystal formed from a 50%:50% $K_3[Cr^{(III)}(C_2O_4)_3]$: $K_3[Fe^{(III)}(C_2O_4)_3]$ solution exhibiting a directional intracrystal concentration gradient.

Acknowledgements: JB acknowledges the APA and DVC scholarships.

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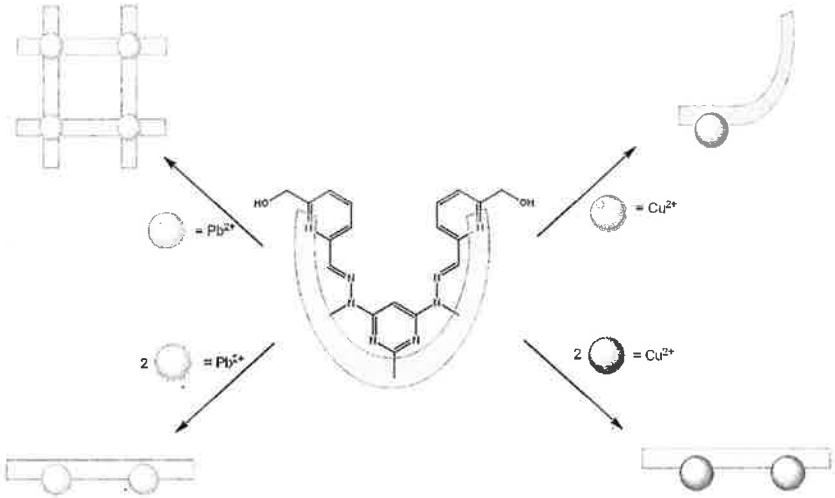
Modified Pyrimidine-Hydrazone Molecular Strands for Supramolecular Acuation

D. J. Hutchinson[1], L. R. Hanton, S. C. Moratti
1. *Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, dhutchinson@chemistry.otago.ac.nz*

In recent years polymer gels have emerged as a new actuating technology due to their characteristically large volume changes that can triggered by a range of external stimuli such as applied voltage, incidence of light, changes in pH and changes in temperature.[1] We are currently working towards creating a polymer gel which exhibits expansion and contraction due to dynamic changes in the ligand component of the gel upon coordination with metal ions.

To this end we have synthesised a series of pyrimidine-hydrazone (pym-hyz) strands that have terminal hydroxymethyl or acryloyl groups. These functional groups allow the pym-hyz strands to be incorporated into a co-polymer gel network. X-ray crystallography studies have shown that the strands are coiled in their free state, with the pym-hyz linkages in a *transoid* conformation. Upon coordination with metal ions the strands uncoil into a linear arrangement as the pym-hyz linkages rotate to a *cisoid* conformation.[2] Copper(II), lead(II), zinc(II) and silver(I) ions have all been shown to cause this dynamic change, resulting in a variety of complex shapes including linear, grid and double helix motifs.

The terminal hydroxymethyl and acryloyl groups have been found to contribute to the supramolecular chemistry of these strands through coordination to the metal ions and intermolecular H-bonding, resulting in interesting supramolecular arrangements. The pym-hyz strands and their varied metal complexes will be presented.



Acknowledgements: The authors would like to acknowledge the Department of Chemistry, University of Otago, and the New Economic Research Fund of the Foundation for Research, Science and Technology (NERF Grant No. UOO-X0808).

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Synthesis of a novel functionalised Cobalt (III) caged surfactant – Coordination Chemistry for the 21st Century

G. E. Jaggernauth[1], R. A. Fairman[1]

1. *The University of the West Indies, St. Augustine.* Gina.Jaggernauth@sta.uwi.edu

We report the synthesis and characterization of a novel amphiphilic derivative of the hexamine cobalt cage ligand known for short as Co[diAMsar],[1] (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane). The sarcophagine cage is a useful head group because it is large, highly charged, redox active and some examples have shown biological activity.[2] Functionalisation of only one terminal amino group was achieved through a modified carboxymethylation [3] procedure and an aza-crown ether attached to the precursor through an amide linkage. The molecule shows dramatic solvatochromism, shifting from the usual orange colour of diAMsar complexes in aqueous solution (λ_{max} 470 nm) to a bright green in organic media (λ_{max} 680nm) below the critical micelle concentration. Surface pressure isotherms were recorded in water (mean molecular area of 84 $Å^2$) and with 1mM $MgSO_4$ subphase (molecular area 116$Å^2$) where selectivity for the Mg^{2+} ion is found. The amphiphilic crown moiety without the cobalt cage shows similar interaction with different metal ions in the subphase.

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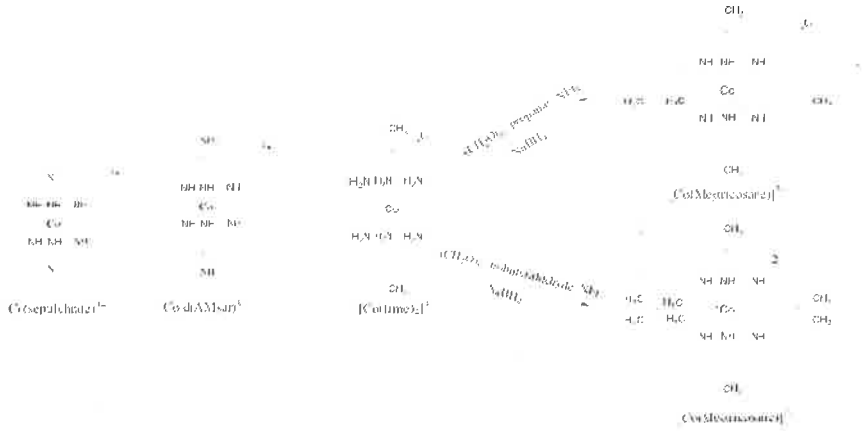
Stretching Metal – Ligand Bonds through Encapsulation of Metals in "Large" Cages

L. James,[1] L. J. Alcock[1], S. F. Ralph,[1] E. M. Bortolus,[1] M. S. B. Mastuli,[1] C. Lloyd,[1] and P. V. Bernhardt[2]

1. *School of Chemistry, University of Wollongong, Wollongong, NSW, 2522*
2. *School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Qld, 4072*

The ability of hexaamine ligands such as sepulchrate and diamsar to complex metal ions, and the properties of the resulting complexes, has been extensively investigated. Initial attempts to adapt the metal template procedure used for preparing these ligands to synthesise analogous cages with larger cavities were unsuccessful. Eventually, however, a procedure using $[Co(tame)_2]^{3+}$ (tame = 1,1,1-tris(aminomethyl)ethane) as a starting material was developed which led to the synthesis of a new cage ligand, Me_5tricosane.[1] Encapsulation of metal ions by Me_5tricosane in some cases confers remarkable properties on the resulting complexes. For example, $[Co(Me_5tricosane)]^{3+}$ has Co-N bond lengths that are ~ 0.05 – 0.06 Å longer than those of typical Co^{III}-N(amine) complexes, resulting in significant changes also to the absorption spectrum and electrochemical properties of the CoN_6 chromophore.[1] Complexation of Cu^{II} by Me_5tricosane results in a complex that displays quasi-reversible Cu^{II}/Cu^{I} electrochemistry from cyclic voltammetry experiments.[2] Both sets of observations are consistent with the idea that Me_5tricosane provides an environment that favours unusually long coordinate bonds.

