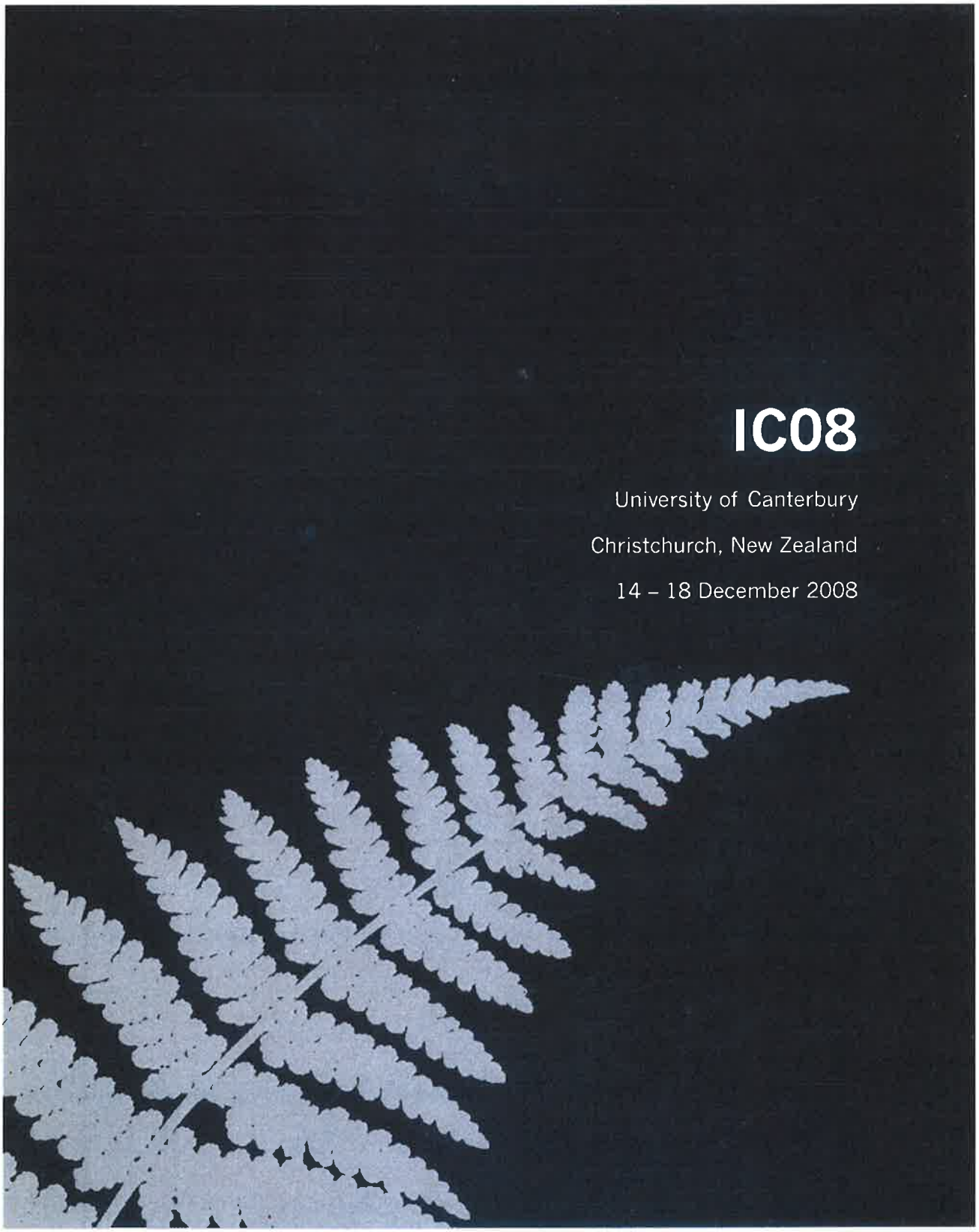
PART 1



PROGRAMME AND BOOK OF ABSTRACTS

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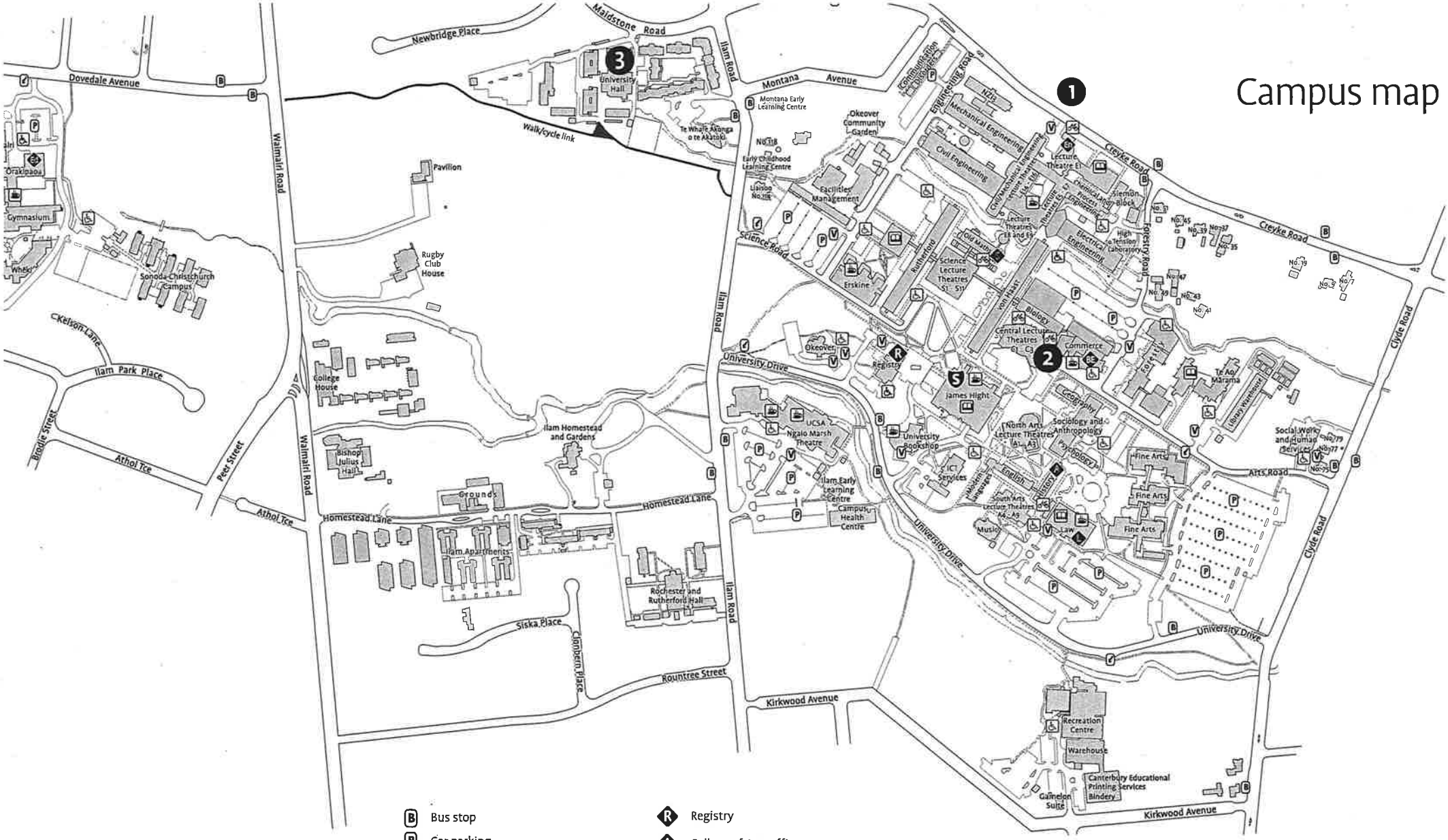
Campus map



1 Academy

2 Central Lecture Theatre Block (C Block)

3 University Hall

- Bus stop
- Car parking
- Visitor car parking
- Disabled car parking
- Library
- Cafe
- Secure cycle stand
- Security

- Registry
- College of Arts office
- College of Business and Economics office
- College of Education office
- College of Engineering office
- School of Law office
- College of Science office

January 2008

Contents

Welcome

Welcome to New Zealand, to Christchurch, to the University of Canterbury, and to IC08. It is some time since a conference from the IC series was last held in New Zealand (IC99, Wellington), but this is a case of regular returns. These conferences are a tangible reminder of the collaboration between the Inorganic Division of the RACI and the Inorganic and Organometallic Specialist Group of the NZIC, and it is important that New Zealand takes it turn. My colleagues on the IC08 Organising Committee and I therefore have much pleasure in welcoming you to the IC08 RACI/NZIC Inorganic Chemistry Conference.

We believe that we have put together an excellent group of plenary speakers – their interests cover many of the specialties within the discipline. Keynote speakers have been selected for sessions on various themes, and these parallel sessions will also represent the diversity of the subject. Conference delegates will be able to attend and participate in sessions on their own specialty, and also sample from sessions that may broaden their knowledge and provide a snapshot of the latest advances in other parts of the field.

Scheduling this conference for December is an innovation for the IC series of meetings, but we believe that such timing offers the opportunity to reinvigorate research programmes after the academic year, avoids pressures of the January-February grant-writing season, and perhaps provides some opportunities to enhance summer holidays! Hopefully many of you have been able to put such plans in place – perhaps to reward yourselves for an active and successful year.

We look forward to hosting you in at the University of Canterbury and promise you the best conference we can possibly manage.

Richard Hartshorn
Chair, IC08 Organising Committee

Local Organizing Committee

Convenor	Richard Hartshorn (University of Canterbury) Peter Steel (University of Canterbury) Jan Wikaira (University of Canterbury) Paul Kruger (University of Canterbury) Vladimir Golovko (University of Canterbury) Owen Curnow (University of Canterbury) David Anderson (University of Canterbury) Lyall Hanton (Otago) Richard Keene (JCU, Townsville)
Organisers	Conference Office, University of Canterbury

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Supporters

RACI

UC UNIVERSITY OF CANTERBURY Te Whare Wānanga o Waitaha CHRISTCHURCH NEW ZEALAND

NZIC

Venue Information

Audio Visual and Speakers Presentation

Student helpers will be available in the lecture theatres to assist you to load your presentation in the break prior to your talk. A vacant lecture theatre, C1, will be available all day Monday after the plenary session for presenters to prepare and check their presentations.

Catering

All catering will take place in the foyer of the Central Lecture Theatre Block. If you have advised of a special dietary requirement, your requirements have been passed on to the caterer. Please make yourself known to the catering staff.

Internet Access

Wireless access is currently not available at the university. You are able to use the Vault Computer Labs in the lower level of the nearby Commerce Building. User codes to access both are available from the conference registration desk at $10.00 per code.

Message Board

Messages can be left or picked up from the message board near the registration desk.

Social Information

Registration Welcome Reception – Sunday 14 December

This will take place on Sunday 14 December from 6pm-7pm in the Central Lecture Theatre Block (C Block) after the Opening Ceremony and Plenary Lecture.

Happy Hour Poster Session 1 – Monday 15 December

Drinks will take place in the venue after the Poster Session from 4.45pm to 6.00pm.

Student BBQ – Monday 15 December

This will take place at the University Staff Club, 87 Ilam Road, between 6.30pm – 9.00pm. Cash bar applies.

Happy Hour Poster Session 2 – Tuesday 16 December

Drinks will take place in the venue after the Poster Session from 4.45pm to 6.00pm.

Social Option – Tuesday 16 December

Gather at the Dux de Lux, at the Christchurch Arts Centre, at 7.30pm until late. Dine in the café, drinks in the courtyard. Everyone is requested to pay their own way.

Conference Dinner – Wednesday 17 December

The Conference dinner will take place at the Antarctic Centre with pre dinner drinks at 7.00pm and an opportunity to walk through the Antarctic Attraction for an hour. Dinner will be served at 8.00pm – the Attraction will remain open during the evening.

Buses will depart UCSA carpark on Ilam Road at 6.45pm to transfer guests to the Antarctic Centre.

For the return trip, one bus will depart at 10.00pm and the second bus will depart at 10.30pm. The second bus will stop at the university and continue on to the city for those who wish to party on!

We look forward to welcoming you to the dinner.

General Information

Banking and Currency

ATM machines are located inside the ground floor entrance of the Commerce Building, outside the University Bookshop, in the foyer of the Central Library, outside the entrance to the Registry Building and at the car park entrance to the Students' Association UCSA building. The nearest branches of major banks are as follows:

Bank of New Zealand (BNZ), Upper Riccarton branch, cnr Riccarton and Waimairi Roads
National Bank, Upper Riccarton branch, 322 Riccarton Road
Westpac, Upper Riccarton branch, 3 Waimairi Road

Normal banking hours are Monday to Friday 9.00am to 4.30pm. Banks are closed on weekends and public holidays. The ASB is open 7 days in the Westfield Shopping Centre, Riccarton Road.

Central Library

During the summer the Central Library hours are 9.00am to 9.00pm Monday to Friday and 10.00am to 4.00pm on Saturday and Sunday.

Emergency Medical Services

Riccarton Clinic, 6 Yaldhurst Road, Church Corner, Upper Riccarton. Phone 03 343 3661. Open 8.00am to 10.00pm Monday to Friday, 8.00am to 8.00pm Saturday, Sunday and public holidays.

After Hours Surgery, corner Bealey Avenue and Colombo Street. Phone 03 365 7777. Open 24 hours, seven days a week.

Pharmacies

Students' Association Building, ground floor. Open Monday to Friday 8.30am to 5.30pm. Phone 364 2215.

Riccarton Radius Pharmacy, 4 Yaldhurst Rd, Church Corner. Phone 03 341 4855, open Monday to Friday 08.30am-8.30pm, Saturday and Sunday 09.00am-8.30pm.

Name Tags

Admission to all sessions including morning and afternoon teas and lunches is by conference name tag. Delegates are requested to wear their name tags at all times.

Parking

Parking is shown on the map at the back of this book. All carparks on campus may be used except those reserved for departments, disabled, University vehicles or individual position-holders.

Photocopying and Fax Facilities

Photocopying and fax facilities are available at the Copy Centre, situated on Level 2 of the Central Library (James Hight Building). Copy Centre hours are 8.30am to 5.00pm weekdays.

Post Office

Postal services are available from the Convenience Store in the Student's Association UCSA building. The nearest NZ Post Shop is corner of Maidstone and Waimairi Roads.

Public Transport

Buses (route 24) depart for the city on weekdays approximately every 30 minutes (on the hour and half hour) from the bus stop opposite the School of Engineering on Creyke Road and approximately every 15 minutes (routes 3 and 21) from the bus stop outside the Student Association Building on Ilam Road (approximately every 30 minutes after 7.00pm). Please check the time of the last bus at night. BusInfo phone: 366 8855.

Smoking Policy

Smoking is not permitted inside any building on campus. Smoking is restricted to outside open areas only. Your cooperation in keeping this a smoke-free conference is appreciated.

Shopping

The closest shopping malls are Fendalton Mall, Memorial Avenue (15 minutes walk); Bush Inn Centre, Riccarton Road (15 minutes walk); Riccarton Mall, Riccarton Road (25 minutes walk).

Taxis

Blue Star	Phone 379-9799
Corporate Cabs	Phone 379-5888
First Direct	Phone 377-5555
Gold Band	Phone 379-5795
Green Cabs	Phone 0508 447336

Door to door shuttle services

Super shuttle	(0800) SHUTTLE	www.supershuttle.co.nz
Airport shuttle	(03) 354 1540	airportshuttles@ihug.co.nz

University Bookshop

Week day hours 8.30am-5.30pm

Accommodation

Academy Motor Lodge
62 Creyke Road, Fendalton
Telephone: 03 351 9347

University Halls
9 Maidstone Road, Ilam.
Telphone: 03 364 2720

Westside Motor Lodge
298 Riccarton Rd, Riccarton
Christchurch
Telephone: 03 347 7254

Chateau on the Park
189 Deans Avenue, Christchurch
Telephone: 03 348 8999

Plenary Speakers

Speaker	Presenting Date(s) and Time(s)
A.P. De Silva **Queen's University Belfast** *2008: A Small Space Odyssey with Luminescent Molecules*	**Sunday 14 December – 5:00pm**
Joe Hupp **Northwestern University** *Functional Metal-Organic Framework Materials*	**Monday 15 December – 9.00am**
Chi-Ming Che **University of Hong Kong** *Atom and Group Transfer Catalysis with Reactive Metal-Ligand Multiple Bonded Complexes*	**Tuesday 16 December – 9.00am**
Franc Meyer **University of Gottingen** *Cooperating Metal Centers: Metalloenzyme Active Sites, Synthetic Models, and Beyond*	**Wednesday 17 December – 9.00am**
Bob Grubbs **California Institute of Technology** *Olefin Metathesis and Discovering New Reactions*	**Thursday 18 December – 9.30am**
Mark Humphrey **Australian National University** *Shedding Light on Organometallics*	**Thursday 18 December – 11.00am**

Presentations

Chair Guidelines

All chairpersons are asked to familiarise themselves with the room and equipment prior to the session. Student helpers will be present to assist with the changeover of speakers (microphones and Powerpoint loading). Chairpersons are asked to keep all presenters strictly to time. Note that the allocated times (Keynote 30 min; Oral 20 min; Stranks 15 min) all INCLUDE time for questions and changeover.

Keynote Presentations (K1-K8)

Abstracts are numbered as they appear in the Programme and Books of Abstracts.

Stranks Finalists (S1-S6)

Abstracts are numbered as they appear in the Programme and Books of Abstracts.

Oral Presentations (O1-76)

Abstracts are numbered as they appear in the Programme and Books of Abstracts.

Poster Sessions (PM1-PM70) (PT1-PT71)

Poster authors are requested to have their poster in place at lunch on the day of their allocated session and should be dismantled by morning tea the next day.

Your poster number can be found in the Poster Index in the Programme and Books of Abstracts. Your poster should be mounted on the board with the corresponding number.

Student Poster Prize

There will be prizes for the best student posters, kindly sponsored by the Australian Journal of Chemistry.

Meetings

The RACI inorganic divisional meeting will take place in C1 after the Closing Ceremony.

	Sunday December 14	Monday December 15	Tuesday December 16	Wednesday December 17	Thursday December 18
9:00		**Plenary Speakser** Hupp (USA)	**Plenary Speaker** Che (Hong Kong)	**Plenary Speaker** Meyer (Germany)	**Plenary Speaker** Grubbs (USA)
10:00		**New Faces** Cole (UNSW) D'Alessandro (USA) Moore (Melb) / **Coordination** Harding P (Thai) Poorters (UNSW) Halet (France)	**Coordination** Young (Melb.) Sykes (USA) Li (Sydney) / **Catalysis** Spiccia (Monash) Zaman (UC NZ) Lein (MU NZ) / **Bioinorganic** Gahan (UQ) Codd (Sydney) Naik (ANSTO)	**Materials** Murray (Monash) Iremonger (Syd.) Price (Sydney) / **Biomedical** Guagliado (WA) Donnelly (Melb.) Sharpe (UQ) / **General** Riley (UQ) Puschmann (UK) Mulyana (Melb.)	
11:00		**Morning Tea**			**Morning Tea**
12:00		**New Faces** Lucas (UO NZ) Telfer (MU NZ) Turner (Monash) / **Bioinorganic** Rendina (Sydney) Wedd (Melb.) Keene (JCU)	**Coordination** Junk (Monash) Lawrance (Newc.) McKee (UK) / **Materials** Soehnel (UA NZ) Anderson (UC NZ) Cook (CSIRO) / **Biomedical** Lay (Sydney) V.-Villegas (USA) Hambley (Syd.)	**Materials** Mume (ANSTO) McMurtrie (QUT) Masters (Sydney) / **Clusters** Boskovic (Melb.) Bircher (ANSTO) Xie (Melb.) / **Sensors** Wenzel (MU NZ) Wainwright (Flin.) Wright G (UK)	**Burrows Lecture** (Humphrey)
13:00		**Lunch**			**Closing Ceremony/ Divisional Meeting**
14:00	**Registration**	**Supramolecular** Janiak (Germ.) Sumby (Adel.) Plieger (MU NZ) Fitzgerald (Melb.) Lincoln (Adel.) / **Organometallic** Wright J (UA NZ) Lapinte (France) Brown (Curtin) Canty (Tasm.) Loughrey (Griff.)	**Coordination** Tasker (UK) Halder (USA) Ainscough (NZ) Harding D (Thai) Gardiner (Tasm.) / **Organometallic** Hahn (Germany) Yen (Singapore) Bhargava (RMIT) Chaplin (UK) Oksakada (Japan) / **Robinson-Simpson** Bruce (Adel.) Nicholson (NZ) Spencer (VU NZ) Golovko (UC NZ)	**Supramolecular** Lindoy (Sydney) Kruger (UC NZ) Latham (RMIT) Abrahams (Melb.) / **Bioinorganic** Bernhardt (UQ) Belousof (Monash) Ikotun (USA) Schilter (Sydney) / **Computational** Yates (Tasm.) Nielson (MU NZ) Brookes (Tasm.) Tonner (MU NZ)	**Rutherford's Den** Arts Centre
15:00				**Afternoon Tea**	
16:00		**Poster Session 1**	**Poster Session 2**	**Stranks Award** Zimmermann (Melbourne) Sciortino (Sydney) Kunnamkumarth (Adelaide) Kitchen (Otago) Ching (Sydney) Argyle (Otago)	
17:00	**Opening Ceremony** / **Plenary Speaker** de Silva (UK)	**Happy Hour**	**Happy Hour**		
18:00	**Mixer**				
19:00		**Student Barbeque** UoC Staff Club		**Conference Dinner and Awards Ceremony** Antarctic Centre	
20:00			**Social** Dux de Lux		

Time	Sunday 14th December 2008
1430 - 1630	**Registration** *C Block Lecture Theatre Foyer*
1630 - 1700	**Opening Ceremony** *Lecture Theatre C1*
1700 - 1800	**Plenary Lecture 1** *Lecture Theatre C1* Chair: Richard Hartshorn *2008: A Small Space Odyssey with Luminescent Molecules* **A. P. de Silva** Queen's University of Belfast, United Kingdom
1800 - 1900	**Mixer** *C Block Lecture Theatre Foyer*