While the coordination chemistry of Me_5tricosane has now been explored with a number of transition metal ions, virtually nothing is known about the properties of complexes of the closely related ligand Me_8tricosane. Despite their structural similarities, it appears that Me_8tricosane may offer an even larger cavity for metal ions than Me_5tricosane. Evidence in support of this is provided by the observation that the Co^{II} ion in $[Co(Me_8tricosane)]^{2+}$ is sufficiently stabilised within this ligand environment that the metal complex is stable towards oxidation in air.[3] This paper will present results obtained from recent investigations into the structural, spectroscopic and chemical properties of metal complexes of both Me_5tricosane and Me_8tricosane.



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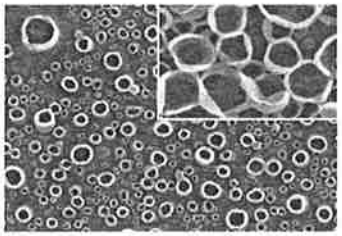
Formation and Related-behavior of Micro-bowl and Micro-sprout Morphology Consisting of Ionic Palladium(II) Complexes

O. S. Jung[1], C. R. Kim[1], Y.-A. Lee[2]

1. *Department of Chemistry, Pusan National University, Pusan 609-735, Korea; e-mail: oksjung@pusan.ac.kr*
2. *Department of Chemistry, Chonbuk National University, Jeonju 570-752, Korea*

Reaction of $[(bpy)Pd](PF_6)_2$ (bpy = 2,2'-bipyridine) with racemic bis(isonicotinoyl)-1,1'-bi-2-naphtholate (L) in acetone, and followed by addition of chloroform and solvent evaporation allows to form amorphous micro-bowl morphology consisting of $[(bpy)PdL]_2(PF_6)_4$ without any template or additive. In contrast, the reaction and recrystallization in acetone for 1 week produce parallel-piped single crystals consisting of $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$. The formations of micro-bowl and parallel-piped single crystal morphologies appear to be primarily associated with the kinetic and thermodynamic control, respectively. The reaction of $(tmeda)Pd(ClO_4)_2$ (tmeda = *N,N,N',N'*-tetramethylethylenediamine) with L (L = bis(4-(4-pyridylcarboxyl)phenyl)methane) affords the ionic cyclodimeric palladium(II) complex $[(tmeda)Pd(L)]_2(ClO_4)_4$. The complex forms an unprecedented micro-sprout morphology via slow evaporation of acetone in a dilute concentration mixture of acetone and water without any template or additive. The formation-process of the micro-sprout morphology has been explained by the stepwise concentration effect.



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Towards Ruthenium-based Metal-Organic Frameworks

J. R. R. Kanga[1], D. M. D'Alessandro[1], C. J. Kepert[1]

1. *Molecular Materials Group, School of Chemistry, The University of Sydney, Camperdown, NSW 2006, Australia*

The past decade has seen remarkable progress in the field of Metal-Organic Frameworks owing to their enormous structural and chemical diversity and their potential applications in gas storage, ion exchange, molecular separation and heterogeneous catalysis. These microporous crystalline solids are composed of organic bridging ligands coordinated to metal-based nodes to form a 3-D extended network with pore diameters in the range 3 to ca.50 Å. The nodes generally consist of one or more metal ions to which the organic bridging ligands coordinate via a specific functional group (e.g., carboxylate, pyridyl). To date, the vast majority of frameworks reported in the literature have consisted of transition metal ions of the first-row (e.g., Fe^{2+}, Co^{2+}, Ni^{2+} Cu^{2+} or Zn^{2+}), while examples of frameworks containing second-row transition metals are extremely rare owing to their relative inertness to ligand substitution.

This presentation will report our efforts towards the design, synthesis and characterisation of 3-D ruthenium-based frameworks based on the diruthenium paddlewheel cluster $[Ru_2(CH_3COO)_4]^{0/+}$, of which only one example has been reported to date.[1] These materials are expected to have significant potential for catalysis, gas sorption and redox switching.

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Double-Activated Supramolecular Reaction in Transesterification of Acyclic Oligoether Substrates and Metal Alkoxides

K. Kawakami[1], Y. Sei[2], K. Yamaguchi[2], A. Tsuda[1]

1. *Graduate School of Science, Kobe University, e-mail : tsuda@harbor.kobe-u.ac.jp*
2. *Kagawa School of Pharmaceutical Sciences, Tokushima Bunri University*

Biomolecules such as proteins dynamically change its conformation by metal ion recognitions to trigger a variety of biomolecular events. It is, thus, worthy to focus the studies on dynamic structure, potential functions, and specific reactions of supramolecular complexes, being constructed by noncovalent interactions.

With this background, we have previously reported a novel supramolecular reaction, where a host reaction substrate, can activate itself upon complexation with a metal ion. For example, our designed supramolecular complex **1**, in which *p*-benzoquinone bearing a long oligoethylene glycol (OEG) chain includes a metal ion, dramatically accelerated its Diels-Alder reaction with cyclopentadiene.[1,2] Effective electron withdrawal from *p*-benzoquinone moiety to metal ion, as Lewis acid, allowed such dramatic acceleration.

As an extension of this study, we will present herein a "Double-activated supramolecular reaction", where the supramolecular complexation activates both the host substrate and counter anion (alkoxide) of guest metal ion. We have designed a series of host substrates **2a–g**, and kinetically investigated their transesterification reactions with univalent or divalent metal alkoxides.

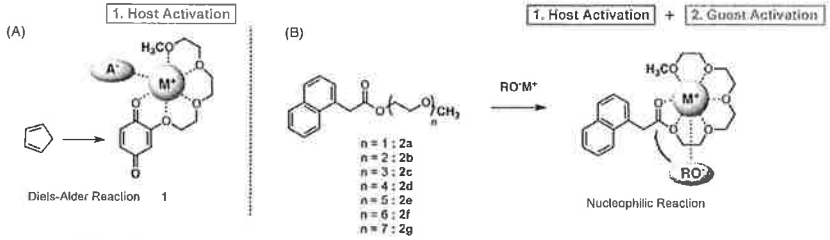

Figure 1. (A) Diels-Alder reaction of a self-activated supramolecular **1** with cyclopentdiene. (B) Double-activated suramlecular reaction upon complexation of host substrate **2** with a metal alkoxide

When the host substrates **2a–g** were mixed with a univalent alkaline metal methoxide in MeCN/MeOH (50:1) at 10 °C, they quantitatively afforded the corresponding methyl ester **3**. The reaction progress was monitored in HPLC, and the rate constant k_{obs} of each reaction could be calculated. The obtained k_{obs} values were plotted in Figure 2B. Interestingly, despite almost linear increase of binding constant of **2** with Na^+ or K^+ by elongation of the side arm, the maximum accelerations were achieved in **2c**/MeONa and **2d**/MeOK (4.3 and 6.7 folds accelerations from the corresponding **2a** complexes, respectively). Just fit complexation, where the carbonyl group participates into the interaction, may allow efficient electron withdrawing from the carbonyl group. In a case of divalent guest, $(EtO)_2Ba$, to our surprise, the longest **2g** gave the largest k_{obs} value, which is 1290 fold acceleration from that of **2a**, due to double activation of host substrate and alkoxide of guest metal ion.