Monday 15th December 2008

Time		
0900 - 1000	**Plenary Lecture 2** *Lecture Theatre C1* Chair: Richard Keene *Functional Metal-Organic Framework Materials* **Joseph Hupp** Northwestern University, USA	
	New Faces in Chemistry *Lecture Theatre C2* Chair: Chris Fitchett	**Coordination Chemistry** *Lecture Theatre C3* Chair: James Wright
1000 - 1020	**Marcus Cole** **O 1** University of New South Wales, Australia *Heavy group 13 halohydrides – not just aspiring trihydrides!*	**Phimphaka Harding** **O 4** Walailak University, Thailand *Electron transfer studies of cobalt(II) and nickel(II) β-diketonate complexes incorporating asymmetric diimine ligands*
1020 - 1040	**Deanna D'Alessandro** **O 2** University of California, USA *CO_2 capture in amine-functionalised metal-organic frameworks*	**Laurent Poorters** **O 5** University of New South Wales, Australia *Versatile early and late transition metal coordination by pyrazolyl-based heteroscorpionate pincers*
1040 - 1100	**Evan Moore** **O 3** University of Melbourne, Australia *From the visible to near infra-red: efficient antennae for sensitised Ln(III) luminescence*	**Jean-François Halet** **O 6** University of Rennes, France *Heteroatom in carbon ligands spanning two metal centers: enhancement or diminution of the electronic communication? The case of di-iron-(bis)acetylide-pyridine species*
1100 - 1130	**Morning Tea**	
	New Faces in Chemistry *Lecture Theatre C2* Chair: Chris Fitchett	**Bioinorganic Chemistry** *Lecture Theatre C3* Chair: Peter Steel
1130 - 1150	**Nigel T. Lucas** **O 7** University of Otago, New Zealand *Hexabenzocoronene ligands for supramolecular ordering*	**Lou Rendina** **O 10** University of Sydney, Australia *Selective aggregation of a Pt-Gd complex within a tumour cell nucleus*
1150 - 1210	**Shane Telfer** **O 8** Massey University, New Zealand *Synthesis and photophysical properties of complexes of dipyrrin ligands*	**Anthony Wedd** **O 11** University of Melbourne, Australia *Control of seven copper sites in a single enzymic reaction of copper resistance*
1210 - 1230	**David Turner** **O 9** Monash University, Australia *Clusters, chains and non-covalent networks: The unpredictable chemistry of dicyanomethanide ligands*	**Richard Keene** **O 12** James Cook University, Australia *Dinuclear ruthenium(II) complexes as potential probes for RNA bulge sites*

1230 - 1330	**Lunch**			
	Supramolecular Chemistry *Lecture Theatre C2* Chair: Paul Kruger		**Organometallic Chemistry** *Lecture Theatre C3* Chair: Owen Curnow	
1330 - 1400	**Christoph Janiak** University of Freiburg, Germany	**K 1**	**James Wright** *University of Auckland, New Zealand*	**K 2**
	From metal-organic to hydrogen-bonded networks		*Metallabenzene ring functionalization reactions*	
1400 - 1420	**Christopher J. Sumby** University of Adelaide, Australia	**O 13**	**Claude Lapinte** University of Rennes, France	**O 17**
	Cross-conjugated and highly conjugated heterocyclic ligands; discrete coordination complexes and metallo-supramolecular assemblies		*Long distance electronic and magnetic interactions between organometallic redox active centres mediated by carbon rich bridges containing aromatic rings*	
1420 - 1440	**Paul Plieger** Massey University, New Zealand	**O 14**	**David Brown** Curtin University of Technology, Australia	**O 18**
	Anion binding utilizing polyammonium transition metal helicates		*Alkoxybenzimidazolium-linked cyclophanes: conformation control and carbene-precursors*	
1440 - 1500	**Nicholas J. Fitzgerald** University of Melbourne, Australia	**O 15**	**Allan Canty** University of Tasmania, Australia	**O 19**
	Novel supramolecular assemblies of cyclotricatechylene		*Miniaturising metal catalysis at the micrometer level in capillaries and glass chips*	
1500 - 1520	**Stephen F. Lincoln** University of Adelaide, Australia	**O 16**	**Bradley T. Loughrey** Griffith University, Australia	**O 20**
	Cyclodextrin [2]- and [3]-Pseudorotaxanes: An UV-vis and 2D 1H NMR ROESY equilibrium and structural study in aqueous solution		*Novel organometallic ruthenium(II) Cp* benzenesulphonamides for the inhibition of carbonic anhydrases*	
1530 - 1700	**Poster Session** **S 1 –S 6 and PM 1 - PM 70** *Mezzanine Floor*			
1700 - 1800	**Happy Hour** *Drinks Served from 1645*			
1830 - 2100	**Student BBQ** *University Staff Club, Ilam Gardens.*			

Tuesday 16th December

Time			
0900-1000	**Plenary Lecture 3** Lecture Theatre C1 Chair: Shane Telfer *Atom and Group Transfer Catalysis with Reactive Metal-Ligand Multiple Bonded Complexes* **Chi-Ming Che** **University of Hong Kong**		
Chair	**Coordination Chemistry** *Lecture Theatre C1* Chair: Shane Telfer	**Catalysis** *Lecture Theatre C2* Chair: Brian Yates	**Bioingoranic Chemistry** *Lecture Theatre C3* Chair: Chris Sumby
1000 - 1020	**Charles Young** O 21 University of Melbourne, Australia *Dioxo- and oxosulfido-Mo(V) radical anions and their conjugate acids*	**Leone Spiccia** O 24 Monash University, Australia *Bioinspired water oxidation catalysis: towards renewable hydrogen generation*	**Lawrence Gahan** O 27 University of Queensland, Australia *Structural and catalytic models for phosphoesterases*
1020 - 1040	**Andrew Sykes** O 22 University of South Dakota, USA *Oxonium ion based molecular switches: large-amplitude changes in molecular geometry within anthraquinone-containing macrocycles*	**Shazia Zaman** O 25 University of Canterbury, New Zealand *Synthesis and reactions of a new soluble-polymer bound ruthenium-carbene catalyst for olefin metathesis*	**Rachel Codd** O 28 University of Sydney, Australia *Chemical biology of siderophores*
1040 - 1100	**Feng Li** O 23 University of Sydney, Australia *Structural and magnetic properties of iron(II) complexes with 2,3-di-2-pyridylpyrazine (DPP)*	**Matthias Lein** O 26 Massey University, New Zealand *The effects of relativity on reaction mechanisms – Gold(III) catalysis as an example*	**Radhika Naik** O 29 ANSTO, *Australia* *Metal absorption on eri and mulberry silk powders: a comparative study*
1100 - 1130	**Morning Tea**		
Chair	**Coordination Chemistry** *Lecture Theatre C1* Chair: Jan Wikaira	**Materials** *Lecture Theatre C2* Chair: Vladimir Golovko	**Biomedical** *Lecture Theatre C3* Chair: Nigel Lucas
1130-1150	**Peter Junk** O 30 Monash University, Australia *Access to heterobimetallic complexes by direct routes*	**Tilo Soehnel** O 33 University of Auckland, New Zealand *The chemical transport and the crystal and electronic structure of Cu_5SbO_6 and $Cu_5Sb_2Si_3O_{12}$*	**Peter Lay** O36 University of Sydney, Australia *Biomedical applications of X-Ray absorption and vibrational spectroscopic microscopies in bioinorganic chemistry*
1150-1210	**Geoffrey Lawrance** O 31 University of Newcastle, United Kingdom *Complexation of deceptively simple and decidedly non-simple ligands: conjoint analysis of kinetic and equilibrium data for mechanistic elucidation*	**David P. Anderson** O 34 University of Canterbury, New Zealand *Effects of metal carbonyl precursor on the formation of metal colloids*	**Nerissa Viola-Villegas** O 37 Syracuse University, USA *Illuminating the cytotoxicity of a novel rhenium(I) bioconjugate of folic acid in folate receptor overexpressing cancer cells*
1210-1230	**Vickie McKee** O 32 Loughborough University, United Kingdom *Double template effect in polynuclear pseudocalixarenes*	**Vernon Cook** O 35 CSIRO, Australia *Tunable photoluminescenct platinum complexes & flexible photonic crystals*	**Trevor Hambley** O 38 University of Sydney, Australia *Metal based drug uptake in tumours, tumour models and cells: imaging and modification*
1230-1330	**Lunch**		

Chair	Coordination Chemistry *Lecture Theatre C1* Chair: David Turner		Organometallic Chemistry *Lecture theatre C2* Chair: Marcus Cole		Robinson-Simpson Symposium *Lecture Theatre C3* Chair: Lyall Hanton	
1330-1400	**Peter Tasker** University of Edinburgh, United Kingdom Using the outer coordination sphere in extractive hydrometallurgy	**K 3**	**Ekkehardt Hahn** University of Münster, Germany *Template synthesis of complexes with cyclic polycarbene ligands*	**K 4**	**Michael Bruce** University of Adelaide, Australia *Oxidation reactions of alkynyl-metal complexes: formation of unusual dimers and acyl complexes*	**K 5**
1400 - 1420	**Gregory Halder** Argonne National Laboratory, USA *Guest-dependent high-pressure behavior in a nanoporous metal-organic framework material*	**O 39**	**Swee Kuan Yen** National University of Singapore, Singapore *Synthesis, structure and catalytic applications of novel palladium(II) carbene complexes with benzothiazolin-2-ylidene ligands*	**O 43**	**Brian Nicholson** University of Waikato, New Zealand *Aryl stibonic acids; precursors to organometallic, high-nuclearity isopolyoxystibonates*	**O 47**
1420 - 1440	**Eric Ainscough** Massey University, New Zealand *Dinuclear copper(II) complexes containing bridging cyclotetraphosphazenes and their metal-metal communication*	**O 40**	**Suresh Bhargava** RMIT University, Australia *The chemistry and reactivity of platinacycles*	**O 44**	**John Spencer** Victoria University, New Zealand *Heterobidentate ligands*	**O 48**
1440 - 1500	**David J. Harding** Walailak University, Thailand *Synthesis and characterization of redox-active tris(pyrazolyl)borate cobalt complexes*	**O 41**	**Adrian B. Chaplin** University of Oxford, United Kindom *Acceptorless alkyl dehydrogention in a Rh(I) complex via an isolated agostic intermediate*	**O 45**	**Vladimir Golovko** University of Canterbury, New Zealand *Polynuclear systems containing dicobalt carbonyl-coordinated alkyne building blocks*	**O 49**
1500 - 1520	**Michael G. Gardiner** University of Tasmania, Australia *Structure and reactivity studies of tethered mixed anion lithium complexes: a rational discovery of a new class of superbase*	**O 42**	**Kohtaro Osakada** Tokyo Institute of Technology, Japan *Organometallic rotaxanes with unique structures and chemical behaviors*	**O 46**		
1530 - 1700	**Poster Session 2** **S 1 –S 6 and PT 1 - PT 70** *Mezzanine Floor*					
1700 - 1800	**Happy Hour** *Drinks served from 1645*					
1930 - Late	**Social** *Dux de Lux,* *Arts Centre*					

Wednesday 16th December

Time			
0900-1000	**Plenary Lecture 4** *Lecture Theatre C1* Chair: Paul Kruger *Cooperating Metal Centers: Metalloenzyme Active Sites, Synthetic Models, and Beyond* **Franc Meyer** University of Göttingen		
Chair	**Materials** *Lecture Theatre C1* Chair: Paul Kruger	**Biomedical** *Lecture Theatre C2* Chair: Lou Rendina	**General** *Lecture Theatre C3* Chair: Jan Wikaira
1000 - 1020	**Keith Murray** O 50 Monash University, Australia *Metallo-supramolecular clusters and frameworks; spin-exchange, SMM and spin-switching*	**Paul Guagliardo** O 53 University of Sydney, Australia *Positron annihilation lifetime spectroscopy: a tool for exploring nanoporosity in biological materials*	**Mark Riley** O 56 University of Queensland, Australia *MCD and EPR of a dynamic copper(II) Jahn-Teller system*
1020 - 1040	**Simon Iremonger** O 51 University of Sydney, Australia *Anions in framework materials: From gas storage to post-synthetic modification*	**Paul S. Donnelly** O 54 University of Melbourne, Australia *Copper radiopharmaceuticals for the molecular imaging of Alzheimer's disease*	**Horst Puschmann** O 57 Durham University, UK *Making crystallography accessible: Olex 2 and the small molecule toolbox*
1040 - 1100	**David J. Price** O 52 University of Sydney, Australia *Spin-crossover Hofmann-type materials structures and magnetism*	**Philip Sharpe** O 55 University of Queensland, Australia *Chelators as medicinal agents: iron and beyond.*	**Yanyan Mulyana** O 58 University of Melbourne, Australia *Valence tautomerism in cobalt complexes*
1100 - 1130	**Morning Tea**		
Chair	**Materials** *Lecture Theatre C1* Chair: Vladimir Golovko	**Inorganic Clusters** *Lecture Theatre C2* Chair: Andy Sykes	**Sensors** *Lecture Theatre C3* Chair: Deanna D'Alessandro
1130-1150	**Eskender Mume** O 59 ANSTO, Australia *Nuclear probes for characterising self-assembled monolayers on silicon surfaces*	**Colette Boskovic** O 62 University of Melbourne, Australia *Polyoxotungstate-encapsulated lanthanoid spin clusters*	**Marco Wenzel** O 65 Massey University, New Zealand *Tripodal polyamine – ambivalent receptors for cations and anions*
1150-1210	**John McMurtrie** O 60 Queensland University of Technology, Australia *Supramolecular selection in metal complex alloys*	**Roland Bircher** O 63 ANSTO, Australia *Twisting molecules - On the effects of hydrostatic pressure on a Mn_6 single-molecule magnet*	**Kevin Wainwright** O 66 Flinders University, Australia *Metal-ion activated molecular receptors immobilised on silica*
1210-1230	**Tony Masters** O 61 University of Sydney, Australia *Bespoke catalytic surfaces – precision nanoengineering*	**Jingli Xie** O 64 University of Melbourne, Australia *Toward a facile one-step construction of quantum dots containing Zn_8S cores*	**Glenn D. Wright** O 67 Queens University of Belfast, UK *Consolidation of molecular computational identification*
1230-1330	**Lunch**		

	Supramolecular Chemistry *Lecture Theatre C1* Chair: Richard Keene	Bioinorganic Chemistry *Lecture Theatre C2* Chair: Evan Moore	Computational *Lecture Theatre C3* Chair: Owen Curnow
1330-1400	**Leonard Lindoy** K 6 University of Sydney, Australia *Strategies for generation of new discrete nano-scale molecular structures via metal-ion directed assembly*	**Paul Bernhardt** K 7 University of Queensland, Australia *Mediated molybdoenzyme electrocatalysis: macrocyclic chemistry meets enzymology*	**Brian Yates** K 8 University of Tasmania, Australia *A computational approach to the activation of strong bonds*
1400 - 1420	**Paul Kruger** O 68 University of Canterbury, New Zealand *Twist and spin: from anion binding to spin crossover in dinuclear Fe(II) helicates*	**Matthew J. Belousoff** O 71 Monash University, Australia *A new macrocyclic terbium(III) complex for use in RNA footprinting experiments*	**Al Nielson** O 74 Massey University , New Zealand *Coordination chemistry by computation; from linear agnostic interactions to weak hydrogen bonds in TM complexes*
1420 - 1440	**Kay Latham** O 69 RMIT University, Australia *Ionic molecular crystals of organophosphonic acids: synthesis, supramolecular motifs and luminescent Behavior*	**Oluwatayo Ikotun** O 72 Syracuse University, USA *Pharmokinetic properties of pyrophosphate-based homodinuclear coordination complexes*	**Nigel Brookes** O 75 University of Tasmania, Australia *Scission of carbon dioxide by transition metal complexes. A DFT investigation*
1440 - 1500	**Brendan Abrahams** O 70 University of Melbourne, Australia *Structural and host-guest studies of novel supramolecular species*	**David Schilter** O 73 University of Sydney, Australia *Synthesis and bio-inorganic chemistry of metallocyclic architectures*	**Ralf Tonner** O 76 Massey University, New Zealand *Adsorption of proline and glycine on the TiO_2(110) surface – a DFT study*
1500 - 1530	**Afternoon Tea**		
	Stranks Award Oral Presentation *Lecture Theatre C1* Chair: Paul Bernhardt		
1535 - 1555	**Matthias Zimmermann**, University of Melbourne, Australia S 1 *The N-terminal domain of the zinc transmembrane transporter HMA4 from Arabidopsis thaliana binds Cu(I) 10^6 times more strongly than Zn(II) and Cd(II)*		
1555 - 1615	**Natasha F. Sciortino,** University of Sydney, Australia S 2 *Multifunctional metal-organic frameworks*		
1615 - 1635	**Sumy Kunnamkumarath,** University of Adelaide, Australia S 3 *Intracellular imaging of anti-cancer NAMI-A analogues*		
1635 - 1655	**Jonathon Kitchen,** University of Otago, New Zealand S 4 *Generating magnetically interesting dinuclear iron(II) complexes with designer 1,2,4-triazole ligands*		
1655 - 1715	**H.Y. Vincent Ching,** University of Sydney, Australia S 5 *Boronated DNA metallointercalators for boron neutron capture therapy*		
1715 - 1735	**Victoria J. Argyle,** University of Otago, New Zealand S 6 *Metal oxime triangles, cages and boxes*		
1845 - 1900	**Buses to Antarctic Centre** *UCSA Car Park*		
1900 – 2200	**Conference Dinner and Awards Ceremony** *Antarctic Centre* *Buses will return guests to the University at 2200 and 2230.*		

Time	Thursday18th December 2008
	Plenary Lecture 5 *Lecture Theatre C1* Chair: Richard Hartshorn
0930-1030	*Olefin Metathesis and Discovering New Reactions*
	Bob Grubbs California Institute of Technology, USA
1030 - 1100	**Morning Tea**
	Burrows Lecture *Lecture Theatre C1* Chair: Paul Bernhardt
1100 - 1200	*Shedding Light on Organometallics*
	Mark Humphrey Australian National University, Australia
1200 - 1300	**Closing Ceremony** **Divisional Meeting** *Lecture Theatre C1*

Sunday 14 December

Plenary Lecture

5.00pm-6.00pm

Plenary 1

2008: A Small Space Odyssey with Luminescent Molecules

Gareth J. Brown,[1] A. Prasanna de Silva,[1] Kaoru Iwai,[2] Gareth D. McClean,[1] Bernadine O.F. McKinney,[1] David C. Magri,[1] Seiichi Uchiyama[3] and Sheenagh M. Weir[1]

1 School of Chemistry and Chemical Engineering, Queen's University, Belfast, Northern Ireland

2 Department of Chemistry, Nara Women's University, Kitauoya-Nishimachi, Nara, Japan

3 Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

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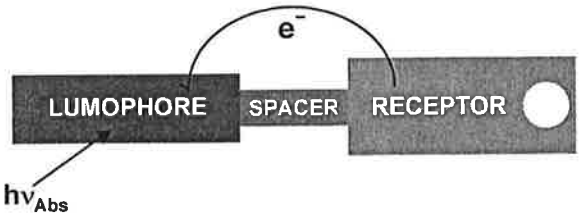
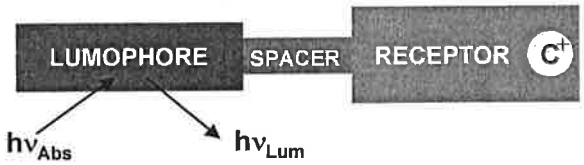
Photoinduced electron transfer (PET) is the heart of photosynthesis and is a major channel of de-exciting excited states.[1] Luminescence is another such channel. The controlled competition of luminescence with photoinduced electron transfer (PET) can switch the luminescence 'on' or 'off' by chemical means in an easy, predictable manner. The modular nature of 'lumophore-spacer-receptor' supramolecular systems is not only vital for the occurrence of PET, but also for the prediction of sensor/switch characteristics such as colours of the optical signals and the concentration range of the analyte (C^+ in the scheme below).





Since switchable light signals carry information, we can enter the subject of information handling. When molecules are gathering information they are *sensors*. When processing information they are *computers*. Chemical scientists have the skills to launch molecular vehicles to explore small inaccessible spaces and to send back information that we can act upon, e.g. in a medical context.

The first-generation systems use a single chemical controller. These give rise to examples which monitor or the sodium levels in blood within millimeter-sized channels cells. status of acidic compartments in micrometer-sized Some of these even map proton distributions in nanometric spaces near membranes.[2] Notably, some of these serve wider society by operating in hospital intensive care units.[3] In general, these are sensors which now form a vibrant field.

The second-generation systems use multiple chemical controllers. These form molecular-scale information processors[4] which employ chemical species as inputs, light as output and wireless interfacing to human operators. These processors operate comfortably in nanometer-sized regions near membranes,[5] for instance. These spaces are far too small for the tiniest silicon-based electronic devices to enter. Such molecular logic devices are continually growing in complexity. Some of these have potential as 'lab-on-a-molecule' systems for intelligent medical diagnostics.[6]

Molecular computation will only grow if robust applications can be found for it in the short term. Molecular computational identification (MCID) of nano/micrometric objects[7] is offered as the first of such applications which addresses a problem that does not currently have solutions from semiconductor computing technology.

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Monday 15 December

Plenary Lecture

9.00am-10.00am

Plenary 2

Functional Metal-Organic Framework Materials

J.Hupp[1],

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This talk will present results of some of our recent successful efforts to design and synthesize metal-organic framework (MOF) materials that are functional for chemical separations, chemical fuel storage and release, and catalysis. The talk will describe the features we believe to be important for eliciting functional behavior. Also to be described will be advances in the activation and purification of high-area MOFs, including separation of otherwise identical catenated versus non-catenated versions of promising framework materials. If time permits, useful post-synthetic tailoring of MOF surfaces and interiors by "click" chemistry and by coordination chemistry will be described.

Monday 15 December

Session 10.00am-11.00am

Session	Chair	Room
New Faces in Chemistry	**Chris Fitchett**	**C2**
Abstracts O 1 to O 3		
Coordination Chemistry	**James Wright**	**C3**
Abstracts O 4 to O 6		

O 1

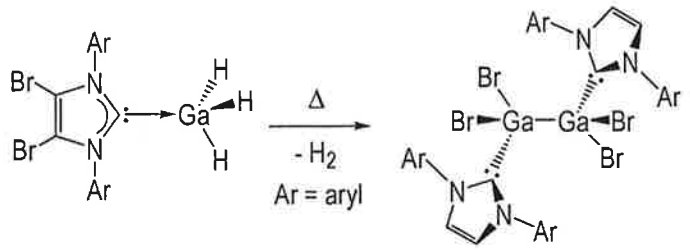
Heavy Group 13 Halohydrides – *Not Just Aspiring Trihydrides!*

Marcus L. Cole

[1]*School of Chemistry, University of New South Wales, Sydney, Australia – m.cole@unsw.edu.au*

The binary hydrides of the metallic group 13 elements have been a source of fundamental interest to main group chemists for over 80 years.[1] By contrast, the study of partially halogenated variants, e.g. the mono- and dihalogenometallanes; MXH_2 and MX_2H, where M = metallic group 13 metal and X = halogen, has received scant interest due to little perceived synthetic benefit.[2]

This presentation seeks to highlight that partial hydride replacement with halides increases the stability of group 13 hydrides, thereby enhancing their synthetic utility. Aspects of note include the tuning of chemoselectivity during hydrometallation, entry to low oxidation state group 13 compounds by reductive dehydrogenation,[3] and synthetic modification by salt-elimination metathesis.