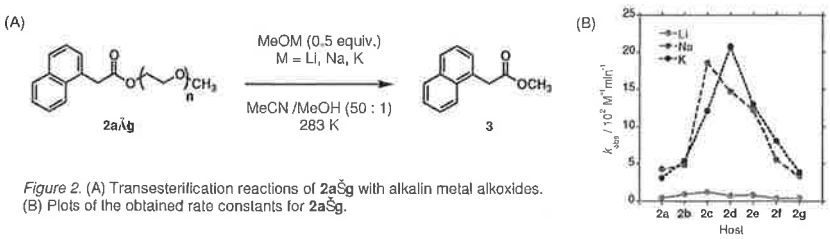

Figure 2. (A) Transesterification reactions of **2a–g** with alkalin metal alkoxides. (B) Plots of the obtained rate constants for **2a–g**.

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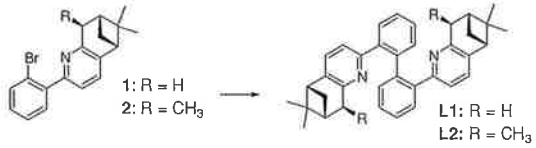
A New Class of Chiral Pyridine-Containing Ligands Base on a 1,1'-Biphenyl Bridge–Coordination Chemistry for the 21st Century

H. L. Kwong[1], K. C. Sham[1], C. S. Lee[1], K. Y. Chan[1], S. M. Yiu[1] and W. T. Wong[2]

1. *Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR (China)*
2. *epartment of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

Pyridine-containing ligands are important ligands in coordination chemistry. These ligands can be constructed by choosing suitable linker.[1-3] New chiral pyridine containing ligand **L1** and **L2**, based of 1,1'-biphenyl bridge, were synthesized by Ullman coupling of chiral bromopyridine.[2] Both **L1** and **L2** give conformers in solution and can be unambiguously assigned by NMR. Silver complexes [Ag(**L**)ClO_4] (**L1** or **L2**) were prepared by stirring the ligands with $AgClO_4$ in methanol. Copper complex, [Cu(**L**)I] of **L1** and **L2** were synthesized by reacting ligands with CuI in degassed acetonitrile under nitrogen. All the complexes were characterized by ESI-MS and elemental analysis. The ^1H NMR spectrum of [Ag(**L1**)(ClO_4)] in $CDCl_3$ shows two sets of signals with a ratio 4:1. These signals are assigned to be two diastereomeric forms of the complexes. The ^1H NMR spectrum of [Ag(**L2**)ClO_4] in $CDCl_3$ gives a single set of peaks. Single crystal of [Ag(**L2**)ClO_4] shows that it has a distorted tetrahedral geometry and suggested that the *S*-isomer is the major isomer observed in solution. Similar to the silver complexes, ^1H NMR spectrum of [Cu(**L1**)I] shows two set of signal in a ratio 2.9:1. The copper complex of more bulky **L2** is diastereoselectively formed with a ratio > 30:1. Single crystal of [Cu(**L2**)I] shows that it has a trigonal planar geometry having *S* planar charity.



Reaction conditions: Cu, degassed DMF, 100 °C.

Acknowledgements: Financial support for this research project from the City University of Hong Kong and the Hong Kong Research Grant council GRF grant (CityU 101108) are gratefully acknowledged.

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Formation and Physical Properties of New Photoluminescent Dithiocarbamate Pt(II) Complexes

Y. A. Lee, A. R. Han
Department of Chemistry, Chonbuk National University, Jeonju 561-756, South Korea, ylee@chonbuk.ac.kr

Reaction of K_2PtCl_4 with functional dithiocarbamate ligands (TC) produced new photoluminescent platinum(II) complexes, $Pt(TC\text{-}X)_2$ (TC-1 = methyl(2-(pyridine-2-yl)ethyl)dithiocarbamate, TC-2 = ethyl(pyridine-2-ylmethyl)dithiocarbamate, TC-3 = bis(pyridine-2-ylmethyl)dithiocarbamate). In crystal structure for $Pt(TC\text{-}1)_2$, each platinum(II) atom adopts a typical square-planar arrangement with four sulfur atoms of two dithiocarbamate ligands. The four pyridine rings of ligands are situated at the upward and downward from the platinum plane, which is possible coordinating site to other transition metals. $Pt(TC\text{-}X)_2$ series is a novel bidentate or tetradentate metallo-ligand to make various macromolecules. Interestingly, $Pt(TC\text{-}1)_2$ and $Pt(TC\text{-}3)_2$ show bright yellow luminescence (λ_{em} = 567 nm for $Pt(TC\text{-}1)_2$, 560 nm for $Pt(TC\text{-}3)_2$) at room temperature and solid state, but $Pt(TC\text{-}2)_2$ didn't show any luminescent properties even low temperature.

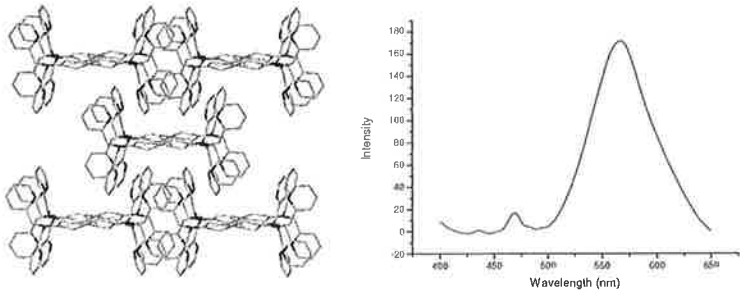

Fig. Packing diagram (left) and emission spectrum (right) for $Pt(TC\text{-}1)_2$

Acknowledgements: The authors thank KOSEF for supporting this work.

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Nuclear Sensors for Probing Chemistry of Nanopores – Optimizing the Engineering of the Next Generation of Nanomaterials.

S. V. Smith[1], E. Mume[1,2] and A. Uedono[3],
1. *Centre of Excellence in Anti-matter Matter Studies, Australian Nuclear Science and Technology Organisation, AUSTRALIA*
2. *Centre of Excellence in Anti-matter Matter Studies, Australian National University, AUSTRALIA*
3. *Institute of Applied Physics, University of Tsukuba, JAPAN.*

Engineering porosity in and functional groups on the surface of materials is used to enhance the absorption and loading capacity of drugs or chemicals or the surface reactivity of materials. It can improve the performance of technologies such as catalysts, filtration membranes, drug delivery vehicles, biosensors, batteries, anti-corrosion or self-healing media. Measuring and predicting how these changes influence the properties of the materials is very difficult, as ideally it requires the probing of solid-liquid interfaces *in situ*.

Transmission Electron Microscopy (TEM), BET, small angle neutron and X-ray scattering as well as positron annihilation lifetime spectroscopy (PALS) all provide valuable information about size of pores and their concentration within of materials. However, extensive sample preparation with some of these techniques, limit the range and or type of pores that can be measured. Furthermore, they generally can not provide information about the availability of the pores or the charge within these pores under conditions that are relevant to their intended application.

We have designed and synthesized a library of radiolabelled metal complexes or nuclear sensor, to probe transport, binding and surface reactivity of materials. Selected examples are given in Figure 1. Because the nuclear sensors are highly sensitivity (up to ppb) and their gamma emissions are independent of media, we are able to measure these interfaces *in situ*. Furthermore we use PALS to determine if and when the nuclear sensors are occupying the pores and under what conditions. This study reports how nuclear sensors and PALS can be used to evaluate the reactivity of pores within materials and the potential they have for application in high-throughput analysis of novel materials.

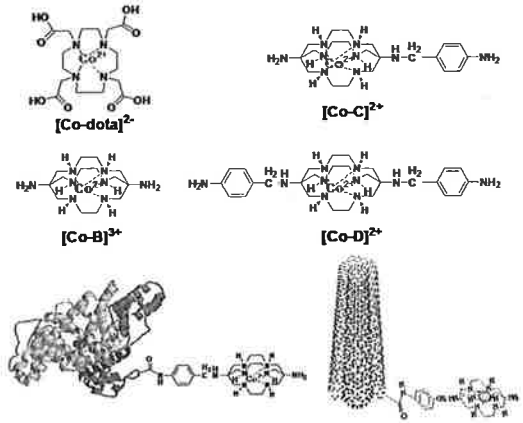

Figure 1. Schematic of nuclear sensors used to probe the surface reactivity and charge of nanopores in novel materials.

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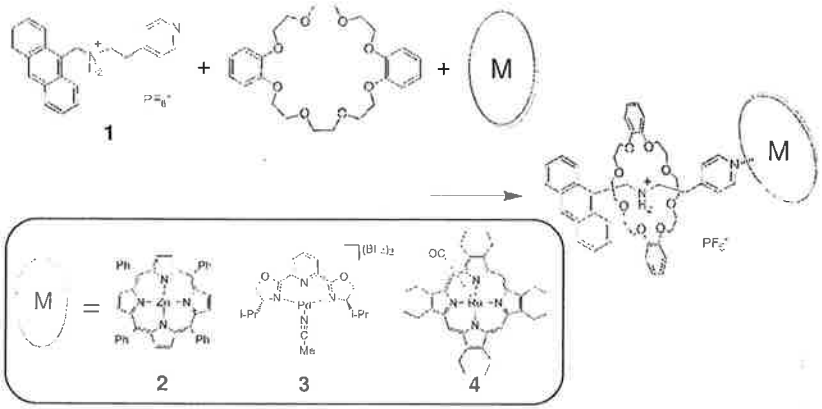
Dynamic Capping in Rotaxane Formation by Coordinate Bond

T. Maeda,[1] S. Shinoda,[1,2] H. Miyake,[1] and H. Tsukube[1,2]

1. *Department of Chemistry, Graduate School of Science, Osaka City University, Osaka, Japan maeda@sci.osaka-cu.ac.jp*
2. *JST, CREST*

Several metal complexes can be used as the stoppers in rotaxane formation by assembling processes.[1] We prepared a new series of metal complex-capped rotaxanes, in which the pseudo-rotaxanes formed between secondary ammonium-type thread **1** and 24-crown-8s were capped by zinc(II), palladium(II), and ruthenium(II) complexes **2–4**.
Dibenzo-24-crown-8 and its parent 24-crown-8 were confirmed to form the pseudorotaxanes with thread **1** in CH_3CN-$CHCl_3$ (3:7, v/v). NMR experiments revealed that the stability constants (log *K*) were 4.2 and 4.6 for dibenzo-24-crown-8 and 24-crown-8, respectively. When metal complex **2**, **3**, or **4** was added to the pseudorotaxane, the metal coordination capping between pyridine end and metal center was detected by NMR spectroscopy. Zinc porphyrin **2** gave a rapidly exchanging mixture in NMR time scale, while the other complexes **3** and **4** showed much slower capping/decapping rates. Chiral Pd(II) complex **3** particularly induced quenching of anthracene fluorescence and large circular dichroism changes at the *d-d* band region. ESI-MS studies indicated that 24-crown-8s gave intense signals corresponding to the rotaxanes, though smaller crown ethers gave only signals of thread **1** + metal complexes. As these metal complexes have enough sizes to cap the end of thread **1**, hydrogen bonding and metal coordination cooperatively promoted the dynamic rotaxane synthesis.



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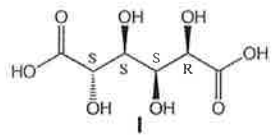
Coordination complexes of deprotonated aldaric acids

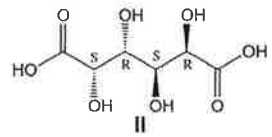
L. J. McCormick[1,2], B. F. Abrahams[1], M. J. Grannas[1], R. Robson[1], T. Waters[1]

1. *University of Melbourne, Victoria, Australia*
2. *l.mccormick2@pgrad.unimelb.edu.au*

Saccharic and mucic acids (I and II, respectively) are dicarboxylic acids that may be used as multidentate bridging ligands. The binding of these ligands is unpredictable due to the large number of potential metal binding sites. By combining saccharate or mucate with metal ions in the presence of terminal ligands such as 2,2`-bipyridine or 1,10-phenanthroline it is possible to generate 1D coordination polymers or discrete species.

Under aqueous conditions, a series of linear coordination polymers of composition M^{II}(sacc)(phen), M^{II}(sacc)(bipy), M^{II}(muc)(phen) or M^{II}(muc)(bipy) are formed (M = Mn, Co, Ni, Cu, Zn or Cd). These polymer chains interact through both hydrogen bonding and face-to-face aromatic interactions to form large channels. These channels are well suited to the incorporation of guest molecules such as H_2O or CO_2.





In methanol, two discrete clusters, both of composition $Cu_{21}(sacc)_6(phen)_{12}(NO_3)_{12}$, can be formed as two distinct phases. We have named these two remarkable clusters the 'Diabolecules'.