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O 2

CO_2 Capture in Amine-Functionalised Metal-Organic Frameworks

Deanna M. D'Alessandro[1], Aude Demessence[1], Maw-Lin Foo[1], Jeffrey R. Long[1]

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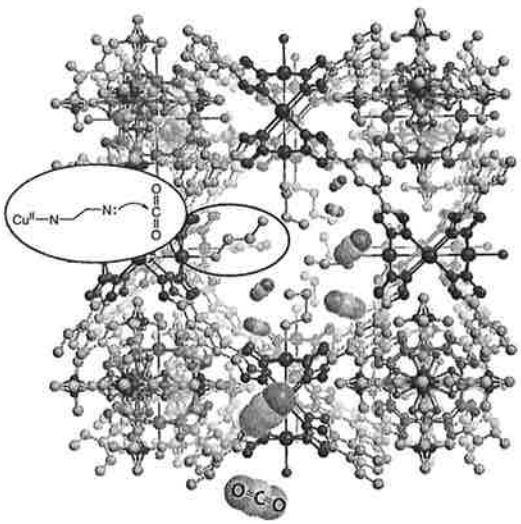
deanna_dalessandro@berkeley.edu

Amongst several candidate groups for CO_2 capture materials, metal-organic frameworks (MOFs) show exceptional promise due to their highly porous structures, high surface areas, and uniform but tunable pore sizes, which give rise to selective gas adsorption properties. We have developed air- and water-stable alkylamine-functionalised MOFs as a new class of materials for CO_2 capture. As a class of solid adsorbents, the materials have the potential to overcome many of the problems associated with conventional amine-based 'wet-scrubbing' methods for CO_2 capture from flue gas streams, whilst exploiting the high affinity of amine-containing functionalities for CO_2.

The use of general postsynthetic functionalisation techniques to graft pendant alkylamine functionalities onto the internal surfaces *following* framework formation has provided access to a range of robust amine-functionalized MOFs based on imidazolate, pyrazolate and triazolate ligands.[1] For example, in the desolvated framework $HCu[(Cu_4Cl)_3(BTTri)_8]$ {H_3BTTri = 1,3,5-tri(1*H*-1,2,3-triazol-4-yl)benzene}, the coordinatively unsaturated Cu^{II} sites can be selectively functionalised by the monodentate coordination of ethylenediamine (as shown below). The new materials have been characterised by X-ray powder diffraction analysis, in addition to gas adsorption and thermogravimetric analyses. To screen the materials for capture applications, the temperature control of the adsorption/desorption processes and the kinetics of the CO_2-amine reactions have been probed under realistic flue gas stream conditions.



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O 3

From the Visible to Near Infra Red: Efficient Antennae for Sensitised Ln(III) Luminescence

Evan G. Moore[1], Kenneth. N. Raymond[2]

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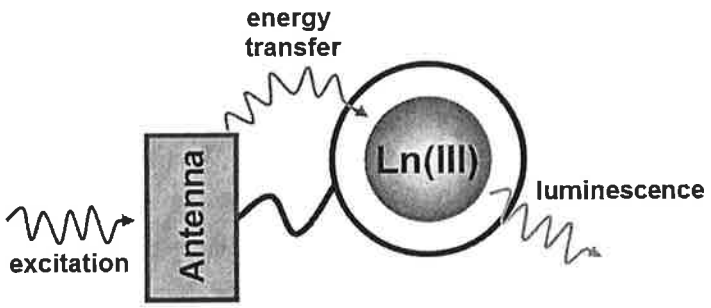
[2]*Department of Chemistry, University of California, Berkeley, CA, 94720, USA.*

Synthetic, structural, and photophysical aspects of recent efforts toward improving the sensitization of trivalent lanthanides using aromatic chelate groups as 'antenna' chromophores will be discussed. A variety of eight and nine coordinate complexes (CN = 8, 9) with bis(tetradentate), tris(tridentate) and octadentate ligand topologies have been prepared and studied. Efficient visible emission from Eu(III) and Tb(III) with quantum yields as high as Φ_{tot} ~ 20% and 60% respectively have been observed.[1,2] Sensitisation of Near Infra Red (NIR) emitters such as Ho(III) and Yb(III) has also been achieved in aqueous solution,[3] with quantum yields for the latter on the order of Φ_{tot} ~ 1%. Accompanying TD-DFT calculations and 77 K studies with Gd(III) have allowed a detailed understanding of the electronic structures. These compounds and their functionalised derivates are attractive as luminescent reporters for time-resolved fluoroimmunoassay and in the developing field of NIR tomography.



Acknowledgements: EGM acknowledges the Australian Research Council for funding (Discovery Project DP0879996). KNR acknowledges support from the Director, Office of Science, Office of Basic Energy Sciences, and the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at LBNL (Contract No. DE-AC02-05CH11231).

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O 4

Electron Transfer Studies of Cobalt(II) and Nickel(II) β-Diketonate Complexes Incorporating Asymmetric Diimine Ligands

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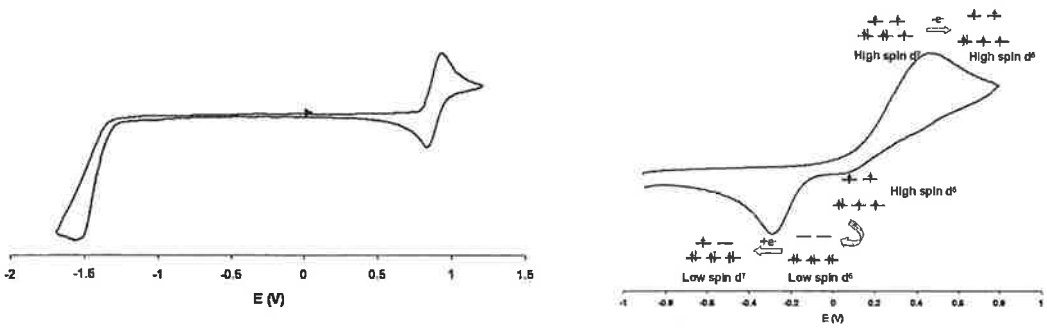
The reaction of ppa^X {(4-X-phenyl)-pyridin-2-ylmethylene-amine; X = H, Me, Et, OMe, F, Cl, Br and I} with $[M(dbm)_2]$, $[M(tmhd)_2]$ or $[M(hfac)_2]$ (M = Ni or Co) yields a series of nickel and cobalt complexes, $[M(\beta\text{-diketonate})_2(ppa^X)]$. X-ray cystallography reveals octahedrally coordinated metal centres with a *cis* arrangement of the β-diketonate ligands. The β-diketonate ligands adopt 'planar' or 'bent' coordination modes while the aryl ring of the ppa^X ligand is twisted with respect to the pyridylimine unit. The complexes have been studied by cyclic voltammetry. The results show that changing the substitutents on the β-diketonate ligands plays a more important role in the electron transfer behaviour than that of the ppa^X ligand. The increase in electron donating ability from hfac to tmhd and the corresponding change in redox-baviour from no oxidation to irreversible oxidation to quasi-reversible oxidation, in case of hfac, dbm and tmhd respectively.[1] Moreover, cyclic voltammograms of $[Co(tmhd)_2(ppa^X)]$ and $[Co(dbm)_2(ppa^X)]$ complexes reveal the spin change upon oxidation from the high spin d^7 to low spin d^6.[2]



(a) (b)

Figure 1 Cyclic voltammograms of (a) $[Ni(tmhd)_2(ppa^F)]$ and (b) $[Co(tmhd)_2(ppa^F)]$.

Acknowledgements:

We would like to thank the Thailand Research Fund and Walailak University for financial support (RSA5080007).

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O 5

Versatile Early and Late Transition Metal Coordination by Pyrazolyl-Based Heteroscorpionate Pincers

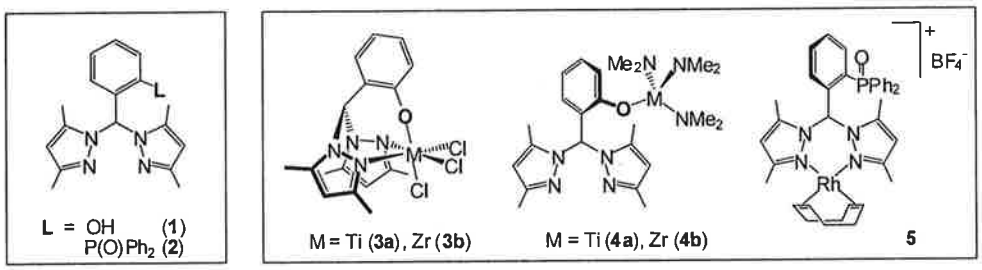
Laurent Poorters, Barbara A. Messerle

University of New South Wales, Sydney 2052, Australia. E-mail: l.poorters@unsw.edu.au

The utilisation of dinitrogen as a feedstock in the generation of sophisticated nitrogen-containing products is appealing for industrial use, as it is abundant, accessible and inexpensive. However, its direct activation still remains a challenge. In nature, nitrogenase enzymes catalyse this process under mild and ambient conditions, but the exact mechanism is still largely unknown. Since the characterisation of the first synthetic dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$ in 1965,[1] a large number of N_2 complexes have been synthesised, bearing either early or late transition metal centres and polydentate ligand systems.

Scorpionate pincers constitute a well established and widely employed family of ligands used in catalytic systems.[2, 3] Traditionally, scorpionates are spectator ligands that use hard nitrogen donors to bind a single metal centre.[4] More recently, there has been interest in the chemistry of scorpionates that incorporate other Lewis donors such as phosphorus, oxygen or sulfur.[5] We have synthesised new (NNO), (NNP) and (NNS) heteroscorpionate ligands for the preparation of early transition metal complexes. The latter will be used as catalyst precursors for the activation of molecular nitrogen.

The heteroscorpionate ligands investigated in this study are built upon a *bis*-(pyrazolyl)methane backbone. Attachment of an *ortho*-substituted phenyl ring to the bridging methylene moiety allowed the introduction of the third coordinating site. When reacted with halogenated early transition metal precursors, ligands **1** and **2** behave as authentic scorpionates, leading to the formation of octahedral metal complexes (e.g. **3a** and **3b**). On the other hand, ligand **1** acts as a mono-dentate ligand in the presence of *tetrakis*(dimethylamido)-titanium and zirconium. Finally, chelation of the metal centre through the *bis*-(pyrazolyl)methane entity occurred after treatment of **2** with the [Rh^{I}(1,8-cyclooctadiene)] cation to form **5**. As shown by low temperature NMR experiments, complex **5** as well as complexes **4a** and **4b** exhibit atropisomeric properties.



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O 6

Heteroatom in Carbon Ligands Spanning two Metal Centers: Enhancement or Diminution of the Electronic Communication? The Case of Di-iron-(bis)acetylide-pyridine Species

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In recent years, molecular compounds in which different carbon-containing units span two redox transition metal groups have received considerable attention, due to the speculation that such assemblies would be well suited for use in a variety of applications, including, for example, information storage devices. The control and manipulation of the interactions between the metal termini of such systems are therefore of great practical importance, but present considerable conceptual challenges. These challenges can be met by combining experimental studies with theoretical methods. We have ourselves analysed and compared the electronic and geometrical structures of a large variety of transition-metal systems containing different all-carbon spacers with the aid of density functional theory tools.[1] More recently, incorporation of hetero-elements such as nitrogen or boron in the carbon spacers has been theoretically studied in order to consider their effects on the electronic interaction between the metal centres.[2] Some recent results obtained for bi-metallic complexes containing (bis)ethynyl-pyridine spacers will be discussed.

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Monday 15 December

Session 11.30am-12.30pm

Session	Chair	Room
New Faces in Chemistry	**Chris Fitchett**	**C2**
Abstracts O 7 to O 9		
Bioinorganic Chemistry	**Peter Steel**	**C3**
Abstracts O 10 to O 12		

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O 7

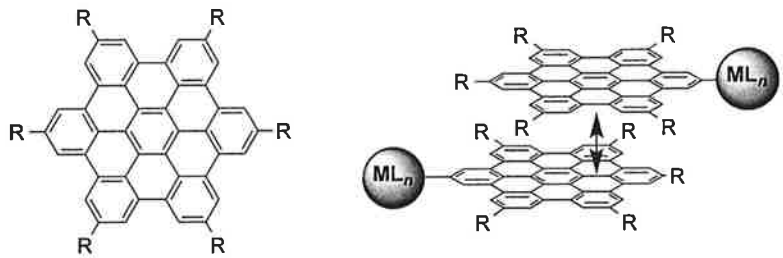
Hexabenzocoronene Ligands for Supramolecular Ordering

N. T. Lucas,[1,2] T. Darwish[1], P. Jensen[2]

[1]*Department of Chemistry, University of Otago, Dunedin, New Zealand*
[2]*School of Chemistry, The University of Sydney, NSW, Australia*

Intra- and intermolecular phenyl-phenyl interactions between metal complexes are well known and are critical in driving the packing of such complexes in the solid-state.[1,2] Although edge-to-face interactions between phenyl groups are the more prevalent, (offset) face-to-face interactions are common in polycyclic aromatic hydrocarbons (PAHs), increasingly so as they become larger.[3]

Large PAHs, often referred to as 'graphenes', can be formally regarded as 2-dimensional fragments of graphite. Advances in the directed synthesis of large PAHs have led to their investigation as new carbon-rich semi-conducting materials that self-organise by virtue of the strong π–π stacking interactions that exist between molecules.[4] One PAH that has recently received much attention for its materials properties is hexa-*peri*-hexabenzocoronene (HBC, **1**) and its alkyl-substituted analogues.[4] The robust supramolecular interactions of HBCs, along with their attractive electronic and optoelectronic properties, have prompted us to investigate them as ligands for metal complexation. The HBC group typically drives ligand conformation and the arrangement of metal complexes in the bulk. Our latest results on the synthesis and structure of HBC-based ligands and complexes will be presented.



1 **2**

R = H, alkyl, aryl

Acknowledgements:

We thank the Australian Research Council, The University of Sydney and University of Otago for financial support.

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O 8

Synthesis and Photophysical Properties of Complexes of Dipyrrin Ligands

Shane G. Telfer

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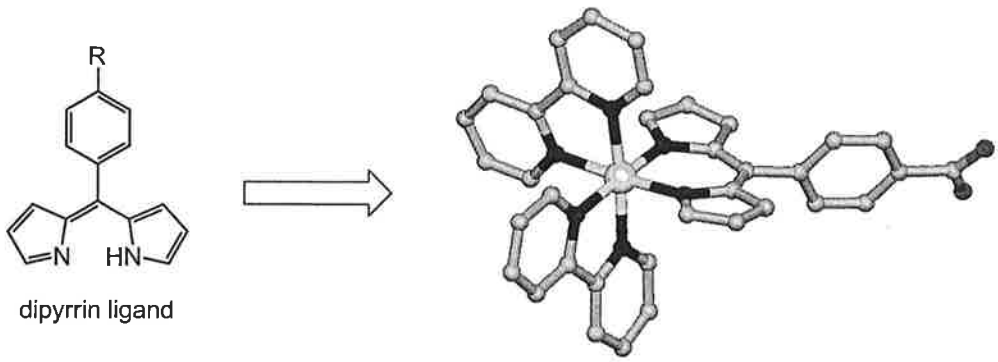
The coordination chemistry of dipyrrinato ligands, first studied several decades ago, is undergoing a rapid resurgence.[1] These ligands possess a conjugated π system akin to porphyrins, which endows their complexes with useful optical properties including intense absorption bands in the visible region of the spectrum and photoluminescence. As such, dipyrrin complexes hold promise as functional components of light harvesting and/or energy transfer systems.

This presentation will detail our investigations into the synthesis of spectroscopically interesting complexes of dipyrrin ligands. Exciton coupling between adjacent ligands has been found to have a significant impact on the absorption, circular dichroism (CD), and Raman spectra of [M(dipyrrin)$_3$] complexes.[2] Absorption spectra of mixed dipyrrin/2,2'-bipyridine complexes of ruthenium(II) indicate that the dipyrrin and Ru/bipy (MLCT) chromophores are essentially uncoupled, and this is further verified by Raman spectroscopy.[3] The application of these latter complexes as dyes for dye-sensitised solar cells will be discussed.



Acknowledgements:

We thank the MacDiarmid Institute for generous financial support.

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O 9

Clusters, Chains and Non-Covalent Networks: The Unpredictable Chemistry of Dicyanomethanide Ligands

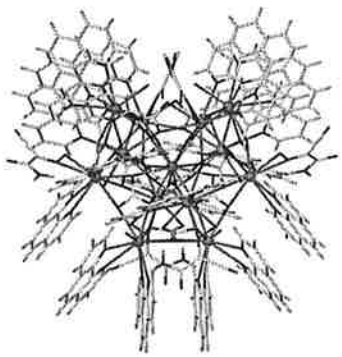
David R. Turner[1], Anthony S.R. Chesman[1], Sze Nee Pek[1], Glen B. Deacon[1], Stuart R. Batten[1]

[1]*School of Chemistry, Monash University, Clayton, VIC 3800, Australia david.turner@sci.monash.edu.au*

The coordination chemistry and reactivity of two anionic dinitrile ligands, $C(CN)_2(NO)^-$ (*dcnm*) and $C(CN)_2(CONH_2)^-$ (*cdm*), has been extensively researched by ourselves over the past few years.[1 - 3] The coordination chemistry of the *dcnm* anion in particular is highly unpredictable with a variety of coordination modes possible, including η^2(NO) bonding to rare-earth elements and nitroso-bridging between transition metals. Adding to this unpredictability is the reactive nature of the *dcnm* anion, which readily undergoes addition of protic solvent across one of the nitrile arms. This addition process has been harnessed to create a variety of novel anionic species, including examples of diamine cyclisation across both nitrile arms yielding anionic, heterocyclic species.

Compounds that have been obtained using the *dcnm* and *cdm* anions, and their derivatives, are too numerous to discuss at length and selected highlights are presented:

- Novel Ln_{13}-carbonate 'lanthaballs' with unprecedented $Ln(CO_3)_6$ cores (**1**).
- Thermal conversion of a molecular species to a magnetically coupled coordination polymer (**2**).
- Construction of a 2D sheets comprising Fe_{10} clusters (**3**).
- Reproducible hydrogen-bonding motifs between discrete complexes and polymeric chains.
- Transition-metal mediated reactivity of nitrile arms with diamines.



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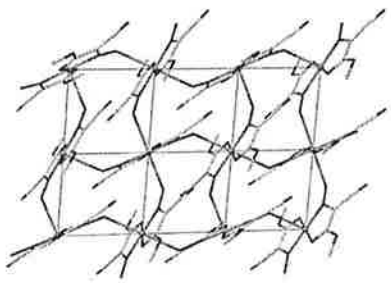

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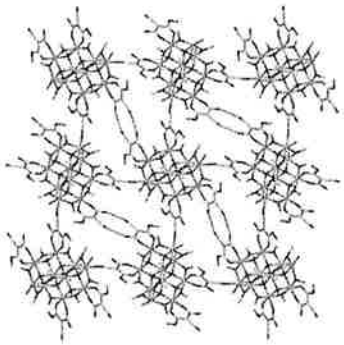

3

Acknowledgements: We acknowledge the ARC for funding and for a post-doctoral fellowship (DRT).

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[3] See also poster at this meeting by D.R. Turner and S.R. Batten for $C(CN)_2(CONH)_2^-$

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O 10

Selective Aggregation of a Pt-Gd Complex Within a Tumour Cell Nucleus

Louis M. Rendina[1], Ellen L. Crossley[1], Jade B. Aitken[1], Stefan Vogt[2], Hugh H. Harris[3]

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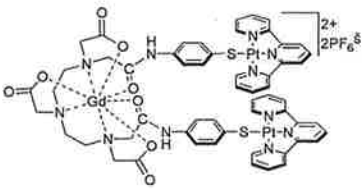
[2]*X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA.*
[3]*School of Chemistry and Physics, The University of Adelaide, Adelaide, SA 5005, Australia.*
Email: rendina@chem.usyd.edu.au

Gadolinium neutron capture therapy (GdNCT) is a relatively unexplored binary therapy which utilises the non-radioactive ^{157}Gd isotope (natural abundance = 15.7%) in a highly-effective thermal neutron capture reaction to destroy tumour cells.[1] ^{157}Gd possesses the largest effective nuclear cross-section of all the naturally-occurring elements (2.55 x 10^5 barns), a figure which is approximately 60 times greater than that of the ^{10}B nucleus which is used in BNCT.[2] In contrast to the ^{10}B isotope, ^{157}Gd undergoes neutron capture to give the products of internal conversion, accompanying Auger and Coster-Kronig electron emission and 7.94 MeV of kinetic energy.[1] However, the limited range of Auger electrons means that the Gd must be localised in close proximity to critical cellular components such as cell nuclei if the neutron capture reaction is to be exploited effectively. Gd may also play an important role in radiosensitising techniques such as synchrotron stereotactic radiotherapy (GdSSR).[3] In both types of therapies, the selective delivery of Gd to the cell nucleus would significantly enhance the efficacy of the treatments.

Treatment of A549 human lung carcinoma cells with **1** resulted in the selective aggregation of the intact drug within the cell nuclei, as determined by synchrotron X-ray Fluorescence (XRF) imaging. This work represents the first example of Gd delivery to a tumour cell nucleus by a Pt complex. The key results of this work will be presented.



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We thank Ms P. MacKay (The University of Sydney) for conducting the *in vitro* cell assays, including the preparation of cells for the XRF studies. This research was supported by the Australian Synchrotron Research Program which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. The use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, under contract no. W-31-109-Eng-38. The research was also supported by ARC grants to LMR (DP0557118) and HHH (DP0664706).