Figure 1: Channels within Cu(muc)(phen)

Figure 2: A $Cu_{21}(sacc)_6(phen)_{12}(NO_3)_{12}$ cluster.

Acknowledgements: The authors would like to thank the Australian Research Council.

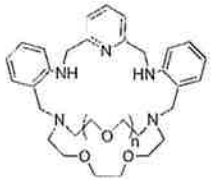
Lead(II) Complexes of Lateral Macrobicyclic Receptors Incorporating a Crown Moiety and a Pyridine Head Unit

T. Rodríguez-Blas[1], R. Ferreirós-Martínez[1], T. Enríquez-Pérez[1], M. Mato-Iglesias[1], C. Platas-Iglesias[1], D. Esteban-Gómez[1] and A. de Blas[1]

1. *Departamento de Química Fundamental, Universidade da Coruña, Alejandro de la Sota 1, 15008 A Coruña (Spain), E-mail: mayter@udc.es*

The interest in lead(II) coordination chemistry is related to the inherent toxicity and health effects of this element, and to the widespread industrial uses of its compounds.[1] Lead poisoning particularly affects young children who can absorb up to 50 % of ingested lead.[2] We are interested in the relation between structure and stability of lead(II) complexes with macrocyclic ligands derived from crown ether platforms, as well as in the role of the lone-pair activity of Pb(II) in these kind of compounds,[3,4] and the coordinative properties towards lead(II) of two lateral macrobicyclic receptors incorporating either a 1,10-diaza-15-crown-5 (**L**^{1}) or a 4,13-diaza-18-crown-6 (**L**^{2}) fragment are reported here.

Lateral macrobicycles are dissymmetrical molecules structurally based on the combination of two different binding subunits, a chelating one and a macrocyclic one. Considering the peculiar structural features shown by lateral macrobicycles, one could anticipate that this type of macropolycyclic architectures offer a range of interesting and potentially useful molecular recognition properties, as they offer the advantage of being preorganized and therefore capable of profiting from the thermodynamic macrobicyclic effect.



L^1: n = 1
L^2: n = 2

Spectrophotometric titrations performed in acetonitrile solution indicate the only formation of mononuclear complexes in solution. The X-ray crystal structures of the two receptors show that the conformation adopted by the ligand is imposed by the presence of intramolecular hydrogen-bonding interactions involving the secondary amine groups and the pivotal nitrogen atoms. The solid state structure of [Pb(**L**^{1})(NCS)](SCN)·0.5H_2O shows that the metal ion is asymmetrically coordinated inside the macrobicyclic cavity. The Pb(II) ion is coordinated to the nitrogen atoms of the pyridine units, the two secondary amine atoms, two oxygen atoms of the crown moiety, and a nitrogen atom of an isothiocyanate group. The distances between the Pb(II) ion and the two pivotal nitrogen atoms and one of the oxygen atoms of the crown moiety are too long (>2.92 Å) to be considered as unequivocal bonds, and must be regarded only as weak interactions. On the other hand, a comparison of the ^{1}H NMR spectra recorded for compounds [Pb(**L**^{2})](SCN)$_2$·0.5H_2O and [Pb(**L**^{2})](ClO_4)$_2$ shows that the nature of the counterion substantially affects the chemical shifts of the proton nuclei of the ligand, concluding that the thiocyanite coordination appears to provoke substantial changes in the structure of the complex.

The protonation constants of **L**^{1} and **L**^{2} and the stability constants of their complexes formed with Pb(II) were determined by potentiometric titrations in 95% methanol (I = 0.1 M, ^{n}Bu$_4$NClO$_4$, 25 ºC). The two receptors undergo two protonation processes in the pH range 2.0 < pH < 12.0, which correspond to the protonation of the nitrogen atoms of the oxa-aza moiety. The log K_{PbL} value obtained for **L**^{1} (9.906(1) is *ca.* 1.1 logK units higher than that determined for **L**^{2} (8.75(1)).

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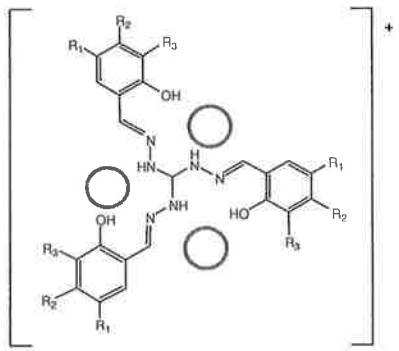
Rational design of heteroleptic complexes as small models for large supramolecular coordination compounds

A. C. Schulze[1], I. M. Oppel[1]

1. *Institute for Inorganic Chemistry, Rheinisch-Westfaelische Technische Hochschule Aachen, Landoltweg 1, 52074 Aachen, Germany, E-Mail: Carina.Schulze@ac.rwth-aachen.de*

We are interested in the coordination chemistry of differently modified derivatives of the C_3-symmetric ligand Tris(2-hydroxybenzylidene) triaminoguanidinium chloride (Figure and Table), which can exist in four different conformations (*aaa*, *aas*, *ass*, *sss*). In the *aaa* conformation the ligand is able to coordinate three metal centres in tris-chelating manner forming in this way building blocks which cover nearly completely a triangular face [1, 2].

Discrete coordination cages with the outer shape of tetrahedra [3, 4], an octahedron [5], a trigonal bipyramid [6] and a double-walled tetrahedron [7] could already be formed using different metal ions as Pd^{2+}, Zn^{2+} or Cd^{2+}. In addition to these compounds, several 'unexpected' complexes with quite flexible coordination modes at the metal centres were observed during the reaction of the ligand with e.g. Ga^{3+}, Zn^{2+} or Sn^{4+} ions [8].



R_1	R_2	R_3	abbreviations
H	H	H	$[H_6L]^+$
Br	H	H	$[H_6Br_3L]^+$
Br	H	Br	$[H_6Br_6L]^+$
Br	OMe	Br	$[H_6(OMe)_3Br_6L]^+$
Br	H	OMe	$[H_6(OMe)_3Br_3L]^+$

In order to learn more about the favoured types of connectivity in these systems and to simplify the sometimes very complex results we decided to block one or two coordination sites of the ligand with MPR_3-fragments (M = Pd^{2+}, Pt^{2+}; R = Et, Ph) leaving two or only one site(s) vacant for the coordination of a different metal centre like Cd^{2+} or Zn^{2+}. The resulting complexes and their characterisation is topic of the poster.

Acknowledgements: We would like to thank W. S. Sheldrick, C. Dietz and R. W. Seidel for support and helpful discussions

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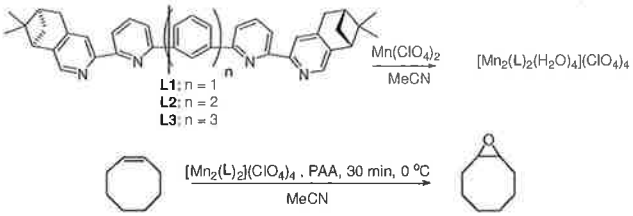
Double-stranded binuclear manganese complexes as catalyst for alkene epoxidation – Coordination Chemistry for the 21st Century

K. C. Sham, H. L. Yeung, S. M. Yiu, H. L. Kwong*
Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR (China)

Manganese-catalyzed epoxidation of alkenes are of great current interest and many manganese complexes have been demonstrated to be active catalyst.[1-3] These manganese complexes have one thing in common; they are all mononuclear in nature. Inspired by the importance of poly-nuclear manganese-containing metalloproteins in biological systems[4] and the well known dissociation of high spin metal ion from ligand, we through it would be interesting to develop supramolecular manganese catalyst for epoxidation.

New binuclear manganese complexes were synthesized by reacting manganese perchlorate with chiral phenyl- and polyphenyl-oligopyridine ligand, **L1–3**. These manganese complexes with formula $[Mn_2(L)_2(H_2O)_4](ClO_4)_4$ were characterized by ESI-MS and elemental analysis. X-ray crystal structures show that some of the manganese complexes are double stranded helicate with *P* charity. The helicates show strong CD absorptions at 230–360 nm which implied that the helical structure is retained in solution. The potential of the manganese double stranded helicates in catalysis was investigated in epoxidation with peractic acid as oxidant. Results shown that the helicates are all active catalysts, they catalyze epoxidation of a wide range of olefin selectively. For example, aliphatic substrate like cyclooctene and 1-hexene are oxidized to epoxide giving excellent selectively (up to 99%), unfortunately, no asymmetric induction was observed (<5% ee in all cases).



Acknowledgements: Financial support for this research project from the City University of Hong Kong and the Hong Kong Research Grant council GRF grant (CityU 101108) are gratefully acknowledged.

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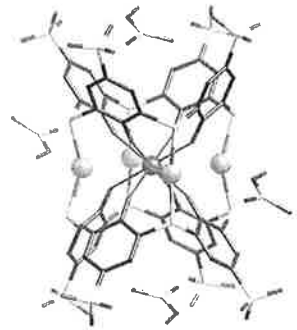
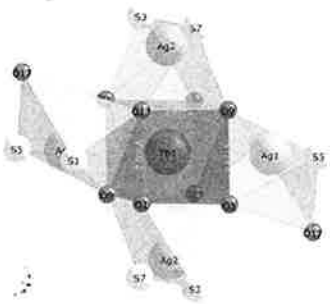
Novel photopysical property and structure of Tb(III)-Ag(I)-Thiacalix[4]arene supramolecular complex

T. Tanaka, N. Iki, H. Hoshino
Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi, Japan

Luminescence of lanthanide complex has many attractive features such as large stokes shift, narrow emission bands and long life time. In general, ligand for luminescent lanthanide complex is designed to connect antenna group enabling excitation of lanthanide and multidentate functional group to expel quenchable water molecules from the lanthanide ion, which leads to efficient and long-lived luminescence. One of drawback of this strategy is the laborious synthesis of such ligand. Here, we report a luminescent complex obtained not with synthesis of sophisticated ligand but with simple self-assembly of a macrocyclic ligand.
Recently, we found that thiacalix[4]arene-*p*-tetrasulfonate (TCAS) spontaneously assembled Tb and Ag in aqueous solution to form a ternary complex, which exhibited exceptionally long-lived luminescence (life time is 4.6 ms) at pH 10.[1] The composition of this complex was determined to be $Ag_2Tb_1TCAS_2$ with ESI-MS. We attempted isolation of single crystals of the ternary complexes to result in obtention of $Ag_4Tb_1TCAS_2$ and revealed the three-dimensional structure by X-ray analysis.[2] The complex shows a typical double cone shape, in which two TCAS sandwich a heterogeneous Ag_4Tb core by forming S-Ag-S and O-Tb-O bridges. An interesting feature of this complex is the supramolecular cage supported by 4-fold S-Ag-S bridges, in which Tb is encapsulated in nearly perfect cubic O_8-coordination geometry and shielded from any coordinating solvent molecules. Although the composition is different from the one in solution state, the structure of this complex suggests that $Ag_2Tb_1TCAS_2$ complex should adopt the same structure but with two instead of four silver bridges. Thus, the non-covalent heterogeneous assembly of Tb, Ag, and TCAS provided Tb ideal coordination environment to expel coordinating water molecules and to emit long-lived luminescence.



Ag_4·Tb·$TCAS_2$ complex



Coordination environment of the Ag_4Tb core

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Self-Assembled Checkerboard Pattern Structures Constructed from One-dimensional Zigzag Chains of Cyclam-Type Complexes

K. Tomono, M. Yamawaki, K. Miyamura
Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
E-mail: tomono@rs.kagu.tus.ac.jp

Metal-organic frameworks (MOFs) are the hybrid materials where metal ions or small clusters are bridged by organic linkers into one-dimensional chains, two-dimensional layers or three-dimensional (3D) network structure. During the past decade, the construction of MOFs through crystal engineering has attracted considerable attention owing to the various intriguing architectures of the frameworks and their potential application as functional materials. [1-3] The synthesis of 3D supramolecular network $[Ni(cyclam)(H_2O)_2]_3[C_6H_3(COO)_3]_2 \cdot 24H_2O$ [3] has aroused our interest in cyclam-type ligand, such as cyclam derivatives with C- and N-substituent groups (L) [4], because such cyclam derivatives may systematically control the size of framework by steric effect of substitutents.

In this study, 1,3-adamantanedicarboxylate (ADC) salts of a series of macrocyclic complexes $[Ni(cyclam)](ADC) \cdot 5H_2O$ (**1**), $[Ni(L_H)](ADC) \cdot 5H_2O$ (**2**), $[Ni(L_{Me})](ADC) \cdot 2H_2O$ (**3**), and $[Ni(L_{Et})](ADC) \cdot 7H_2O$ (**4**) in figure 1a were synthesized and characterized by single-crystal X-ray diffraction. Suffix of L indicates the N-substituents (R_1) of the macrocyclic ligand. Systematic change in crystal structure arose from the difference in the N-substitutents (hydrogen, methyl, ethyl).

In all complexes, each ADC^{2-} ligand binds two Ni^{II} ions in a bis-monodentate mode, and each Ni^{II} macrocyclic complex with a square-planar coordination geometry is coordinated to two carboxylate oxygen atoms of ADC^{2-} at trans positions, which results in a one-dimensional zigzag chain (see figure 1b). Each intrachain Ni···Ni separations of **1**, **2**, **3**, and **4** are 8.47, 8.61, 11.25, and 11.30 Å, respectively. Three-dimensional supramolecular network structure constructed by one-dimensional chains, incorporated many water molecules within its one-dimensional channel. Hydrogen bonding with the guest water molecules was present (figure 1c). The each shortest interchain Ni···Ni distances of **1**, **2**, **3**, and **4** are 8.98, 9.81, 9.53, and 9.67 Å, respectively.