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O 11

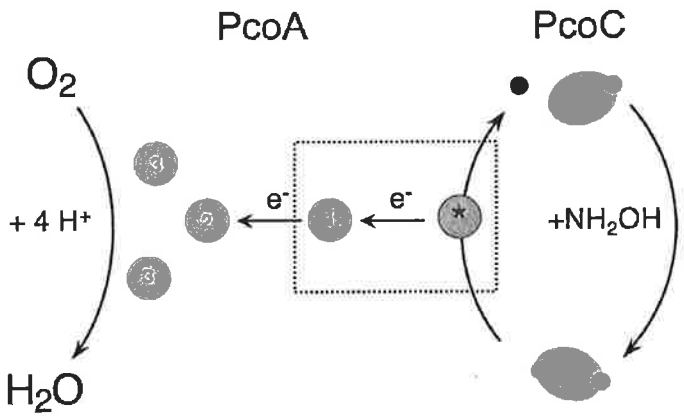
Control of seven copper sites in a single enzymic reaction of copper resistance. The multicopper oxidase PcoA catalyses oxidation of Copper(I) in $Cu^{I}Cu^{II}$-PcoC

Anthony G. Wedd, Karrera Y. Djoko, Matthias Zimmermann, Lee Xin Chong and Zhiguang Xiao

School of Chemistry, Bio21 Research Institute, University of Melbourne, Parkville, Victoria 3010, Australia

Nutrient copper is essential but toxic in excess. PcoA and PcoC are two of the soluble proteins expressed to the periplasm as part of the copper resistance response of *E. coli*. PcoC binds both copper(I) and copper(II) to form air-stable $Cu^{I}Cu^{II}$-PcoC. The blue multicopper oxidase PcoA is shown to catalyze oxidation of copper(I) bound in $Cu^{I}Cu^{II}$-PcoC to less toxic copper(II) which is released into solution (Figure).[1] This activity requires tight control of seven copper atoms. These two proteins may interact with the outer membrane protein PcoB to export excess copper from the periplasm.

PcoC and CopK are upregulated when *Cupriavidus metalliduran* CH34 is challenged with environmental copper. Remarkably, binding of Cu(I) in a $[Cu(S\text{-}Met)_3]^+$ site induces cooperative binding of Cu(II). The affinity for Cu(II) increases by a factor of 10^6 upon binding of Cu(I).[2] The respective roles of these proteins in protection against toxic copper levels will be discussed.



Acknowledgements: The Australian Research Council is thanked for support of this research.

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O 12

Dinuclear Ruthenium(Ii) Complexes As Potential Probes For Rna Bulge Sites

F. Richard Keene[1], Caitriona B. Spillane[1], Damian P. Buck[2], Jayden A. Smith[1], J. Grant Collins[2]

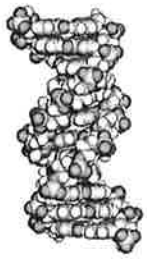
[1] *School of Pharmacy & Molecular Sciences, James Cook University, Townsville, Qld.4811, Australia; Email: richard.keene@jcu.edu.au*

[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.*

We have previously demonstrated that inert dinuclear ruthenium(II) complexes preferentially bind DNA at non-duplex structures, such as bulges and hairpin-loops.[1] Such perturbations to the canonical double-helical nucleic acid structure occur in both DNA and RNA, but are more frequent in RNA; they play an important role as secondary structure elements for specific recognition by proteins, RNA splicing and RNA-folding, thereby making them promising targets for potential diagnostics and therapeutic agents, including metallopharmaceuticals.

The groove dimensions for RNA are significantly different than for DNA (see figure), so our earlier results cannot be extrapolated to RNA. This paper will report on our NMR spectroscopy and molecular modelling studies of the binding of the stereoisomers of $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-bpm})]^{4+}$ {Me_2bpy = 4,4'-dimethyl-2,2'-bipyridine; bpm = 2,2'-bipyrimidine} to an RNA tridecanucleotide duplex containing a single-base bulge, which show that the complex binds the bulge-containing RNA with a significantly greater affinity than the non-bulge control RNA duplex.[2] Preliminary binding models, consistent with the NMR data, show that the ruthenium complex can effectively associate in the RNA minor groove at the bulge site.

The study has been extended[3] to investigate the HIV-1 trans-activation response (TAR) region of the RNA from the HIV-1 virus, which has been previously characterised and is biologically important. Bases in the bulge region are vital for effective protein recognition: if the protein (Tat) cannot bind at the bulge region of the HIV-1 TAR sequence the virus can not replicate, so there is considerable interest in developing small molecules that can selectively bind to such features as they would have potential as powerful anti-HIV drugs. The preliminary NMR results of this study strongly suggest that the tridecanucleotide bulge region of the HIV-1 TAR sequence is a recognition site for dinuclear ruthenium complexes. Molecular modelling has identified a new RNA conformational feature created by the insertion of bulge residues into duplex regions that may act as a recognition site for small molecule binding, in particular for inert dinuclear ruthenium complexes.



B-form DNA

Wide major groove
Narrow minor groove

A-form RNA

Deep, narrow major groove
Wide, shallow minor groove
Shorter, wider helix than B-form DNA

References:

[1] J.L. Morgan, D.P. Buck, A.G. Turley, J.G. Collins and F.R. Keene, *Inorg. Chim. Acta*, **2006**, *359*, 888. J.A. Smith, J.L. Morgan, A.G. Turley, J.G. Collins, and F.R. Keene, *Dalton Trans.*, **2006**, 3179.

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Monday 15 December

Session 1.30pm-3.20pm

Session	Chair	Room
Supramolecular Chemistry	**Paul Kruger**	**C2**
Abstracts K 1, O 13 to O 16		
Organometallic Chemistry	**Owen Curnow**	**C3**
Abstracts K 2, O 17 to O 20		

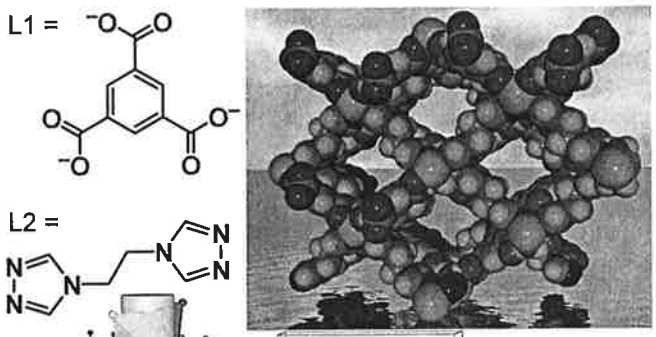
K 1

From Metal-Organic to Hydrogen-Bonded Networks

Christoph Janiak

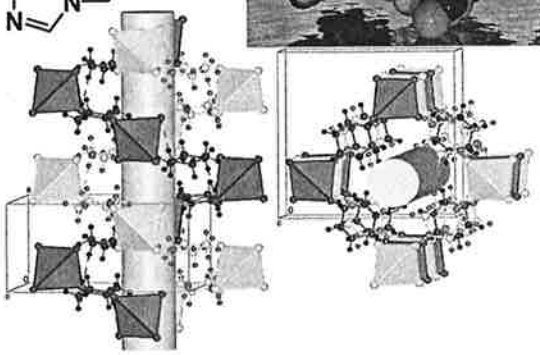
Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany. janiak@uni-freiburg.de

The last years have seen competitive research in the field of molecular-based extended framework materials, ranging from coordination polymers/metal-organic networks (e.g. **1**) to the supramolecular arrangement of metal complexes through hydrogen-bonding (e.g. **2**, **3**) and the application of C-H···F bonded ionic liquids as templates for nanoparticle syntheses [1].



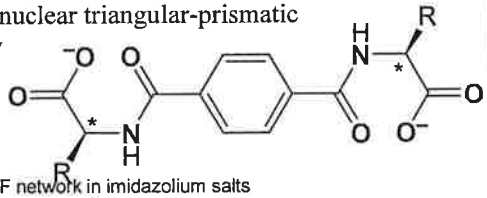
1: 3D-framework $^{3}{}_{\infty}\{[Ni_3(\mu_3\text{-}L1)_2(\mu_4\text{-}L2)L2(\mu\text{-}H_2O)_2]\cdot\sim 22H_2O\}$

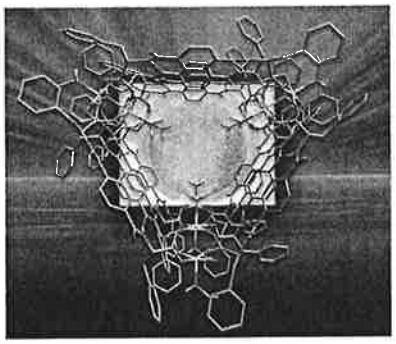
with a solvent volume of 1621 Å^3/unit cell (52%),
crystal-to-crystal transition,
Ni_3-SBU with antiferromagnetic coupling



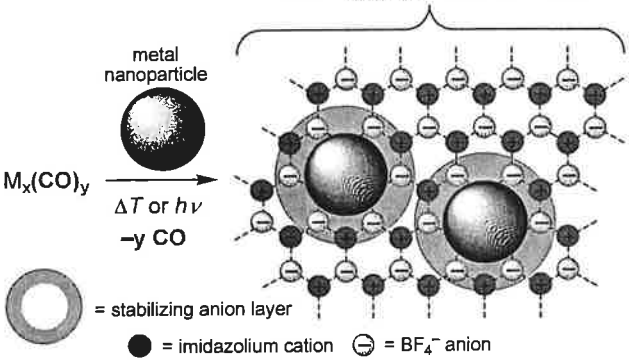
2: Piperazinium-halogenocuprates, $\{(C_4H_{12}N_2^{2+})_2[Cu^II_4^{3-}](I)_2^-\}_n$ – an inorganic model for the elusive iodine-starch complex.

3: Chiral C_3-symmetric hexanuclear triangular-prismatic cluster derived from a highly dipeptidic ligand:





copper(II) modular



4: Ionic liquid as templates for the synthesis of stable metal nanoparticles from metal carbonyl precursors without the need of additive stabilizers

[1] C. Janiak, *Dalton Trans.* **2003**, 2781. H. A. Habib, J. Sanchiz, C. Janiak, *Dalton Trans.* **2008**, 1734. B. Wisser, C. Janiak et al., *CrystEngComm* **2008**, *10*, 461. E. Redel et al., *Chem. Commun.* **2008**, 1789. J. Krämer et al., *Organometallics* **2008**, *27*, 1976.

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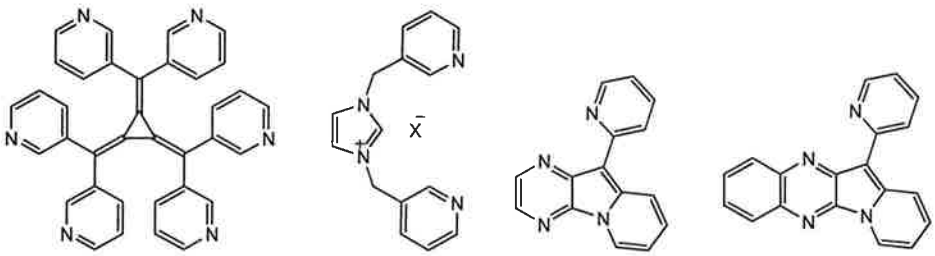
O 13

Cross-Conjugated And Highly Conjugated Heterocyclic Ligands; Discrete Coordination Complexes And Metallo-Supramolecular Assemblies

Christopher J. Sumby[1], Courtney Hollis[1], Lyall R. Hanton[2]

[1]*School of Chemistry & Physics, The University of Adelaide, Adelaide, Australia*
[2]*Department of Chemistry, University of Otago, Dunedin, New Zealand*

Over the last decade enormous strides have been made towards establishing the self-assembly criteria for the assembly of metallo-supramolecular species.[1] Against this backdrop of success in synthesis, the focus has shifted to investigating, tailoring and advancing the characteristics of these assemblies for new applications.[2] The properties of transition metal complexes and/or metallo-supramolecular assemblies can be readily tailored by the choice of heterocyclic ligand.[1, 2] For example, electron deficient or cationic ligands can be utilized to generate metallo-supramolecular receptors for anions. Electron deficient heterocyclic ligands include compounds based around a [3]-radialene core, or those based on an imidazolium core; for example compounds **1** and **2**, respectively. Electron rich chelating ligands such as 5-(2-pyridyl)indolizino[2,3-b]pyrazine **3** and 5-(2-pyridyl)indolizino[2,3-b]quinoxaline **4** can be used in place of 2,2'-bipyridine for example to modify the redox properties of ruthenium(II) complexes. This paper will describe the syntheses of these and other heterocyclic ligands, the preparation of complexes and metallo-supramolecular assemblies, and studies on these compounds.



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

Acknowledgements: The authors thank the University of Adelaide and the ARC for funding to support this research. C.J.S. acknowledges the ARC for a ARC Australian Post-doctoral Fellowship. The University of Otago is acknowledged for providing access to X-ray crystallography facilities.

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O 14

Anion Binding Utilizing Polyammonium Transition Metal Helicates

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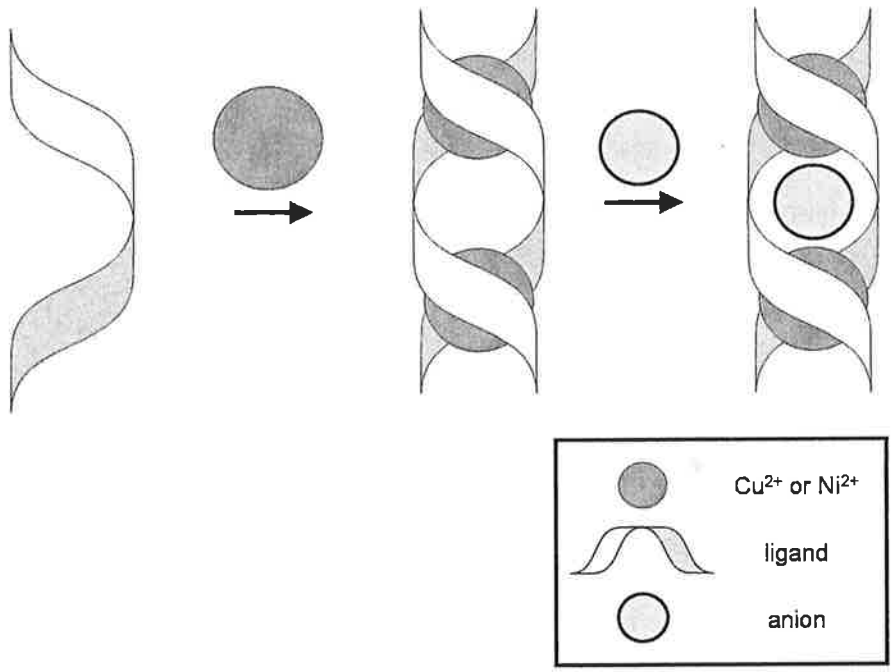
Supramolecular architectures continue to find utility as hosts for anionic guests. Frequently, these structures self assemble, trapping or encapsulating the anion within,[1] and, depending on the design of the ligand can form a myriad of supramolecular shapes including helicates.[2, 3]

By linking salicylaldimine units via a strap containing tertiary amines, we have shown that these ligands adopt a helical supramolecular cage upon complexation with transition metal cations.[4] The now protonated amines of the zwitterionic form of the ligand are available for anion binding. The structures and anion binding properties of these complexes will be discussed.



Acknowledgements:

Supported by the Marsden Fund Council from Government funding, administered by the Royal Society of New Zealand. PGP acknowledges the support of a Massey University PDF.

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O 15

Novel Supramolecular Assemblies Of Cyclotricatechylene

Nicholas J. FitzGerald, Brendan F. Abrahams, Timothy A. Hudson, Richard Robson

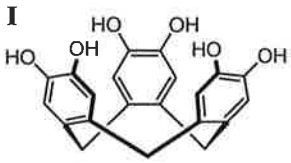
School of Chemistry, University of Melbourne, Victoria 3010, Australia

Over the last few years we have been interested in employing ligands that contain two or more catechol units as building blocks in the generation of both finite and infinite metallosupramolecular assemblies. The catechol unit offers the advantage that it binds strongly and predictably to metal centres and the incorporation of two or more catechol units in a single molecule provides an opportunity to place metal centres in a desired arrangement. One species that we have recently focussed upon is cyclotricatechylene (**I**, H_6CTC), which is closely related to cyclotriveratrylene (**II**) – a species that has been the focus of considerable attention within the field of supramolecular chemistry.[1] Here we report some novel supramolecular assemblies involving the H_6CTC unit that has been deprotonated to varying extents.

The combination of vanadyl with H_6CTC under basic conditions in the presence of appropriate cations yields tetrahedral $[(VO)_6CTC_4]^{12-}$ units (**III**). Other metals including Co, Mn and Cu also yield similar tetrahedral enclosures. In the case of the Co compound, metal centres belonging to adjacent tetrahedra are linked by oxide bridges, resulting in the formation of a cubic-type network containing very large voids. Cubes and trigonal prisms can also be formed by changing metal ions and/or reaction conditions.

Under weakly basic conditions and in the presence of an appropriately-sized cation a clam type structure is formed in which two partially deprotonated H_6CTC shell-like units hydrogen bond to each other and either fully or partially encapsulate the cation. Relatively small cations such as Rb^+ and Cs^+ appear to be ideally suited to the internal void of the clam (**IV**) whilst larger cations such as NMe_4^+ (**V**) and NEt_4^+ have the effect of causing the clam to partially open. These solid state structures are supported by mass spectral studies.

I



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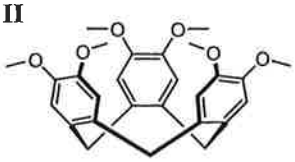

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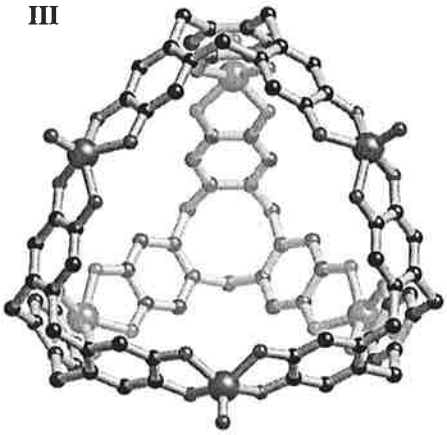

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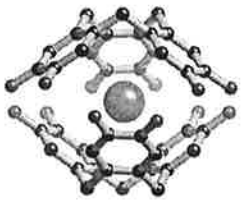

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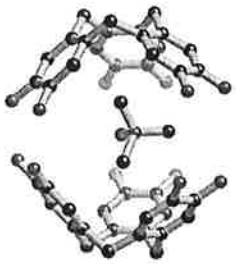

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O 16

Cyclodextrin [2]- and [3]-Pseudorotaxanes: An UV-vis and 2D ^{1}H NMR ROESY Equilibrium and Structural Study in Aqueous Solution

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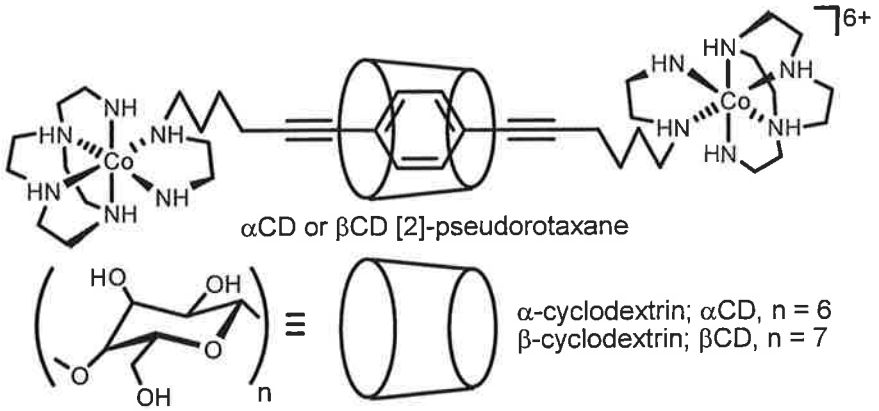
[2]- and [3]-pseudorotaxanes are two and three component host-guest complexes, in which a guest, or axle, with bulky end groups is threaded through one or more cyclic hosts. They are sufficiently facile to allow the guest to thread into and dethread from the host(s) in solution through a "slippage" mechanism. (This contrasts with [2]- and [3]-rotaxanes in which the end groups of the axle are sufficiently large to prevent the operation of a slippage mechanism and which are instead assembled by attachment of the end groups to the axle after it threads the cyclic host(s) in a "self-assembly" mechanism.) In this study α-cyclodextrin and β-cyclodextrin, αCD and βCD, act as the cyclic hosts and the axle end groups are cobalt(III) complexes as exemplified by the [2]-pseudorotaxane shown below. The correlation of the sizes of the cyclodextrins and the cobalt(III) complex end groups and the formation of [2]- and [3]-pseudorotaxanes and their stabilities determined by UV-vis spectroscopy are discussed, as are the broad structural factors deduced from 2D ^{1}H NMR ROESY spectroscopy .



Acknowledgements:

We gratefully acknowledge support from the Australian Research Council and The University of Adelaide

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K 2

Metallabenzene Ring Functionalization Reactions

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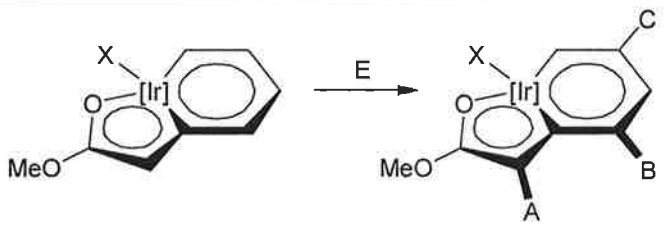
Although numerous studies have appeared concerning the structural features, spectroscopic properties, bonding, aromaticity and aspects of the chemistry of metallabenzenes, very few reports of metallabenzene ring substitution reactions have appeared.[1] In an extension of our original report that describes the first metallabenzene electrophilic aromatic bromination and nitration reactions,[2] we now report that the selective mono- di- and tri-bromination, mono- and tri-mercuration and mono-nitration of iridabenzofurans (see Figure 1) and related metalloaromatic compounds can be achieved. The mercurated derivatives in particular serve as useful precursors to other functionalized metallabenzenes. We also report that in a new type of reaction for metallabenzenes, nucleophiles add to the γ ring carbon atoms of the cationic species $[Os(CSMe\{CH\}_4)(CO)_2(PPh_3)_2]^+$ or $[Ir(CSMe\{CH\}_4)(S_2CNEt_2)(PPh_3)_2]^+$ to form the corresponding neutral metallacyclohexadiene complexes. Subsequent treatment of these neutral complexes with a suitable oxidant removes the hydrogen from the saturated γ carbon atoms and this restores the delocalized bonding within the metallacyclic rings to yield new, cationic, substituted metallabenzenes.



[Ir] = $Ir(PPh_3)_2$

X = CO; E = Br_2; A = Br, B,C = H
X = CO; E = $Cu(NO_3)_2$, C = NO_2, A,B = H
X = Br; E = Br_2; A,C = Br, B = H
X = Br; E = $Hg(O_2CCF_3)_2$, B = HgX, A,C = H
X = Cl; E = $Hg(O_2CCF_3)_2$, A,B,C = HgX

Figure 1

Acknowledgements:

University of Auckland Doctoral Scholarships for L. A. F. and A. F. D. are gratefully acknowledged.