In conclusion, the present results indicated that N-substituent groups tend to expand the channel size for water molecules.

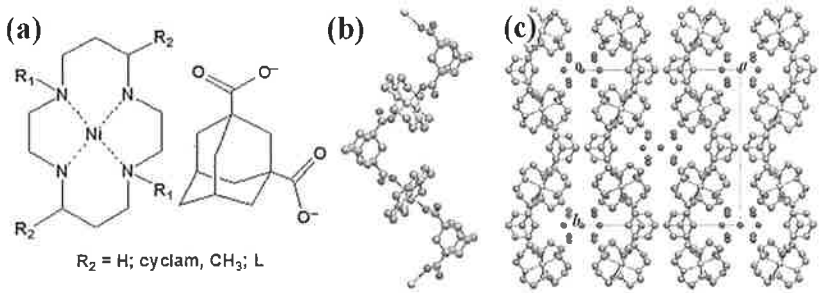

Figure 1. (a) Structural formula of 1-4. (b) Structure of the one-dimensional zigzag chain. (c) View showing the stacking of the zigzag chains, which generates checkerboard pattern structure, and water molecules occupy the 1D channels.

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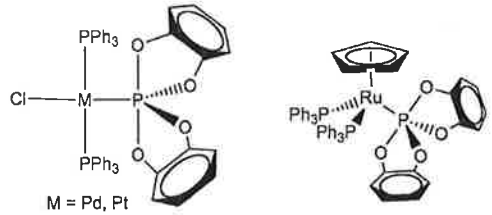
Synthesis of Platinum Metal Phosphoranide Complexes by Deprotonation of the Hydrophosphorane $HP(OC_6H_4O)_2$

C. D. Montgomery[1], B. J. Jelier[1]
1. *Trinity Western University, Langley, BC, Canada montgome@twu.ca*

Metal phosphoranides or metallophosphoranes are five-coordinate phosphorus compounds that feature a M-P bond. Various synthetic routes have been employed to this class of compounds including the use of hydrophosphoranes. In this work, proton abstraction from $HP(OC_6H_4O)_2$ using *n*-BuLi, followed by metathesis with platinum metal chlorides has yielded the phosphoranide complexes *trans*-$[MCl\{P(OC_6H_4O)_2\}(PPh_3)_2]$ where M=Pd, Pt and $[RuCp\{P(OC_6H_4O)_2\}(PPh_3)_2]$. The characterization of these compounds is done by NMR. Stereochemical and bonding features of these complexes will be discussed.



Acknowledgements: The authors are grateful for the financial support of Trinity Western University and the Natural Sciences and Engineering Research Council of Canada.

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Synthesis and Characterisation of Ruthenium Dithiolato Complexes.

B. Morton-Fernandez[1*], J. A. Crayston[1], J. D. Woollins[1], M. J. Duncan[2]
School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, Scotland.
Ceimig Limited, Units 1-3 Smeaton Road, Wester Gourdie Industrial Estate, Dundee, DD2 4UT, Scotland.
*bm324@st-andrews.ac.uk

Ruthenium complexes with aromatic sulfur-donor ligands had not been reported until recently. [1] These complexes may possess interesting properties due to the ruthenium centre's low redox potential and multiple stable oxidation states.

Here we report novel ruthenium complexes with dithiolato ligands which have been synthesised and characterised in order to study their behaviour.
Two classes of complexes have so far been synthesised. The first with the general formula of $[Ru(bpy)_2(SS)]$ (***Fig.1***), where bpy = 2,2'bipyridine and SS = aromatic dithiol ligand.
These complexes were found to be very polar and sparingly soluble in most solvents as well as being very sterically hindered. The solubility of these complexes was increased by the introduction of tert-butyl groups on the bipyridine (***Fig. 2***). The complexes obtained were also found to be oxygen sensitive leading to the doubly-oxidised mono-sulfinate product ($[Ru(bpy)_2(S{\cdot}SO_2)]$) in atmospheric oxygen and the disulfinate product ($[Ru(bpy)_2(S\,O_2{\cdot}SO_2)]$) in a strong oxidising agent like H_2O_2.[1]
The second class of compounds are of the form [Cp*Ru(SS)], where Cp* = 1,2,3,4,5-pentamethylcyclopentadiene and SS = aromatic dithiol ligand. These complexes are very different to those of the latter kind and possess high solubility in many non-polar solvents. Although they are not oxygen sensitive, they produce the dimerised product $[Cp^*(S)Ru\text{-}\eta^2S_2\text{-}Ru(S)Cp^*]$ (***Fig. 3***).

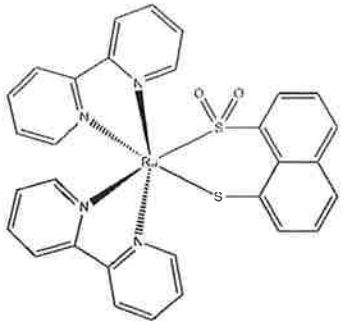

Fig. 1

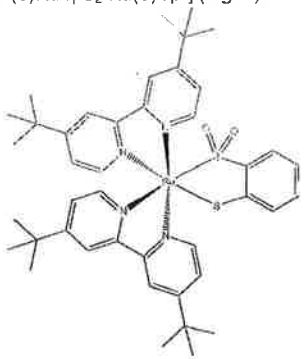

Fig. 2

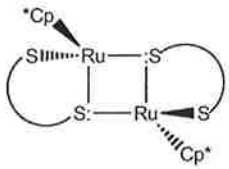

Fig. 3

Acknowledgements: Ceimig Limited, Dundee, Scotland.
ScotCHEM SPIRIT Funding.

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Communication between Carbonyl Groups and 1,8-Naphthylidyl Frameworks of Polypyridyl Ligands in Ruthenium Complexes

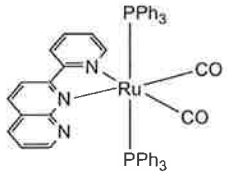
D. Oyama[1], T. Hamada[2], T. Yamanaka[2], T. Takase[1]
1. *Cluster of Science and Technology, Fukushima University, daio@sss.fukushima-u.ac.jp*
2. *Graduate School of Science and Technology, Fukushima University*

Intramolecular cyclometallations are fundamental reactions which play an important role such as activation of C-H bonds, leading to metallacycles and ligand transformations within the metal coordination sphere.[1]

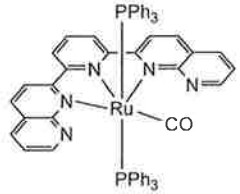
For example, Tanaka and co-workers have reported reversible intramolecular cyclometallation driven by redox reactions of the monodentate 1,8-naphthyridine ligand in ruthenium carbonyl complexes to depress the Ru-CO bond cleavage under the reductive conditions.[2]

Terminal carbonyl ligands, on the other hand, showing higher CO stretching frequencies (over *ca.* 2000 cm^{-1}) undergo nucleophilic attacks by various nucleophiles (OH^-, CH_3O^-, *etc.*).[3]

We have designed and prepared two ruthenium carbonyl complex systems with multidentate polypyridyl ligands containing a single or double naphthyridyl frameworks (see below) to investigate geometric or electronic communications between CO and 1,8-naphthylidyl moieties in different oxidation states.