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O 17

Long Distance Electronic and Magnetic Interactions between Organometallic Redox Active Centres Mediated by Carbon Rich Bridges Containing Aromatic Rings

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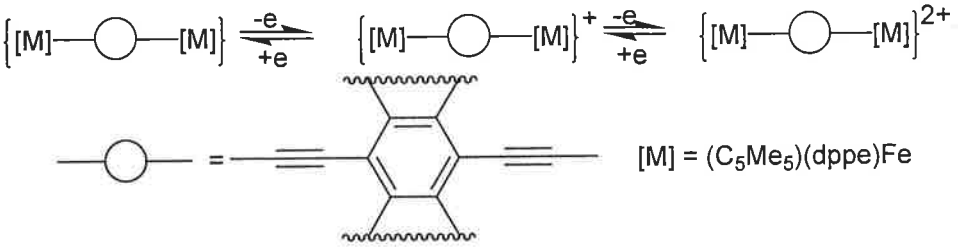
The design, the synthesis and the study of new nanoscale-sized "smart" organic or organometallic molecules with tailor-made switching ability constitute a key step toward creating tomorrow's molecular electronic devices including electroactive and photoresponsive metal-containing polymers.[1] In this field, a very appealing class of composite molecules can be obtained by linking two redox-active inorganic building blocks with unsaturated organic ligands. These molecules can be isolated in several oxidation states, each of them exhibiting different physical properties, like for example, photoluminescence,[2] photo-induced electron transfer,[3, 4] hyperpolarizability[5] or magnetic properties.[6] These physical properties can be easily switched on or off by single electron transfers.



The valence flexibility of the carbon chain ligands and the ability of carbon to form single (M-C), double (M=C) and triple (M≡C) bonds to metals allows intimate combination of the properties of the different metal centers through the carbon bridge. This feature will be illustrated with several examples.

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O 18

Alkoxybenzimidazolium-linked cyclophanes: Conformation control and carbene-precursors

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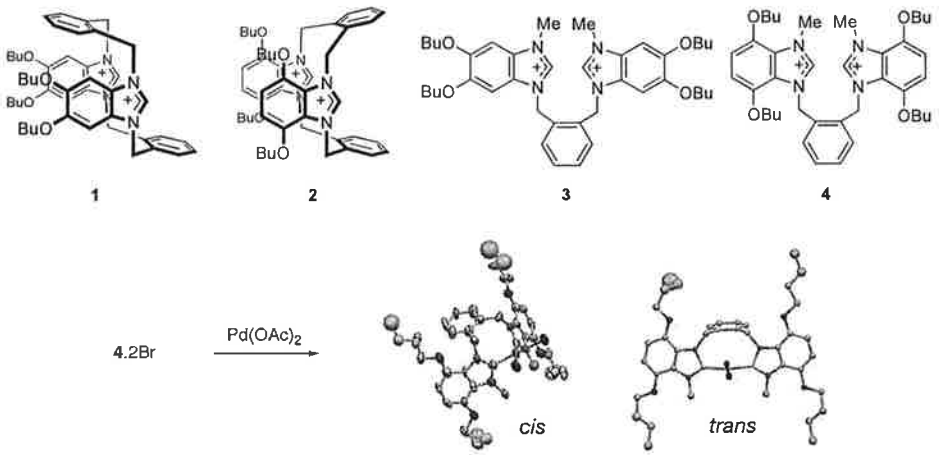
We are interested in azolium cyclophanes and their ability to act as *N*-heterocyclic carbene (NHC) precursors.[1,2] Metal complexes bearing NHC-linked cyclophane ligands display properties that are relevant to catalysis and biological application.[2,3]

Azolium-linked cyclophanes based on 5,6-dibutoxybenzimidazole and 4,7-dibutoxybenzimidazole, such as **1** and **2** have been synthesised, as have their non-cyclophane analogues **3** and **4**. The addition of butoxy-groups allow for some potentially enhanced properties, in particular conformational control of the cyclophane structure and improved-donor propertied of NHC ligands. The solution conformations of the cyclophanes depend on the positions of the substituents and the solvent in which they are studied. Metal complexation studies with palladium have been conducted and the structure of the complexes, and the conformations of the ligands, appears dependant on both the substitution pattern on the ligand and the presence of the metal centre. The ability of these complexes to act as pre-catalysts in coupling reactions will also be discussed.



Acknowledgements:

We thank the Australian Research Council for a Discovery Grant (to M.V.B. and A.H.W.) and an Australian Postgraduate Award (to P.V.S.), and Curtin University of Technology for a Research and Teaching Fellowship (to D.H.B.).

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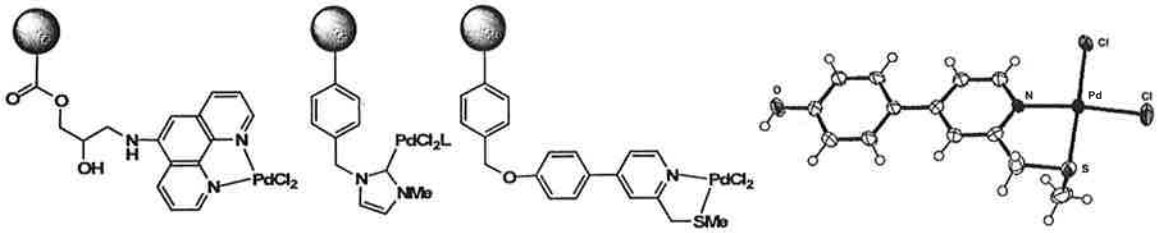
O 19

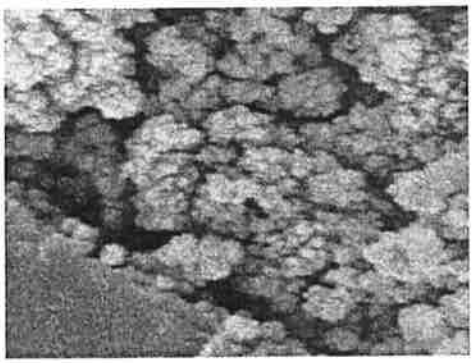
Miniaturising Metal Catalysis at the Micrometre Level in Capillaries and Glass Chips

Allan J. Canty[1], Jeremy A. Deverell[2], Michael G. Gardiner[1], Anissa Gömann[1,2], Rosanne M. Guijt[2], Roderick C. Jones[1], Thomas Rodemann[3], Jason A. Smith[1], Vicki-Anne Tolhurst[1]

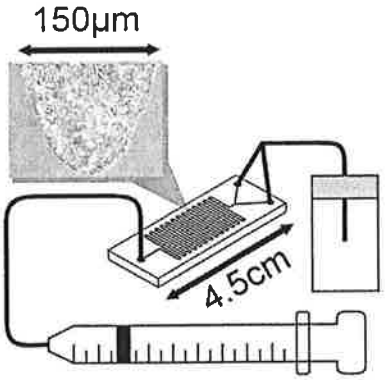
[1]*School of Chemistry, University of Tasmania, Hobart, Tasmania, Australia, allan.canty@utas.edu.au*
[2]*Australian Centre for Research on Separation Science, University of Tasmania*
[3]*Central Science Laboratory, University of Tasmania*

Technologies for the development of supported catalysis in fused silica capillaries and glass chips are described, where catalytic centres are anchored on organic polymer monolith.[1-3] The organic monolith is a continuous molecular solid filling the capillary (Internal Diameter 100 μm) or chip (ID ~150 μm). It is bonded to the walls, highly porous (void volume ~60%) and has high surface area allowing flow-through catalysis. Nitrogen donor, carbene, and nitrogen/sulfur heteroleptic ligand systems have been explored for palladium catalysed Suzuki-Miyaura, Sonogashira and Mizoroki-Heck reactions. The new reagent HOC_6H_4-$pyCH_2SMe$ was synthesised for pre-catalyst anchoring, and its $PdCl_2$ complex is shown below. Comparisons of the new technology with conventional catalysis on bulk solid supports including polystyrene beads will be described.





SEM of monolith in channel of chip



Acknowledgements:
Support from the Australian Research Council is acknowledged.

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O 20

Novel Organometallic Ruthenium(II) Cp* Benzenesulphonamides for the Inhibition of Carbonic Anhydrases

Bradley T. Loughrey[1], Peter C. Healy[1], Peter G. Parsons[2], Sally-Ann Poulsen[1], Claudio T. Supuran[3], Michael L. Williams[1]

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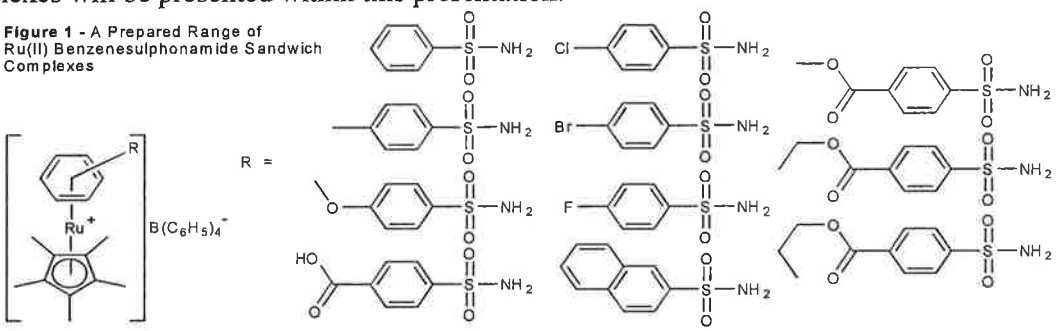
E-mail Address : Bradley.Loughrey@student.gu.edu.au
[2] *Drug Discovery Group, Queensland Institute of Medical Research, Brisbane, Australia*
[3]*Università degli Studi di Firenze, Polo Scientifico, Laboratorio di Chimica Bioinorganica, Sesto Fiorentino (Florence), Italy*

Ruthenium(II) organometallic complexes have gained recent acceptance as potential anti-cancer agents.[1,2] The promising biological effects displayed by these complexes both *in vitro* and *in vivo* prompted our research group to synthesize and structurally characterize a series of ionic Ru(II) arene Cp* (η^5-$C_5(CH_3)_5$) complexes [R-PhRuCp*]$^+$X$^-$.[3] In a series of cellular cytotoxicity assays, these ruthenium sandwich complexes exhibited a potent and selective antiproliferative effect towards a range of tumourigenic cell lines, achieving IC50 values comparable to cisplatin.[3] We hypothesised that similarly ionic Ru(II) organometallic Cp* sandwich complexes, prepared through coordination to a pre-existing therapeutic scaffold, may further optimize the activity of this class of compound.[3]

An aromatic or heteroaromatic sulphonamide moiety ($ArSO_2NH_2$) is the classical recognition fragment necessary for small molecules to bind the active site of carbonic anhydrase (CA).[4] Here we present our synthetic methodology to prepare a range of novel Ru(II) benzenesulphonamide Cp* sandwich complexes (**Figure 1**). These have been screened for enzymatic inhibition of the physiologically dominant CA isozymes: hCA I, II and cancer-associated isozyme IX. Isozyme IX is over-expressed in many solid tumours and inhibition of this CA has been linked to growth cessation in several forms of tumour cell line both *in vitro* and *in vivo*.[4]

Through coordination of the aromatic sulphonamide ligand to a RuCp* moiety, it was proposed that the resulting complex would retain affinity for the CA enzyme, while maintaining the cytotoxicity observed for the earlier [R-PhRuCp*]$^+$X$^-$ complexes . In this way, we endeavored to achieve a dual antiproliferative effect towards tumour cell lines that overexpress the carbonic anhydrase enzyme: inhibiting both enzyme mediated tumour growth and prompting apoptosis through cytotoxicity. The synthesis, enzyme inhibition data and cytotoxic evaluation of this range of complexes will be presented within this presentation.

Figure 1 - A Prepared Range of Ru(II) Benzenesulphonamide Sandwich Complexes



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Stranks Poster Index (Monday and Tuesday Poster Sessions)

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S2	N	Sciortino	Multifunctional Metal-Organic Frameworks - Interplay Between Spin-Crossover and Host-Guest Chemistry in Nanoporous Materials
S3	S	Kunnamkumarath	Intracellular imaging of anti-cancer NAMI-A analogues.
S4		Kitchen	Generating Magnetically Interesting Dinuclear Iron(II) Complexes with Designer 1,2,4-Triazole Ligands
S5		Ching	Boronated DNA Metallointercalators for Boron Neutron Capture Therapy
S6		Argyle	Metal Oxime Triangles, Cages and Boxes

For full abstracts see Wednesday afternoon session.

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PM9	Y.M.	Lee	Unsymmetrical Bidentate Ligands in the Coordination-Driven Self-Assembly of Discrete Supramolecules
PM10	L.O.	Kadidae	New Aromatic Anion Receptors Holding the Dansyl Fluorophore
PM11	H	Feltham	Polynuclear complexes of transition metal ions: towards Single Molecule Magnets
PM12	W	Gobeze	Dinuclear Metal Complexes Incorporating a Pyrimidine Bridge
PM13	O	Ujam	Electrospray Ionisation Mass Spectrometry (ESI-MS) Monitored Synthesis and Characterization of Multifunctional Alkylated Derivatives of [Pt2(μ-S)2(PPh3)4]
PM14	G.V.	Prabhu	Synthesis and characterization of 1,3-Bis-[phenyl-(pyridin-2-ylamino)-methyl]- thiourea and its Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} metal ion complexes
PM15	M	Agahi	Synthesis & coating of ZnS nanosemiconductors on QCM substrate for diagnostic applications
PM16	A	Gharib	Catalytic Performance of Mixed-addenda Heteropolyanions as Inorganic Solid Catalysts in Lactonization of Various Diols
PM17	M	Sokolova	Synthesis, Crystal Structure and Some Properties of Tetravalent Uranium and Plutonium Compounds $[An(DMSO)_8](ClO_4)_4 \cdot CH_3CN$ (An = U, Pu)
PM18	M	Sokolova	Systematic Study of $(HIm)_2[An(di\text{-}Pic)_3] \cdot 3H_2O$ Compounds, An = Th, U, Np, Pu (H_2di-Pic = pyridine-2,6-dicarboxylic acid, $C_5H_3N(COOH)_2$)
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PM21	R	Davidson	Iron (II) complexes of phosphazenes substituted with tridentate ligands
PM22	O	Curnow	Structural, Theoretical and Spectroscopic Properties of Chloride Hydrates: The S_6 Symmetric $[Cl_2(H_2O)_6]^{2-}$ Cube
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PM54	T.J.	Hseuh	Zno Nanowires with Pt Adsorption Using a Photochemical Reduction Mechanism
PM55	H	Kunttu	Relaxation dynamics of $Cr(acac)_3$ probed by ultrafast IR and UV/Vis spectroscopy
PM56	T.K.	Venkatachalam	Synthesis and fluorescence studies on macrocyclic derivatives bearing aminophenylbenzothiazole functionalities: Identification of a potential "OFF-ON-OFF" fluorescent sensor probe for zinc ions
PM57	J	Stevens	Enhanced Anion selectivity and strength of binding by the incorporation of neutral H-bond donors
PM58	S	Hoyte	Structures and Reactions of New Osmium Polyhydride Complexes
PM59	M	Ogawa	Synthesis, Photophysical Properties, and Photocatalytic Activities of Tris(2,2'-bipyridine)ruthenium(II) Derivatives Tethered to Peptide Residues with Viologen Moieties
PM60	S	Kunnas-Hiltunen	X-ray diffraction study of bisphosphonate metal complexes: Mg, Sr and Ba complexes of (dichloromethylene) bisphosphonic acid *P,P'*-dibenzoyl anhydride
PM61	C.H.	Chen	Highly sensitive ZnO nanowire ammonia sensor with Pt adsorption
PM62	K	Allan	Novel *Si,P* Hybrid Ligands
PM63	J	Bull	Mössbauer and X-ray Single Crystal Determination of Microscopic EFG and MSD Tensors in Ferrous High Spin Salts
PM64	L	Kuntz	Green oxidation technologies: Immobilization of Fe-TAML catalysts
PM65	D	Hutchinson	Influence of Terminal OH Groups on the Metal Complexes of Pyrimidine-Hydrazone Strands
PM66	M	Massi	Synthesis and Characterisation of Novel Bismuth β-diketonate Precursors
PM67	P	Simpson	The Effect of Ancillary Ligands on the Behaviour of Alkoxybenzimidazolin-2-ylidene-Palladium Complexes as Pre-Catalysts
PM68	S.Y.	New	Supramolecular Assembly Using Amino Acid Schiff Bases
PM69	T	Vaughan	New Platinum(II) and Platinum(0) Complexes of Bulky Iminophosphine ligands
PM70	M	Schultz	Towards metal helicates: polystranded ligands containing multiple amino acids

Monday Poster Session Abstracts

Poster PM7

Synthesis of Alkynylplatinum(IV) Complexes and Selectivity in Reductive Elimination from Platinum(IV) Centres Containing Varied Combinations of Organic Groups

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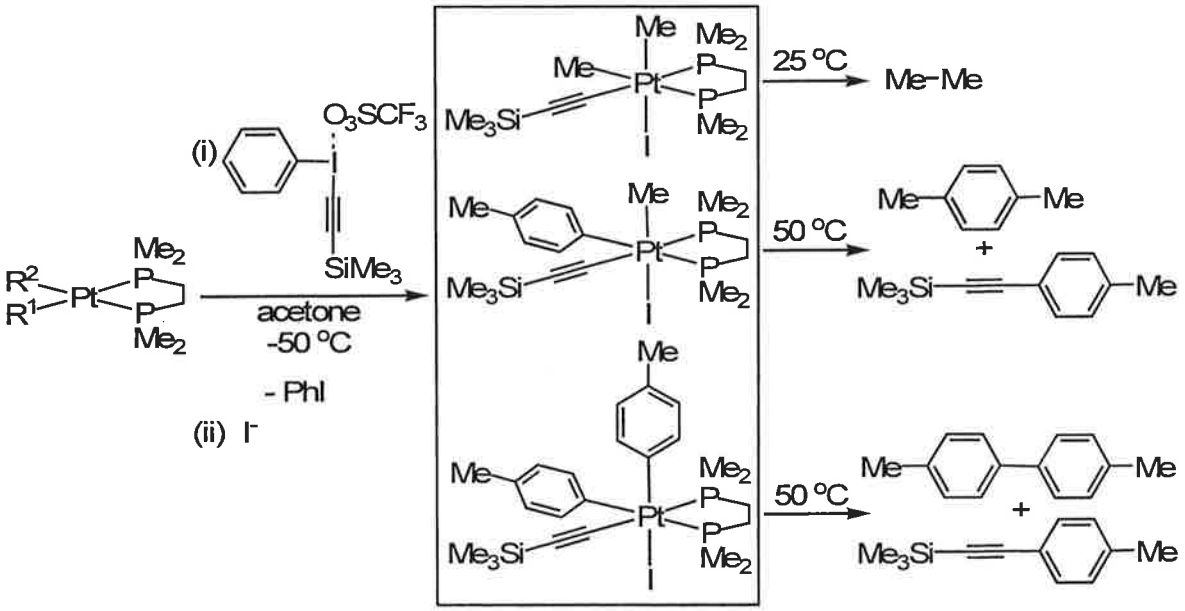
Development of a synthetic route to monoalkynylplatinum(IV) complexes using hypervalent iodonium reagents allows a study of selectivity in carbon-carbon bond formation from complexes containing combinations of alkyl, aryl, and alkynyl groups (Scheme).[1] Minor amounts of $Me_3SiC{\equiv}CI$ are also formed from the tolylplatinum(IV) complexes. Intermediate triflate complexes $Pt(O_3SCF_3)R^1R^2(C{\equiv}CSiMe_3)(dmpe)$, formed en route to the iodo complexes, were characterised in solution and give exclusively R^1-R^2 on decomposition at -10 °C. Alkynylplatinum(IV) intermediates may occur in organic synthesis,[2,3] and decomposition under mild conditions involving unrestrained and "innocent" organic groups at the metal centre provide guidance for possible future advances in organic synthesis applications.



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Support from the Australian Research Council is acknowledged.

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PM8

Crystal structure of a virulence factor HlyU from *Vibrio Vulnificus*

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arsR transcription family frequently operates in stress-response to heavy metal ions. HlyU transcription factor that belongs to arsR family is a key regulator for introducing the expression of the *V. vulnificus* RTX toxin and is specific because it is independent on heavy metal ions [1]. To understand the molecular background, we elucidated the crystal structure of HlyU from *V. vulnificus* CMCP6. The monomeric HlyU structure is composed of five α-helices and two β-strands, where three α-helices together with two β-strands constitute a typical winged helix-turn-helix (HTH) motif. At the dimeric interface, four helices from both monomers are intercalated and form a large hydrophobic pocket. Another hydrophobic interaction for the dimerization was constructed between the extreme N-terminus and the neighboring winged HTH. Two putative DNA binding sites on the dimeric HlyU structure are similarly oriented, implying a normal B-DNA binding without large perturbations of the bound DNA. There is no metal-sensing amino acid in HlyU family and a significant structural difference in the dimeric interaction mode compared with other arsR family proteins. The structural feature of HlyU will be discussed.

Acknowledgements:

We wish to thank Dr. K. J. Kim at the Pohang Accelerator Laboratory for helping with the data collection.

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PM9

Unsymmetrical Bidentate Ligands in the Coordination-Driven Self-Assembly of Discrete Supramolecules

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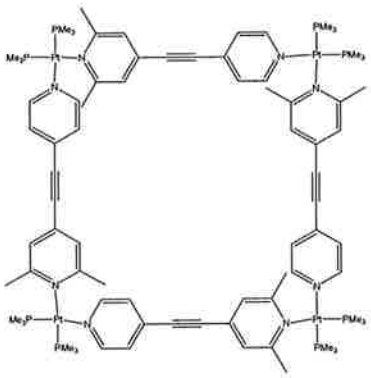
Discrete supramolecules are successfully prepared from ambidentate donor ligands and platinum containing acceptors.[1] Despite the possibility of forming more than one product, ambidentate ligands prefer to self-assemble predominantly into one species. Flexible, ambidentate pyridyl-carboxylate based donor ligands like sodium 3-(3-pyridyl)benzoate, sodium 4-(3-pyridyl)benzoate and potassium 4-(3-pyridyl)ethynylbenzoate self-assemble into discrete [2+2] macrocyclic species instead of infinite networks when combined with a 90 degree organoplatinum acceptor.[2] In each case only one isomeric ensemble is selectively formed in high yield. They are the first examples of discrete supramolecules incorporating flexible, bidentate donor ligands. Despite their potential versatility, these flexible donors adjust their bonding directionality to accommodate a rigid acceptor in the formation of one discrete ensemble. These results provide further evidence of thermodynamic control favoring formation of discrete entities over oligomeric networks, presumably due to the added gain in enthalpy from the additional coordination bond to platinum or palladium in the closed system. We have recently utilized steric effects between substituents of unsymmetrical bis(4-pyridyl)acetylene ligands to control the degree of self-selection in the self-assembly of [4+4] supramolecular squares. The collective ^{31}P and ^{1}H NMR spectra indicate that the efficiency of self-selection of isomers is greater when substituents of greater steric bulk are located at positions proximal to the Pt-N bonding motif and efficiency decreases as the size of substituents is decreased or the substituents are moved further from the Pt–N coordination site. Molecular modeling using the MMFF force field allows for the relative energy of each isomer of the supramolecular squares to be compared and the results support the experimental trend in self-selectivity from complete self-selectivity to the absence of self-selectivity depending upon the ligand we used.



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PM10

New Aromatic Anion Receptors Holding the Dansyl Fluorophore

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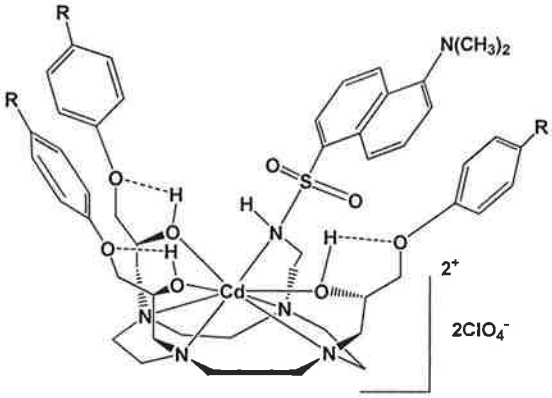
The development of novel, artificial, receptors for recognition and sensing of aromatic anions has been at the centre of considerable research over many years. Owing to both high sensitivity and ease of transduction, receptors involving fluorescent compounds, such as 5-(dimethylamino)naphthalene-1-sulfonamide (dansyl group), have become favourable in supramolecular chemistry.[1] A novel fluorescent host, **1**, as shown below, is reported. This is a cyclen-based molecular receptor system[2], with phenoxy pendant-arms, that has been linked to a dansyl fluorophore.



R: H, $O(CH_2)_2O(CH_2)_2OH$

1

The coordination of the free ligand with a metal ion causes all four pendant arms to project in the same direction, leading to the formation of a 'basket like' cavity. Consequently it has been found that **1** binds to (for example): p-nitrophenolate, p-nitrobenzoate, acetate, p-hydoxybenzoate and p-methoxybenzoate with log *K* values of 4.9, 5.0, 5.6, 5.9 and 4.5, respectively. In some cases quite significant fluorescent changes occur.

Acknowledgements: Flinders University that provides me a conference travel grant.

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PM11

Polynuclear complexes of transition metal ions: towards Single Molecule Magnets

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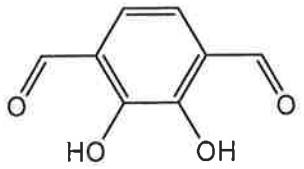
Complexes containing large numbers of paramagnetic metal ions have recently attracted interest for their potential to act as Single Molecule Magnets (SMM).[1] At low temperatures, SMMs exhibit slow relaxation of their magnetization after removal of the external magnetic field. In contrast to traditional bulk magnetism, Single Molecule Magnetism is a property of individual molecules, and SMMs therefore have potential in nano-memory storage (treating each molecule as one memory 'bit'). However, SMMs will only exhibit appreciable retention of their magnetization below a certain "blocking temperature". To date, no SMM has been synthesized that possesses a blocking temperature above 5 K so, clearly, significant research advances are required before a practical SMM is developed.

1,4-Diformyl-2,3-dihydroxybenzene (**1**) is a convenient precursor to diimine ligands with functionality that should be conducive to the formation of metal ion clusters. Several polynuclear complexes derived from **1** have been prepared by Nabeshima[2, 3] and MacLachlan,[4] but no SMM behaviour has been reported. New ligands have been prepared from **1** and a selection of the resulting polynuclear complexes will be presented and discussed here.



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PM12

Dinuclear Metal Complexes Incorporating a Pyrimidine Bridge

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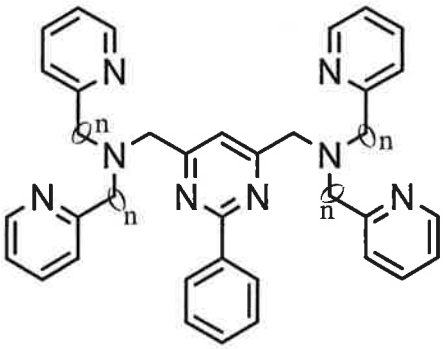
The expansion of novel classes of dinuclear transition metal complexes incorporating suitable bridging ligands is of considerable interest. Studies in this area have been driven by the desire to understand the possible effects of metal-metal interactions on, for example, electron transfer events and/or catalysis in biological processes, and on the spin crossover phenomenon. We are currently focusing on exploring the use of heterocyclic diazines (e.g pyrazine[1], pyridazine[2], and pyrimidine[3]) as bridging units between metal ions. As an extension of our work on tetrametallic [2x2] grids of bis-terdentate pyrimidine ligands we are now studying dinuclear complexes of some related pyrimidine ligands.

Two bis-tetradentate ligands L^{Me} and L^{Et} (figure) and the resulting transition metal (Mn, Fe, Co, Ni, Cu, Zn) complexes have been synthesized. The crystal structures and properties of this family of complexes will be presented and discussed.



L^{Me}, n = 1

L^{Et}, n = 2

Acknowledgements:

We are grateful for the award of a University of Otago Postgraduate Scholarship to WAG.

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PM13

Electrospray Ionisation Mass Spectrometry (ESI-MS) Monitored Synthesis and Characterization of Multifunctional Alkylated Derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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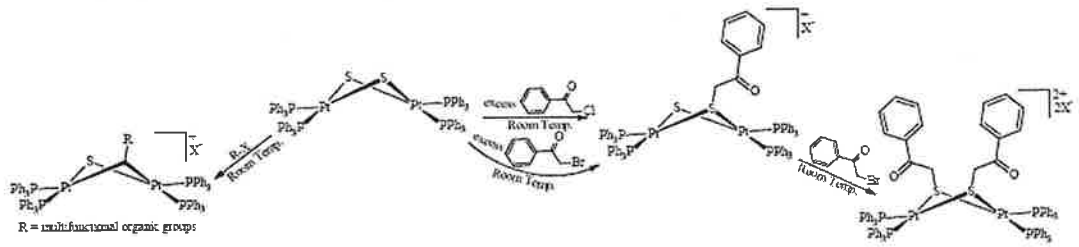
Electrospray Ionisation Mass Spectrometry (ESI-MS) offers a very convenient and efficient screening and monitoring tool for the alkylation of the metalloligand bis(μ-sulfido)tetrakis(triphenylphosphine)diplatinum $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$[1]. This method has been used to construct multifunctional monoalkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ which include $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4](PF_6)$, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(NH_2)_2)Ph\}(PPh_3)_4](PF_6)_2$, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2NHC(O)NCH_2CH_2SCH_2CH_2\}(PPh_3)_4](PF_6)$, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)NHC(O)NHCH_2CH_3\}(PPh_3)_4](PF_6)$, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NOH)Ph\}(PPh_3)_4](PF_6)$ etc.

The reactions between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and electrophiles mostly lead to selective monoalkylation of the sulfide centres to give monocations, $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$. The seemingly trivial conversion of the monocations to dications $[Pt_2(\mu\text{-}SR)_2(PPh_3)_4]^{2+}$ has been plagued with problems due to the reduced affinity of cationic $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)]^+$ towards another electrophile, R-X. However, our investigations show that the leaving group[2], structure of the electrophile, groups around the α-halocarbon ($-CH_2-X$) and electron density of the residual part of an electrophile[3] are complementary factors that enhance the ability of an electrophile to further activate the monocation $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^{2+}$ towards another electrophile R-X. Syntheses based on these factors explains why the reaction of a large excess of $PhC(O)CH_2Cl$ with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ gives $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C(O)Ph)(PPh_3)_4](PF_6)_4$ but $PhC(O)CH_2Br$ gives $[Pt_2(\mu\text{-}SCH_2C(O)Ph)_2(PPh_3)_4](PF_6)_2$. The isolation and characterization of further dialkylated derivatives $[Pt_2(\mu\text{-}SR)_2(PPh_3)_4]^{2+}$ synthesised from 2-bromoacetyl pyrene and 2-bromoacetyl coumarin will also be discussed.



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PM14

Synthesis and Characterization of 1,3-Bis-[phenyl-(pyridin-2-ylamino)-methyl]- thiourea and its Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} metal ion complexes

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The chemistry of coordination of thioureas has attracted considerable attention in view of their growing industrial and biological importance. The Mannich bases of thiourea are potentially very versatile ligands, able to coordinate to a range of metal centers. In the present study, we report the synthesis, characterization and antimicrobial activity of a new Mannich base 1,3-Bis-[phenyl-(pyridin-2-ylamino)-methyl]- thiourea (L) and its metal ion complexes with Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} salts. The ligand was synthesized by condensing thiourea, benzaldehyde and 2-aminopyridine in aqueous medium at ice cold condition through Mannich condensation. The structure of this ligand is established from IR, Raman, ^{1}H, & ^{13}C NMR, mass spectral data and micro elemental analysis. All the 18 complexes were isolated from non-aqueous media. Percentages of the metal ions & anions from chemical analyses, the molar conductance data (Λ_M), effective magnetic moment values ($\mu_{eff.}$) ,micro elemental analyses, IR, UV-Visible, diffused reflectance spectra, ^{1}H NMR, ESR, TG & DTA reveal the bonding sites and possible structure of the metal complexes. The stoichiometry of the complexes were found to be $MX_2.L$ (M = Cd and X = NO_3, 0.5 SO_4), $2MX_2.L$ (M = Co, Ni and X = Cl, NO_3, 0.5 SO_4; M = Cu and X = I, NO_3; M = Zn and X = NO_3, 0.5 SO_4; M = Hg and X = Cl), $MX_2.L.H_2O$ (M = Cu, Cd and X = Cl), $2MX_2.L.2H_2O$ (M = Cu and X = Br, 0.5 SO_4; M = Zn and X = Cl). A tetrahedral or distorted tetrahedral geometry was assigned to Co^{II} chloro, Co^{II} nitrato, Ni^{II} chloro, Ni^{II} sulphato, Cu^{II} iodo and Cu^{II} nitrato complexes and six-coordinate geometry was proposed to the remaining complexes. From the TG/DTA studies, the thermodynamic and kinetic parameters for the thermal decompositions were evaluated using Coats-Redfern and Madhusudanan-Krishnan-Ninan equations. The antimicrobial studies against *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas fluorescens* and *Aspergillus niger* show that the metal complexes have higher antibacterial and antifungal activities compared with that of the ligand.

PM15

Synthesis & coating of ZnS nanosemiconductors on QCM substrate for diagnostic applications

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The synthesis of phosphorescent zinc sulphide nanoparticles (ZnS NPs) by chemical bath deposition (CBD) method was studied in this research. Deposition was carried out at pH ranging from 8.1 to 12.3.

By using sodium hexametaphosphate as stabilizer, particles were prevented of being aggregated. The X-ray diffraction analysis revealed formation of ZnS with cubic zincblende crystal structure. Particle size of crystallite calculated bye Debye-scherrer was in the range of 13- 21 nanometer. Due to dimentional confinement they showed blue shifted emission compared to the bulk material in spectrophotometery analysis. Afterwards in the optimum pH i.e. 9.8 to 10.3, deposition of zinc sulphide on the surface of quartz crystal microbalance accomplished.

QCMs are based on these principles wherein a shift in the resonant frequency of the QCM can be attributed to the mass bound on the sensor membrane as per the sauerbrey equation.

QCMs can be used as biosensors by selective adsorption of the target on their surface which binds with biological element coated on the electrod of QCMs. Spectrophotometry analysis of QCMs' surfaces revealed that the purity of deposited particles are more than solution samples & distribution of particles are better.

Keywords: Semiconductor nanoparticles, Zinc sulphide, Chemical bath deposition, QCM, Biosensors

PM16

Catalytic Performance of Mixed-addenda Heteropolyanions as Inorganic Solid Catalysts in Lactonization of Various Diols

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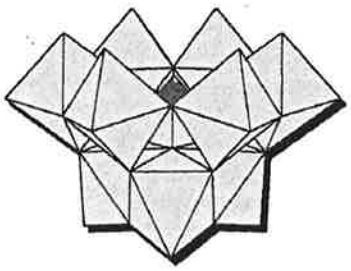
Lactones have deserved great interest in synthetic and natural products chemistry.

These structures occur extensively in the natural world and their biological and pharmacological activities have been widely studied.[1-3] They can be also used for the synthesis of polyesters. [4]

Several catalytic synthetic methods for lactones have been developed and reported during these recent years. [1,5,6] In two last decades research on heteropolyacids, which are a type of inorganic solid catalysts has attracted much attention. A heteropolyacids is an oxide cluster, which has a type of phosphorus/silicon oxo acid and oxo acids with molybdenum, tungsten and other elements. In this research potasium salts of the monosubstituted Keggin polyoxometalates, $[PW_{11}MO_{40}]^{7-}$, (M= Co(II) , Ni (II), Cu(II) , Zn(II), were used as catalysts for lactonization of 1, 4-butane diol, 1, 6 hexane diol and 1, 2-benzene dimethanol, in the presence of hydrogen peroxide as an oxidant . The effects of various parameters such as amount of the oxidant and diol, solvent type, temperature and reaction time have been studied.



Lacunary structures
$XM_9O_{34}^{n-}$

Acknowledgements:

Author is thankful from Dr. Mina Roshani and F.F. Bamoharram and Islamic Azad University, Mashhad.

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PM17

Synthesis, Crystal Structure and Some Properties of Tetravalent Uranium and Plutonium Compounds $[An(DMSO)_8](ClO_4)_4 \cdot CH_3CN$ (An = U, Pu)

M.N. Sokolova,[1] Ph. Moisy[2], M.S. Grigoriev[1], N.A. Budantseva[1], A.M. Fedoseev[1]

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[2]*Commissariat à l'Énergy Atomique (CEA), Valrhô Marcoule, France*

Complexes of composition $An(DMSO)_x(ClO_4)_4 \cdot$could be useful in some applications as a starting material for purpose of synthesis and introduction of tetravalent actinides without acid and strong acido-ligands into organic solutions due to sufficiently high solubility of these complexes in polar solvents. It was found that such complexes are obtainable by very easy and fast procedure: to aqueous solution of An(IV) perchlorate at the concentration more than 0.2 *M* of An and $HClO_4$ about 1 *M* should be added DMSO up to molar ratio An:DMSO = 1:10 and ethanol or methanol to precipitate complex, precipitate could be washed by alcohol, centrifuged and dissolved in minimal quantity of CH_3CN at heating to temperature not more then 50°C, after cooling to ambient temperature well formed large crystals are obtainable.

X-ray diffraction experiments were carried out on a Bruker KAPPA APEX II area detector diffractometer at 100(2) K for uranium complex and at 273(2) K for plutonium complex (at lower temperature it undergoes a phase transition). Absorption correction was made using *SADABS* procedure [1]. The structures were solved by direct method (*SHELXS97* [2]) and refined on F^2 with the full-matrix least-squares procedure (*SHELXL97* [2]) using all reflections.

The compounds are isostructural and crystallize in a triclinic *P*-1 space group with $Z = 2$. The actinide atoms in complex cations are eight-coordinated, their coordination sphere contains eight oxygen atoms from DMSO molecules. Four ClO_4^- anion are present as counterions. The structures contain also one solvate molecule of acetonitrile. The coordination polyhedra of central atoms can be described as bisdisphenoid (trigondodecahedron) **(Fig. 1)**. The An-O distance are from 2.3143(12) to 2.3925(11) Å for U and 2.2912(12) to 2.3634(11) Å for Pu. The average An-O distances are 2.351(11) and 2.327(10) Å for U and Pu, respectively, in agreement with actinide contraction.

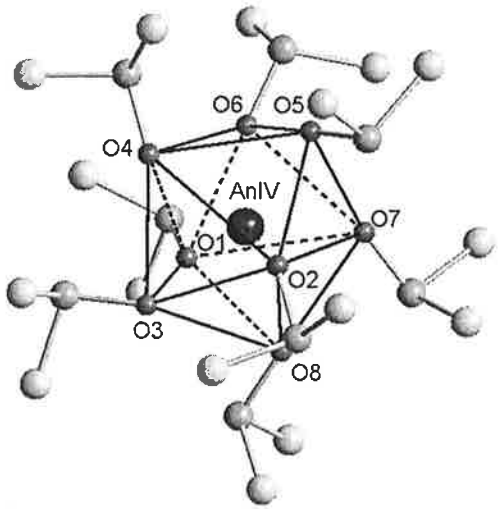

Fig 1. $[An(DMSO)_8]^{4+}$ complex cation in the structures of $[An(DMSO)_8](ClO_4)_4 \cdot CH_3CN$ compounds.

Complexes are characterized by visible and IR spectra. The IR spectra of $[An(DMSO)_8](ClO_4)_4 \cdot CH_3CN$ where An = U(IV), Np(IV) and Pu(IV) are rather identical in the region of 4000 – 400 cm^{-1} and consist of characteristic bands of all groups included in the composition of compounds.

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PM18

Systematic Study of $(HIm)_2[An(di\text{-}Pic)_3]\cdot 3H_2O$ Compounds, An = Th, U, Np, Pu (H_2di-Pic = pyridine-2,6-dicarboxylic acid, $C_5H_3N(COOH)_2$)

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[2]*Commissariat à l'Énergy Atomique (CEA), Valrhô Marcoule, France*

Dipicolinic (pyridine-2,6-dicarboxylic) acid strongly interacts with actinides in different oxidation states and is used in some technological applications, such as decontamination of industrial equipment. The data on the complexation, especially structural investigation, is very poor, so it is interesting to study the coordination interactions of transuranium elements with dipicolinic acid. Complexes were synthesized by treatment of solid $An(C_2O_4)_2\cdot 6H_2O$ with aqueous ~ 1 *M* $(HIm)_2$di-Pic at molar ratio An:$(HIm)_2$di-Pic of about 1:3÷4 at room temperature, large well shaped crystals were obtained in a few minutes.

All the compounds are isostructural and crystallize in a monoclinic $P2_1/c$ space group with $Z = 4$. The actinide atoms in complex anions are nine-coordinated, their coordination sphere contains six oxygen atoms and three nitrogen atoms from three 2,6-di-pyridinedicarbxylate anions. The formula units contain also two imidazolium cations and three crystallization water molecules. The coordination polyhedra of central atom can be described as distorted tricapped trigonal prisms with N atoms occupying capping positions.

The An-O and An-N distances show monotonic decrease in the series Th-U-Np-Pu due to actinide contraction **(fig, 1)**. It is significant, that the overall decrease in An-N distances is higher than in An-O ones. Such behaviour can be explained by influence of 5*f*-electrons. Similar phenomena were observed in some other An complexes with N-bearing ligands [1,2].

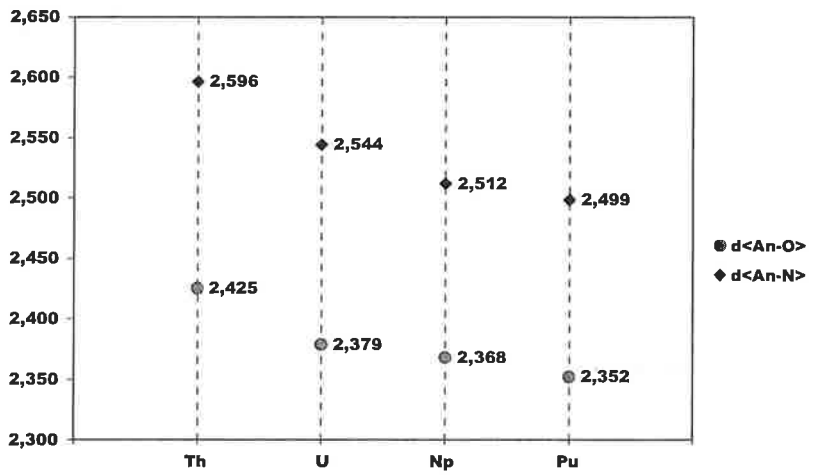

Fig. 1. Average An-O and An-N distances (Å) in $(HIm)_2[An(di\text{-}Pic)_3]\cdot 3H_2O$ compounds.

At room temperature were registered spectra of complexes in visible and near IR ranges presented by broad bands of low intensity with maxima – U: 513, 558, 680, 1076, 1162 nm; Np : 509, 728, 750, 831, 969 nm; Pu: 454, 494, 650, 677, 796, 1093 nm

All complexes are characterized by the thermogravimetric analysis.

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PM19

Azoporphyrins from 5,10-Diaryl- and 5,10,15-Triphenylporphyrins

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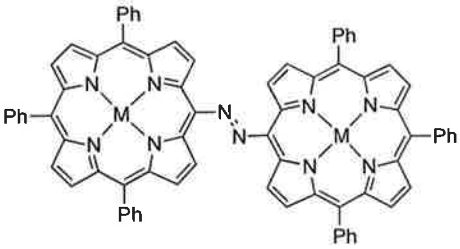
Many examples of covalently-linked porphyrin dimers and higher arrays have been prepared in recent years. These constructs have been investigated for two main reasons: (i) because of their relevance to the natural photosynthetic apparatus and (ii) because of possible applications in molecular electronic devices. We prepared the first examples of azoporphyrins (**1**), the porphyrin analogue of azobenzene, and showed that the azo linker affords excellent electronic communication between the macrocycles.[1] We are now extending this work to the 5,10-diarylporphyrins ("corner porphyrins"), with the aim of preparing square or rectangular tetramers joined by azo or butadiyne bridges, e.g. (**2**), and will report our latest results on these endeavours.



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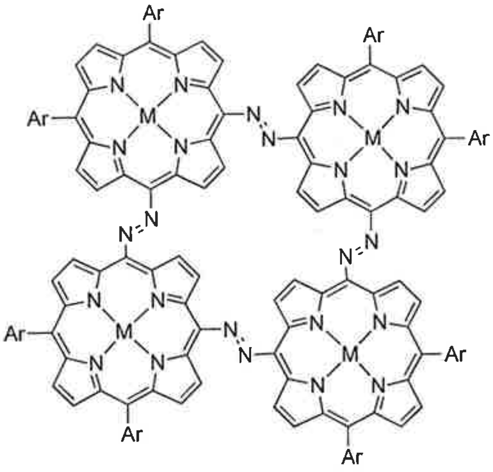

2

Acknowledgements: We thank the Australian Research Council for financial support and Prof. Ken-ichi Sugiura for collaboration on the corner porphyrin synthesis.