$[1]^{2+}$



$[2]^{2+}$

Molecular structures of both complexes were determined by X-ray crystallography: both complexes contain the carbonyl(s) and the naphthylidyl framework(s) on the same plane and two PPh_3 ligands at axial positions. More remarkable is the interatomic distance between the carbonyl carbon and the noncoordinating nitrogen atom of naphthylidyl frameworks: fairly short distances (2.490 Å in $[1]^{2+}$, 2.710 Å in $[2]^{2+}$) may indicate a significant communication between these ligands.

In addition to structural discussions, redox properties and reactivities of the complexes with some nucleophiles will be presented.

Acknowledgements: We thank Professor K. Tanaka, Professor T. Wada, and Dr. T. Fukushima of the Institute for Molecular Science for their helpful advice and discussion.

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A Hexadentate Bis(thiosemicarbazone) Ligand: Rhenium(V), Iron(III) and Cobalt(III) Complexes

B. M. Paterson, J. M. White and P. S. Donnelly
School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Parkville, Melbourne, Victoria, 3010, Australia.

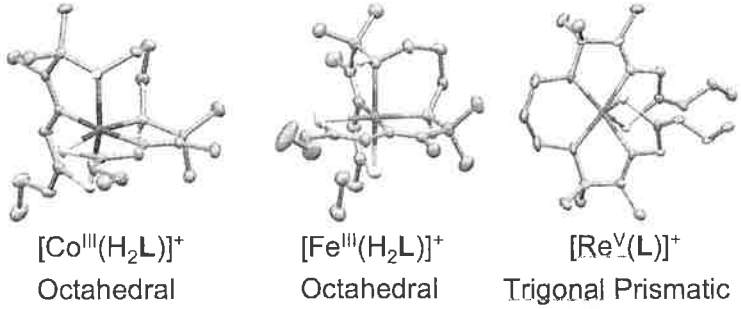
Thiosemicarbazones (TSCs) and their transition metal complexes have a wide range of pharmacological activity that has stimulated continued interest in their synthesis and interactions with biological systems.

Rhenium has two β-emitting isotopes, ^{186}Re and ^{188}Re, that have the potential to be used to treat cancer provided they are effectively targeted *in vivo*. A possible method for targeting rhenium radiopharmaceuticals is to incorporate them into stable bifunctional chelates that contain a functional group for the conjugation of targeting molecules.

Iron has been implicated in the antitumour activity of *N*-heterocyclic thiosemicarbazones such as Triapine. The enzyme ribonucleoside reductase (RR) provides the precursors required for both synthesis and repair of DNA and is found at high concentrations in rapidly proliferating tumour cells. Reduction of the tyrosine free radical, which is essential for the activity of RR, by FeTSCs and oxygen leads to inhibition of tumour cell growth.

A new 1,3-diaminopropane bridged bis(thiosemicarbazone) ligand (H_4**L**) has been synthesised.[1] The new hexadentate ligand is capable of forming six coordinate complexes with rhenium(V), iron(III) and cobalt(III). It was anticipated that a hexadentate ligand would provide increased stability *in vivo*, a desirable property for pharmaceutical applications.

In the case of the isostructural iron(III) and cobalt(III) complexes the ligand doubly deprotonates to give the monocations $[Fe^{III}(H_2L)]^+$ and $[Co^{III}(H_2L)]^+$ in which the metal ion is in a distorted octahedral environment. In the case of rhenium(V) the ligand loses four protons by deprotonation of both secondary amine nitrogen atoms to give $[Re^{V}(L)]^+$ with the metal ion in a distorted trigonal prismatic coordination environment. $[Re^{V}(L)]^+$ represents a rare example of a rhenium(V) complex that does not contain one of the $Re^{V}O^{3+}$, $Re^{V}N^{2+}$, or $Re^{V}(NPh)^{2+}$ cores. The new ligand and metal complexes have been characterised by a combination of NMR spectroscopy, X-ray crystallography and mass spectrometry. The electrochemistry of $[Fe^{III}(H_2L)]^+$, $[Co^{III}(H_2L)]^+$ and $[Re^{V}(L)]^+$ has been investigated by cyclic voltammetry with each complex undergoing a single electron reduction event. It is possible to prepare the rhenium(V) complex from $ReOCl_3(PPh_3)_2$ or directly from $[ReO^4]^-$ with the addition of a reductant, which suggests the new ligand may be of interest in the development of rhenium radiopharmaceuticals.



Acknowledgements: Australian Research Council

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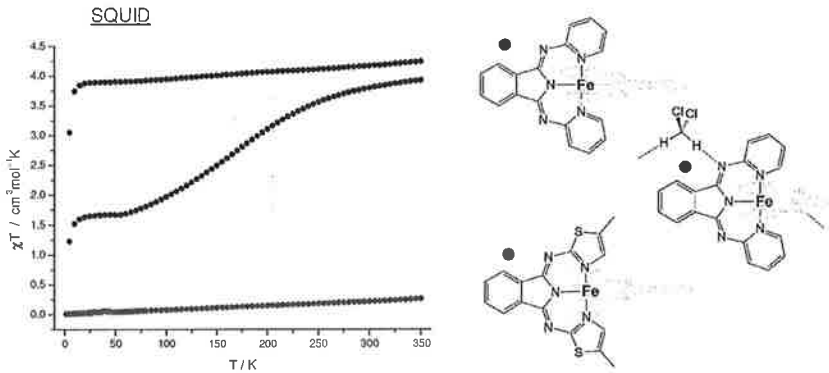
Spin crossover of iron(II)-bai-complexes

A. Scheja[1], M. Bröring[1]
1. *Institute of Inorganic and Analytical Chemistry, TU Braunschweig, Germany, a.scheja@tu-bs.de*

The spin crossover phenomenon of iron(II) in octahedral surrounding was invested intensely in the past, but is not yet completely understood. The reversible transition of the diamagnetic low spin to the paramagnetic high spin configuration could be mostly induced by variation of temperature, its transition temperature and shape could be modified e. g. by alteration of ligands and the degree of cooperativity.[1]

The class of planar tridentate bis(arylimino)isoindolines (bai) offers the possibility to create a wealth of ligands with various electronic and steric properties.[2] Thus, the preparation of homoleptic iron(II)-bai-complexes with different magnetic behaviour was achieved. (see fig.)



Especially a with dichloromethane co-crystallised iron(II)-bis(pyridylimino)isoindoline-complex shows interesting magnetic behaviour, which was investigated further. The current results of our research will be presented.

Acknowledgements: We are grateful to Clemes Pietzonka for the magnetic measurements.

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