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PM20

Synthesis, characterisation and phosphate ester cleavage properties of copper(II) complexes featuring guanidinium pendant groups

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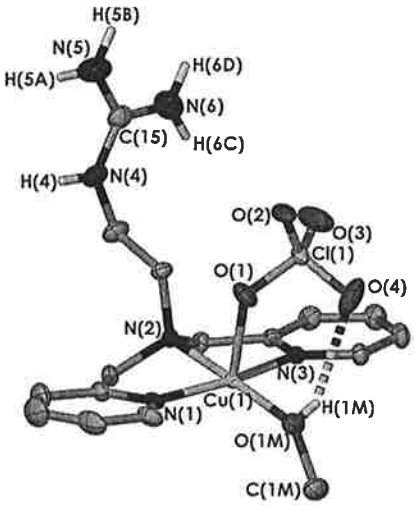
Reactions involving the formation or cleavage of phosphate ester linkages underpin many fundamental biological processes, e.g. cellular signalling, energy storage and production, and nucleic acid synthesis, degradation and repair. Many of these reactions are catalysed by enzymes containing one or more metal ions at their active site. The last two decades have seen an escalating interest in the design of low-molecular weight metal complexes that are able to mimic the activity of these enzymes because of their potential application as artificial restriction enzymes, decontamination agents, etc. A fairly recent development has been the elaboration of metal complexes to include auxiliary groups that complement the hydrolytic action of the metal ion(s). Here we report the synthesis, characterisation and hydrolytic properties of several new copper(II) complexes of *bis*(2-pyridylmethyl)amine (DPA) and 1,4,7-triazacyclononane (tacn) ligands featuring alkyl-guanidinium pendant groups of varying length. These complexes are generally found to promote the cleavage of the model ribose phosphate diester, uridine-3′-*p*-nitrophenylphosphate (UpNP), and super-coiled plasmid DNA (pBR 322) at significantly faster rates than the non-functionalised parent copper(II) complexes. The guanidinium pendants appear to assist cleavage by activating the substrate, promoting protonation/deprotonation processes and/or stabilising transition states, thus mimicking the functional role played by key arginine residues found at the active sites of many nucleases and ribonucleases.



Acknowledgements:

LT and MJB are recipients of Australian Post Graduate Awards. MJB is also the recipient of a Fulbright Fellowship.

PM21

Iron (II) complexes of phosphazenes substituted with tridentate ligands

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Phosphazenes provide a convenient method of polymerizing groups that would otherwise be difficult using other polymer back-bones. This project has focused on the addition of terpyridine and 2,6-benzimidazole pyridine to a phosphazene, then forming iron (II) complexes with the ligands, in the attempt to produce a polymer that contains spin crossover (SCO). Studies have been preformed on the phosphazene trimer as a model for the polymer. These complexes have shown a dependence on temperature (suggesting SCO behaviour), which is affected by its anions (ClO_4^-, OTf^-, PF_6^-, BF_4^-, and BPh_4^-) and the peripheral substituents (2,2'- biphenol and phenol) due to the pockets formed by the phosphazene. These pockets have also given rise to unusual electrochemical behavior. These results have shown the addition of a phosphazene to a seemingly simple system can result in unusual properties.

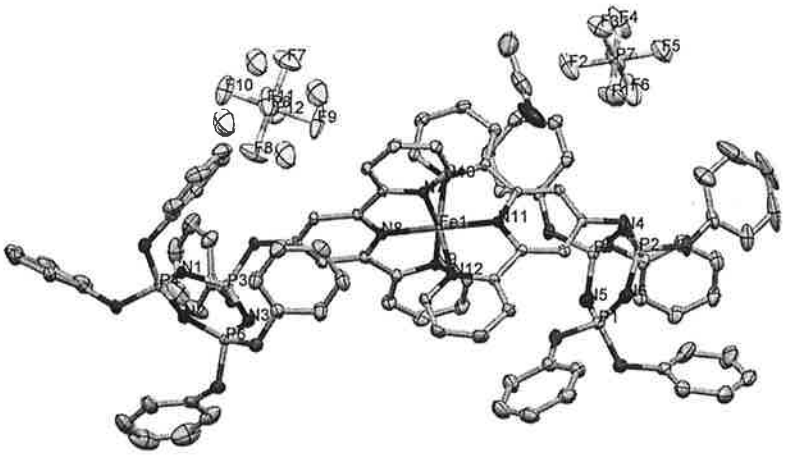

Figure 1 Terpyridine-Phosphazene iron (II) complex

Acknowledgements
Professor Geoff B. Jameson for his assistance with solving crystal structures.
Professor Simon B. Hall for his assistance with electrochemical analysis.
Professor Jeff Tallon for access to a SQUID.

PM22

Structural, Theoretical and Spectroscopic Properties of Chloride Hydrates:

The S_6 Symmetric $[Cl_2(H_2O)_6]^{2-}$ Cube

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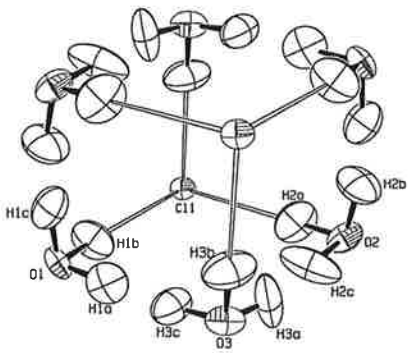
Chloride hydrates are ubiquitous. They are major components of sea water, are present in all biological systems, and are important to our understanding of solvation phenomena.[1] Consequently, there have been many efforts to understand chloride-water interactions.[2] Curiously, however, there have been essentially no studies on dichloride hydrates, undoubtedly due to the probably erroneous assumption that chloride-chloride electrostatic repulsions make such species irrelevant. In this poster, we report on the X-ray[3] and neutron diffraction studies of a dichloride hexahydrate and well as infrared spectroscopic properties and theoretical calculations[3] on this and related species.



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[2] See, for example: a) D. D. Kemp, M. S. Gordon, *J. Phys. Chem. A*, **2005**, *109*, 7688; b) W. H. Robertson, M. A. Johnson, *Annu. Rev. Phys. Chem.*, **2003**, *54*, 173; c) R. Ayala, J. M. Martinez, R. R. Pappalardo, E. S. Marcos, *J. Chem. Phys.*, **2003**, *119*, 9538; d) R. Custelcean, M. G. Gorbunova, *J. Am. Chem. Soc.*, **2005**, *127*, 16362; e) P. S. Lakshminarayanan, E. Suresh, P. Ghosh, *Angew. Chem.*, 2006, *118*, 3891; *Angew. Chem. Int. Ed.*, **2006**, *45*, 3807.

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PM23

Fluorescent redox state sensors with tuneable oxidation potentials for live cell applications

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The cellular redox status influences many processes in plants, including apoptosis, oxidative defence mechanisms, senescence, allosteric control of enzyme activities, transcription and translation, and a variety of signal transduction pathways. Small-molecule fluorescent probes which reversibly respond to subtle changes of intracellular redox levels would be of great value for the dynamic subcellular determination of redox potentials.

The synthesis of conjugates of a fluorescent dye and a quinone-type redox-active moiety, which quenches the fluorophore in the oxidized (quinone) but not in the reduced (hydroquinone) state, yield such redox sensors.[1]

To build up a library of sensors with different applicable potentials the electron density within the aromatic system of the redox active moiety has to be altered.

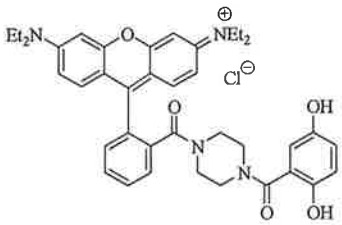

fig. 1: hydroquinone-rhodamine B-piperazinebisamide (**HC**)

Various dyes like hydroquinone- (**HC**), methoxy-hydroquinone-, homogentisic acid-, and anthraquinone-, anthraquinone-carboxylic acid-, nitro-anthraquinone-, and nitro-anthraquinone-carboxylic acid-rhodamine B-piperazinebisamide have been synthesized and characterized.

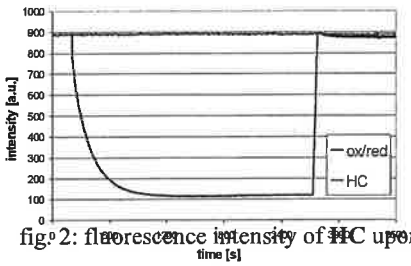

fig. 2: fluorescence intensity of **HC** upon chemical oxidation (t=200s) and reduction (t=2600s) with $[Cu(phen)_2]^{2+}$ and cysteine, respectively

HC proofed in *in vitro* experiments to respond reversibly to chemical or enzymatic oxidation and rereduction. Oxidation can be carried out either chemically with Cu(II)phenanthroline-complex as reagent or catalyst or enzymatically using hydrogen peroxide and HRP (horse radish peroxidise) as catalyst. Rereduction is achieved by a variety of thiols. Subsequent cell experiments are currently carried out.

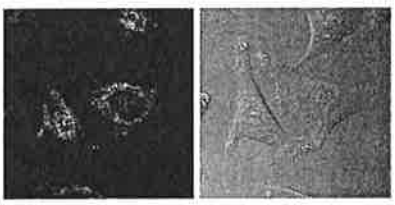

fig. 3: HeLa cells incubated with **HC** (7.5µM, 30min, 37°C)

Acknowledgements:

B. Thaler is grateful to the Landesgraduiertenförderung Baden-Württemberg, Germany for PhD fellowship, special thanks to Z. Kaya, A. Waleska and R. Ahmad for preparative assistance.

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PM24

Towards ruthenium bipyridyl complexes as selective fluorescent sensor for biomolecules in living cells

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Anions play important roles in biological processes. For instance, DNA and RNA are polyanionic. Considering the importance of these systems, there are already many optical recognition systems to detect anions for example based on ruthenium(II) bipyridyl complexes. These sensors detect different kinds of anions in organic solvents and even in biological environment system.[1] But using ruthenium(II) bipyridyl complexes as anion-selective sensors in living cells is not well established. Their main drawback is the slow penetration of $[Ru(bpy)_3]^{2+}$ (100 µM, 6 h, 37 °C) into cells.[2]

Ruthenium(II) bipyridyl complex **1** has an anthraquinone united attached and shows better cell penetration (10 µM, 20 min, 37 °C).[3] To achieve anion selectivity typical anion sensor units should be attached to the remaining two bipyridyl moieties. In complex **2** diethylamine is bound to bis-(carboxy)-bipyridine. Complex **2** penetrates cells in 2 h at a concentration of 20 µM and shows nearly the distribution of $[Ru(bpy)_3]^{2+}$ (Figure 1).

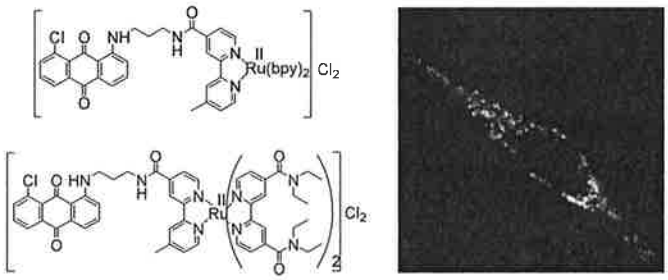

Figure 1 Complex **1** (top) and **2** (bottom) and fluorescence picture of **2**

In vitro titration experiments show selectivity for DNA and RNA over Cl^-, Br^-, SO_4^{2-}, $H_2PO_4^-$, $P_2O_7^{4-}$ and ATP. Whereas control experiments with $[Ru(bpy)_3]^{2+}$ and complex **1** show no such or minor effects, respectively (Figure 2).

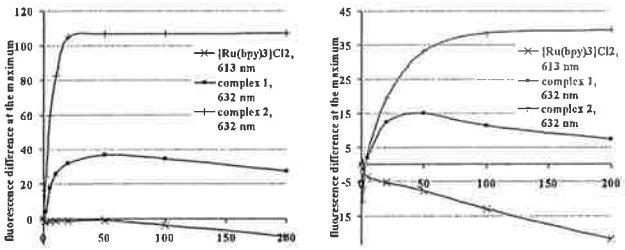

Figure 2 Titration of ruthenium bipyridyl complexes with DNA (left) and RNA (right)

Colocalization experiments are planned.

Acknowledgements: A. Schwarz is grateful to the Landesgraduiertenförderung Baden-Württemberg, Germany for PhD fellowship, special thanks to J. Barth for preparative assistance and Z. Kaya and H. Szelke for scientific advice.

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PM25

Self-assembly of multi-component systems from supramolecular building blocks

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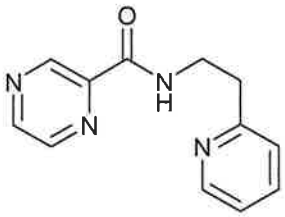
An important objective in crystal engineering is the construction of multi-component systems. In previous work we have produced families of tetrametallic complexes from ligand strands which contain two binding pockets.[1] Our next aim is to construct larger, regular arrays of metal ions. Two routes to such arrays can be readily identified:

(a) Design and preparation of ligand strands with more binding pockets in order to generate larger supramolecular structures.

(b) Design and preparation of ligand strands with 'spare' donor atoms available for coordination after self assembly of the initial complex, allowing higher order assemblies to be generated by the addition of a suitable metal ion.[2,3]

The potentially terdentate ligand **HL** was prepared as a test system for route (b). Discrete mononuclear complexes that feature 'spare' nitrogen donors are accessible. These complexes were then tested as building blocks for generating higher order assemblies.[2] The results of this study will be presented and discussed.



HL

Acknowledgements:

This research was supported by the University of Otago and the Marsden fund (Royal Society of New Zealand), including a Marsden-funded PhD scholarship (RMH).

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PM26

Effects of Geometry on Intervalence Charge Transfer in Trinuclear Complexes

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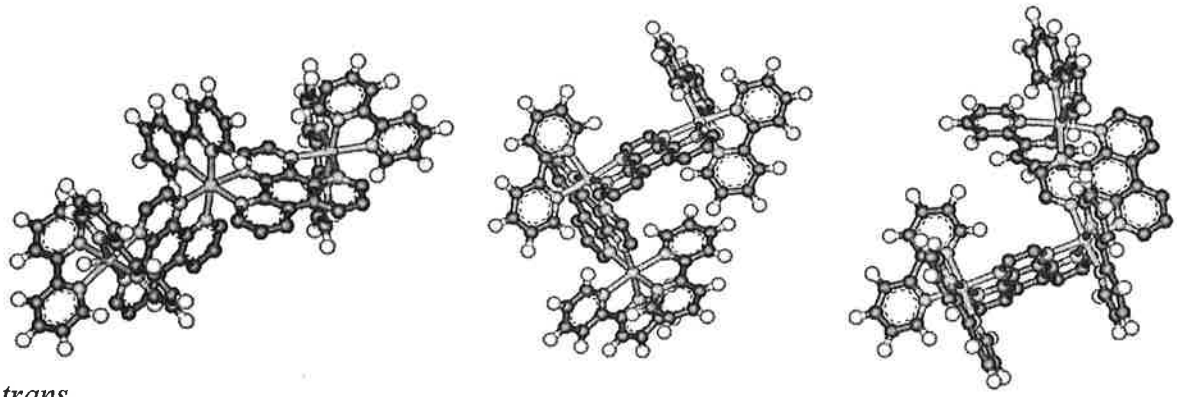
The study of intervalence charge transfer (IVCT) in mixed-valence complexes (comprising two or more metal centres of the same element in different formal oxidation states) provides direct and valuable insight into the nature and behaviour of intramolecular electron transfer. Trinuclear assemblies represent the conceptual link between well-understood dinuclear systems and metallosupramolecular arrays; significantly however, the effect of changing complex geometry (through appropriate ligation and the phenomenon of geometric isomerism) on the inter-metal electronic communication within trinuclear species is unclear.

Homonuclear polypyridyl complexes of ruthenium(II) have been extensively employed as a basis for IVCT transition studies because of their unique and favourable combination of photochemical, photophysical and redox properties, their inertness and their established and accessible synthetic routes.

We have previously reported IVCT studies of "cluster-like" and "chain-like" trinuclear species.[1,2] To extend this work, we are investigating the characteristics of the geometric isomers of the complex $[\{Ru(bpy)_2\}_2\{Ru(bpy)(ppz)_2\}]^{n+}$ (bpy = 2,2'-bipyridine, ppz = 4,7-phenanthrolino-5,6:5'6'-pyrazine), shown in the figure.

For the mononuclear species, $[Ru(bpy)(ppz)_2]^{2+}$, we have isolated three geometric isomers, providing an effective precursor for 'chain-like' trinuclear complexes of both linear (*trans*) and bent (*cis*) configurations – facilitating a comparative analysis of the modes of electron transfer within variable complex geometries.

The presentation will address the synthetic strategy and the spectroelectrochemical techniques employed to investigate the IVCT characteristics of these mixed-valence complexes.



trans *cis (1)* *cis (2)*

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PM27

Structural and magnetic properties of new dinuclear triazole-bridged first row transition metal complexes

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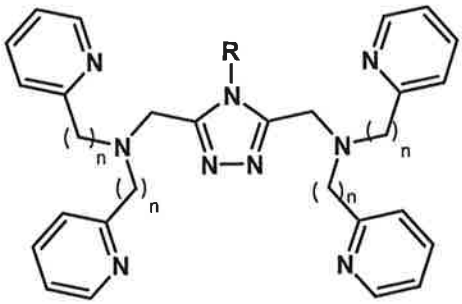
Spin crossover (SCO) between low-spin and high-spin states in octahedral d^4-d^7 first row transition metal ions is an important phenomenon due to its possible applications in molecular switches, data storage and other devices.[1] Particularly some triazole and triazolate-based Fe(II) complexes are SCO active.[2] SCO complexes that present in the solid state a co-operative spin transition have a defined transition temperature ($T_{½}$) and some of them show thermal hysteresis. The presence or absence of thermal hysteresis depends on intramolecular and/or intermolecular cooperative interactions between the SCO centres. The ligand design is a key factor for developing SCO active complexes. This is why we have developed a series of bis-tetradentate triazole-based ligands (Figure 1) capable of forming binuclear metal complexes, where the metal ion is coordinated to the four nitrogen atoms belonging to the ligand and the two vacant positions are completed by solvent molecules and/or counterions. The triazole bridging ligand facilitates communication between the two metal centres, resulting in interesting magnetic properties. We present some dinuclear complexes of these new bis-tetradentate triazole-based ligands.



R = aliphatic, aromatic

n =1,2

Acknowledgements:

We are grateful for the award of a MacDiarmid Institute PhD Scholarship to JO.

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PM28

A Metal-Ion-Releasing Probe for DNA Detection by Catalytic Signal Amplification

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Rapid and specific detection of nucleic acid sequences is an important tool in molecular biology and biotechnology.[1] Methods including target amplification (e.g. PCR) compete against signal amplification systems which possibly decrease the time for one experiment down to minutes.

We developed a bioinspired homogeneous DNA detection system based on allosteric release of metal ions. These metal ions form catalytical active compounds with chemical precatalysts or apoenzymes which create fluorescent signals in presence of appropriate substrates (Fig. 1).[3]

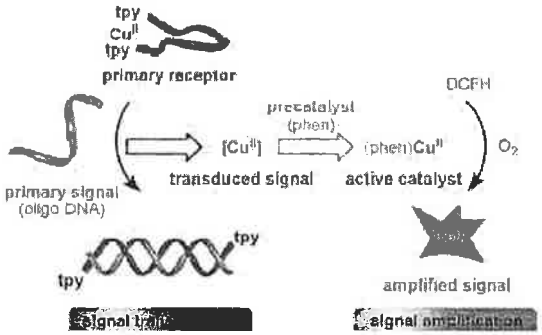

Fig. 1: DNA detection by signal amplification.

To tap full potential of this system competitive kinetic experiments with our probe and N,N,N',N'-tetrakis(2-pyridylmethyl)-ethylene-diamine (TPEN) were carried out to provide further information about the signal transduction step (Fig. 2). Compared to free 2,2':6',2''-terpyridine[3] (tpy) dissociation and stability constants of the $[(tpy)_2DNA]Zn^{2+}$-system are higher (see Fig. 3).[4] Variation of length, sequence and secondary structure (hairpin) of $[(tpy)_2DNA]M^{2+}$ showed no influence on stability or kinetic properties.

On the opposite, the use of other metal ions results in decreased (Cu^{2+}) or increased (Fe^{2+}) stability constants.[4]

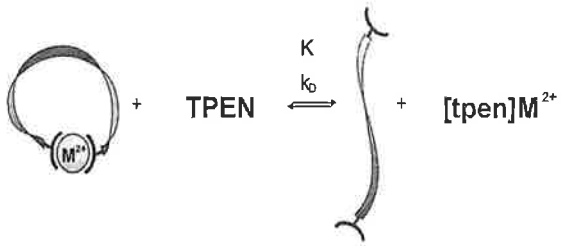

Fig. 2: Kinetic experiments with $[(tpy)_2DNA]M^{2+}$.

	bp	k_D (h^{-1})	log K
DNA1	15	0.16	15.4
DNA2	20	0.18	15.1
DNA3	20	0.17	15.2
DNA4	25	0.31	15.2
DNA5	28	0.27	15.7

Fig.3: Kinetic and thermodynamic constants for $[(tpy)_2DNA]Zn^{2+}$.

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PM29

Theoretical studies on the near-linear agostic interaction in the complexes {M(CpSiMe2H)Cl3]2 (M = Ti, Zr, Hf and Mo).

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An X-ray crystal structure determination of $[Zr(CpSiMe_2H)Cl_3]_2$ shows the possibility of a near-linear Zr---H-Si agostic interaction across the dimer but the structure is not maintained in solution.[1] Synthesis of this complex by computation (Fig 1) shows that the model is in good agreement with the X-ray structure. NBO analysis indicates a near-linear interaction between the Si-H σ NBO and the Zr dz^2 orbital {$E(2)$ = 37 kcal mol^{-1}} with the spatial nature of the overlap being 32%. An AIM analysis indicates a bonding path between the Si-H bond hydrogen and the Zr metal center and there is a lowering of the calculated ^1JSi-H coupling constant compared with the free ligand. Synthesis by computation for the Hf analogue shows similar features as for Zr but for the Ti analogue there is a distortion in the molecule that removes the interaction although the Si-H bond still points towards the adjacent Ti atom due to methyl groups preventing rotation. The effect on the interaction when the metal center is changed to d^2 Mo will also be presented.

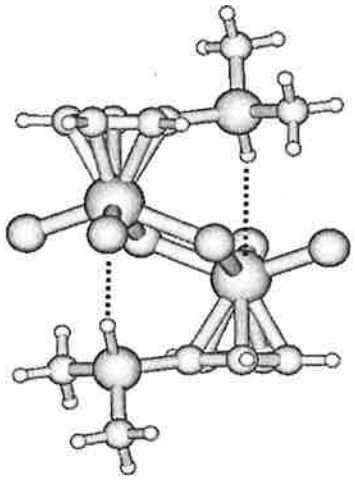

Fig 1. Computed structure of $[Zr(CpSiMe_2H)Cl_3]_2$

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PM30

Dinuclear ruthenium(II) complexes with flexible bridges as DNA bulge-selective probes, and confocal microscopy studies of their cellular uptake

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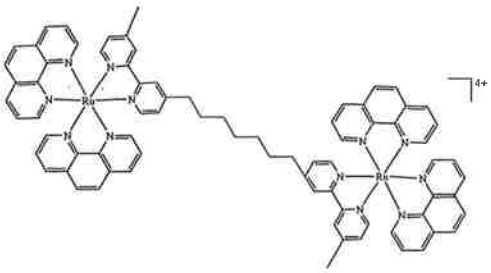
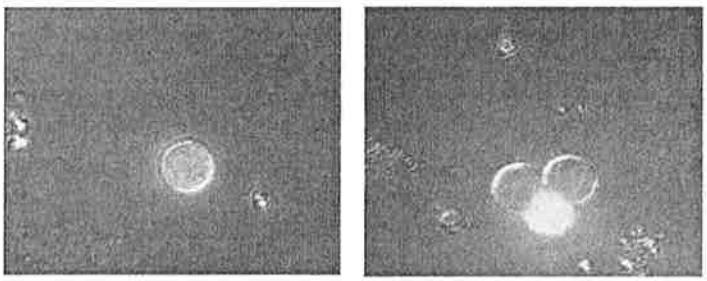
There has been significant interest in the use of a variety of transition metal complexes as alternatives to platinum-based anticancer agents, in an attempt to overcome the high-dose limiting side effects and the acquired resistance associated with their use. Among these alternatives have been ruthenium(II)-based metallopharmaceuticals which have shown activity through various modes of action – including induction of SOS repair system, reduction in RNA synthesis, binding to nuclear DNA and reduced DNA repair – so that there is considerable potential for ruthenium(II) complexes as therapeutic agents.

We recently reported studies of the binding of $[\{Ru(phen)_2\}_2(\mu\text{-bb7})]^{4+}$ {phen = 1,10-phenanthroline; bb7 = 1,7-bis[4(4'-methyl-2,2'-bipyridyl)]heptane} to DNA and DNA bulge sites, which took place with a greater affinity than for analogues with shorter or longer methylene chains in the bridge, or for dinuclear complexes with rigid linkers.[1] Our particular interest in this species for diagnostic or therapeutic applications was its specificity for bulge sites, which are important in both DNA (where they sometimes are associated with mutation) and also RNA where they important in protein recognition.

An important aspect in such applications is the cellular uptake of such complexes, and given the highly fluorescent nature of this genre of dinuclear species, we have also undertaken confocal microscopy studies of their uptake into a mouse leukemia cell line. Accumulation was observed, often at a single site – thought to be the nucleus – but sometimes at multiple sites of accumulation.



The structure of $[\{Ru(phen)_2\}_2(\mu\text{-bb7})]^{4+}$



Confocal microscopy images of L1210 cancer cells incubated with $[\{Ru(phen)_2\}_2(\mu\text{-bb7})]^{4+}$, growing individually (left) and in a cluster surrounded by non-fluorescing cells (right).

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PM31

Synthesis, characterization and anticancer property of dinuclear zinc complex with 2,4-dihydroxybenzaldehyde N(4)-ethylthiosemicarbazone

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A new dinuclear zinc complex with N(4)-ethylthiosemicarbazone with the formulation $[Zn(H24E)Cl]_2.O_2$ ($H_2$24E = 2,4-dihydroxybenzaldehyde N(4)-ethylthiosemicarbazone) has been prepared and characterized by elemental analysis, spectroscopic analyses (IR, UV and NMR) and single crystal X-ray crystallography. The thiosemicarbazone is coordinated to zinc as a monocationic ONS ligand. The coordination geometry around Zn in the dinuclear complex can be described as distorted square pyramid. Three atoms O, N and S from the monodeprotonated ligand and one phenolic oxygen from the neighboring ligand lies at the basal plane, while Cl atom lies at the axial position. The Zn—O...Zn bridging is achieved through a three fold coordinated oxygen atom C-O-Zn_2 from the ligand. The complex and its ligand were screened for anticancer property against MCF-7 breast cancer cell line.

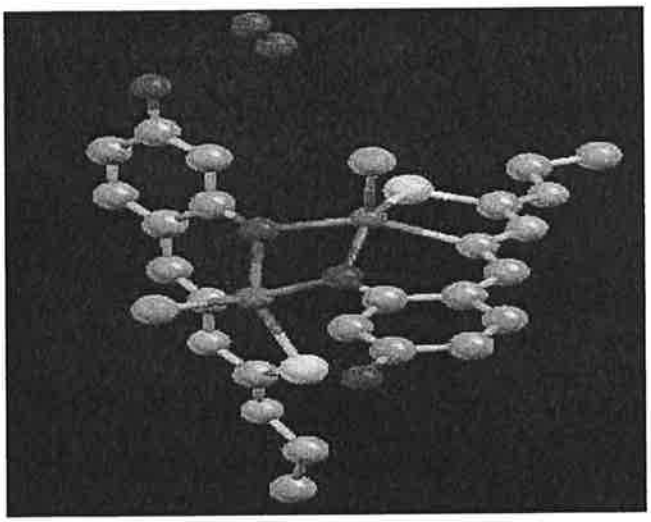

Fig. 1. Structure of $[Zn(H24E)Cl]_2.O2$

Acknowledgements:

We would like to thank University Malaya (PS197/2008A) for supporting this study; KWT thanks University Malaya and the Ministry of Higher Education for SLAI scholarship in this research.

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PM32

Selection of small-molecule-binders for biopolymers from dynamic combinatorial libraries

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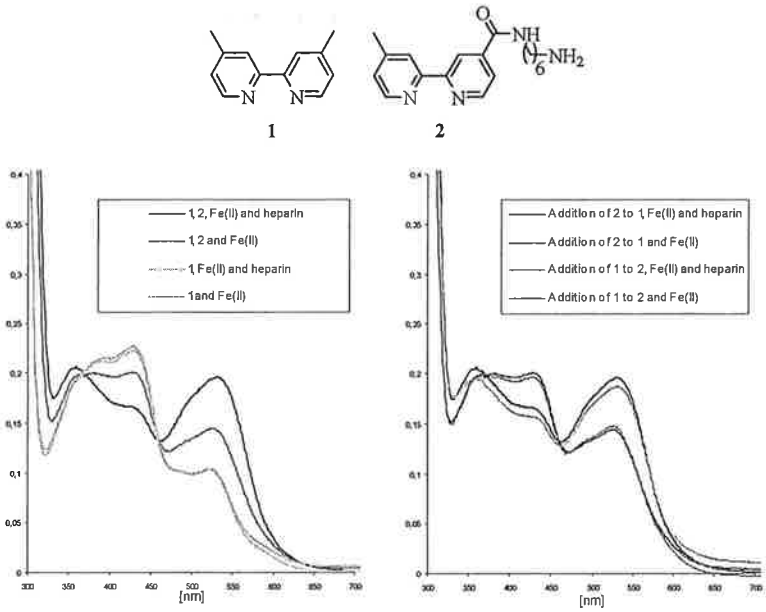
Dynamic combinatorial chemistry (DCC) is a powerful tool for discovering small molecules which bind selectively to biopolymers. Applying combinatorial chemistry under thermodynamic control allows testing more than just one compound per assay: An equilibrated mixture is exposed to an external stimulus by a template and shifts in ideal case to the enrichment of one specific library-member that interacts best with the template.[1]

So far, metal-ligand coordination is only sparsely exploited for the built-up of the exchange-labile system required in DCC. Here we introduce the dynamic combinatorial chemistry of the Fe(II)-bipyridine system. The 2,2'-bipyridine building block can be readily modified and mixtures of just a few different ligands already provide an extensive number of possible complexes. Visualizing changes in equi-librium can be realized by adding a competing ligand, dipicolyl-amine (DPA), which binds stronger to Fe(II) than **1** and **2** in the absence of target. Adding polyanionic heparin to a mixture containing both compounds results in a shift from yellow ($[Fe(dpa)_2]^{2+}$) to red ($[Fe(\mathbf{2})_3]^{5+}$).

Our experiments demonstrate an enrichment of the best heparin binder and show the dynamic nature of the process.



Enrichment of $[Fe(\mathbf{2})_3]^{5+}$ by heparin from a DCC containing 1, 2 and Fe(II) and its dynamic nature (all spectra of equilibrated mixtures)

Acknowledgements:

K. Müller-Graff thanks "Landesgraduiertenförderung Baden-Württemberg" and "Konrad-Adenauer-Stiftung" for financial support.

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PM33

Solid-Bound Logic Gates for use in Molecular Computational Identification

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Inorganic chemists have been amongst the most enthusiastic with regard to the emerging field of molecular logic and computation. In particular, the fields of supramolecular and coordination chemistry have been used to provide an easy way of introducing chemical inputs into a system that can then be converted to a fluorescence output.[1] This is the basis by which molecular logic gates function, and although many logic types have been demonstrated in the past decade,[2][3] there is a pressing need to show that molecular computation can be used in real life applications.

The first such application is Molecular Computational Identification (MCID),[4] whereby large populations of small objects, such as polymer beads, can be easily identified by observing the photophysical properties of their chemical 'tags' in various environments. With potential uses in combinatorial chemistry and medical diagnostics, MCID has the potential to become an incredibly useful tool. Here we will describe a new family of these tags, which will incorporate various fluorophores and receptors, resulting in behavior such as YES, PASS 1 and AND logic.

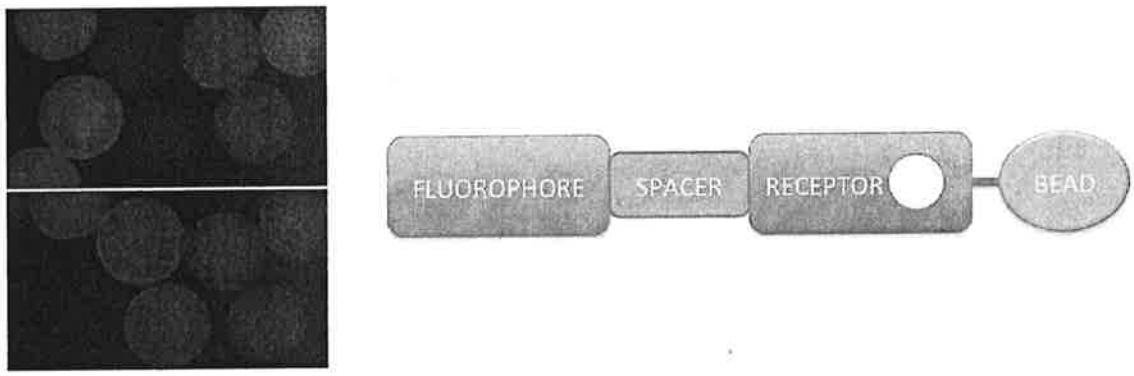

Fig. 1 - Demonstration of single-bead logic operations. The pattern of 'on' and 'off' beads changes in acidic (top) and alkaline (bottom) conditions. A cartoon representation of single bead logic is shown on the right.

Acknowledgements: Great thanks to Paul Vance and Matthew West for their help in the lab and to the Allen McClay Trust for financial support.

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PM34

Towards New Families of Expanded Porphyrin-like Ligands and Complexes

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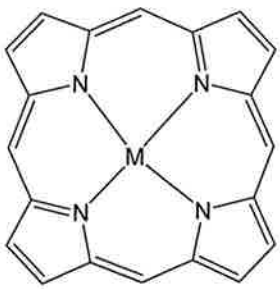
Some of the most important biomolecules in nature are N_4 porphyrin based macrocyclic complexes (I). There are also countless examples of simple synthetic porphyrin based transition metal complexes, many which exhibit interesting properties such as catalytic or single molecule magnet behaviour. Larger 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].



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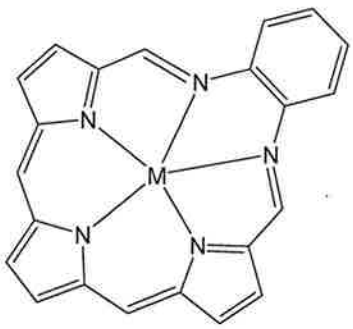

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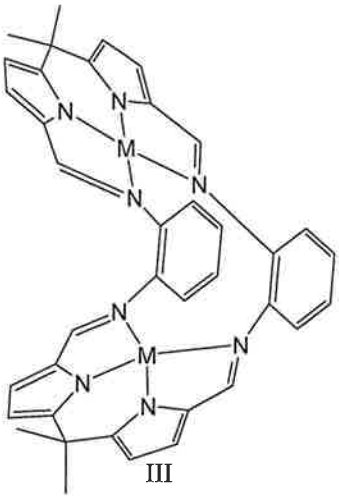

III

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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[4] R. Li, PhD thesis, University of Otago, New Zealand, **2004**

PM35

Controlling Dimensionality in 'Engineered Crystals' by Varying the Hydrogen-Bonding Ability of Counter-Cations

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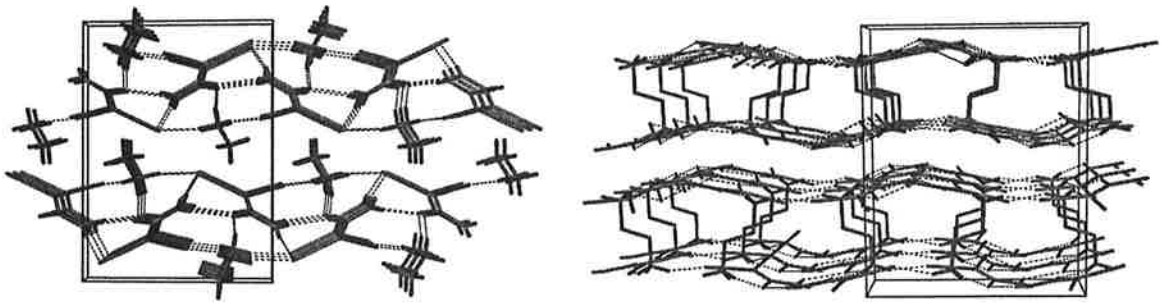
A fundamental goal in supramolecular chemistry and crystal engineering is the understanding the interactions between molecular species and how this can be influenced by judicious choices on the behalf of the experimental chemist. Recently we reported that the anionic species $C(CN)_2(CONH_2)^-$ (*cdm*) could form hydrogen-bonded tapes in salts containing alkali-metal/crown ether sandwich cations.[1] This same tape motif was found to persist in the presence of competing species to bridge between mono- and di-nuclear Cu(II) complexes.[2]

Our recent research has examined to what extent the hydrogen-bonding motifs of the *cdm* anion can be disrupted by competitive species, in this case the presence of ammonium cations. Compounds of the form $Me_xH_{4-x}N$(*cdm*) (x = 0 – 4) have been synthesized and structurally characterized. The NH_4(cdm) compound displays few *cdm*···*cdm* interactions due to competition from the 'hydrogen bond rich' cation. Reducing the number of acidic protons around the ammonium cation (*i.e.* increasing the value of x) results in networks of lower dimensionality; 2D sheets with MeH_3N^+ (see below, left) and 1D chains for $Me_2H_2N^+$ and Me_3HN^+. Studies have also been carried out using diammonioalkane cations to utilize the observed motifs in creating networks with bridging cations, such as the pillared bilayer using the 1,2-diammonioethane cation (see below, right).



Acknowledgements: We acknowledge the ARC for funding and for a post-doctoral fellowship (DRT) and CSIRO for organization of the Student Research Scheme.

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PM36

Luminescence Sensors, Supramolecular Complexes and Large Amplitude Molecular Switches from a Common Anthraquinone Framework

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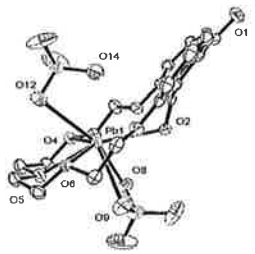
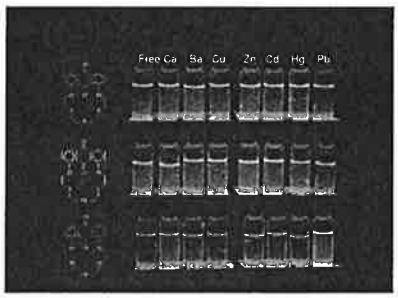
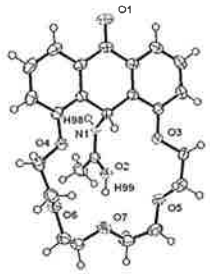
We have employed an anthraquinone scaffold to conduct a variety of different investigations including: ion selective luminescence [1,2], large amplitude molecular switches [3], and coordination chemistry/supramolecular chemistry [4,5]. Synthesis of an anthraquinone-polyether macrocycle that incorporates an intraannular carbonyl group, allows for selective detection of Cd(II), Hg(II) or Pb(II), depending on the substituents incorporated within the polyether ring. Reduction of an anthraquinone macrocycle containing a cyclic polyether ring and reaction with nitriles under Ritter amide conditions yields protonated oxonium ions stabilized by an intramolecular hydrogen bond. Short, Low-Barrier Hydrogen Bonds (LBHB) are formed, averaging ~2.5 Å in length. Crystallography and NMR spectroscopy characterize "open" and "closed" states of deprotonated and protonated adducts that comprise a large amplitude molecular switch. Lastly, condensation of nicotinic and isonicotinic acids with anthraquinones produce bidentate ligands that exhibit a number of different chelating and bridging modes of binding with transition metals. The poster provides an overview of all of these projects.







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PM37

Thiophene-functionalised tetraaza macrocyclic complexes: precursors for chemically modified electrodes

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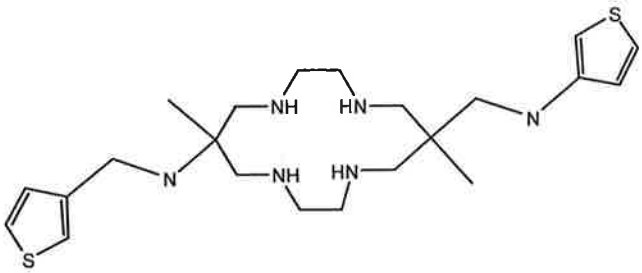
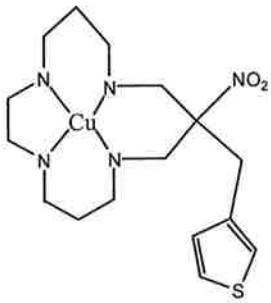
ABSTRACT

Recently, poly-thiophene and its derivatives have been used to deposit metal complexes on electrodes[1,2]. In this study, two synthesis strategies have been applied to attach the thiophene moiety to tetraaza macrocyclic ligands: (i) reductive alkylation of pendent primary amine(s) substitutents attached to a tetraaza macrocycle and (ii) Cu(II)-templated Mannich reactions involving a nitroethyl thiophene, formaldehyde and a linear tetraamine.

Complexation of the bis-thiophene-appended diammac with Co(III) yield tetradentate coordination and hexadentate coordinated macrocyclic complexes ammines. Cyclic voltammetry revealed that the cobalt complex of hexadentate coordinated bis-thiophene diammac has more positive potential compared to parent ligand *i.e.* -250mV *vs* -750 mV vs Ag/AgCl respectively. The ability to tune the redox potential of the monomer and in turn the poly-thiophene derivative offers new ways of producing chemically modified electrodes containing centres with precisely defined redox potentials which may be applied in areas such as bioelectrocatalysis.





Acknowledgements:

The authors would like to thank Malaysian Government for the doctoral scholarship for Sharizal which this study is based upon

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PM38

DNA– detection by lanthanide binding PNA-probes

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Luminescent lanthanide complexes have been receiving increasing attention because of their applications as luminescent probes for highly sensitive time-resolved fluoroimmunoassays, DNA hybridization assays, fluorescence microscopy bioimaging, and other analytical techniques. They show large Stokes shifts (> 150 nm), long luminescence lifetimes (up to ms) and sharp emission bands, which makes them a useful tool for time-resolved spectroscopic or microscopic detection with high signal-to-background ratio.
We recently have introduced a dual labeled DNA- probe for the transduction of a primary signal (a DNA oligonucleotide) in a metal-ion signal which triggers a catalytic amplification step and can sense DNA in nanomolar concentrations. [1]
Here we describe a chemically modified single-stranded PNA- probe (PNA = peptide nucleic acid, a biostable DNA analogue with a polyamide backbone), which upon hybridization with complementary DNA releases a lanthanide ion (Eu^{3+}) forming a luminescent complex with a sensitizer in solution **(Fig. 1)**.

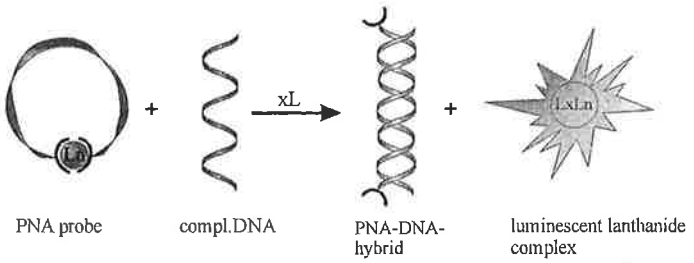
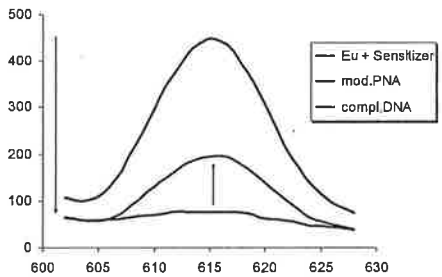


Fig.1: Schematic representation of a PNA-probe which releases a lanthanide ion upon binding to complementary DNA. Lanthanide luminescence is enabled through a sensitizer in solution.

PNA can be labeled on its 3'- and 5' end with lanthanide chelates bearing carboxylic acid groups and amines like DOTA (1, 4, 7, 10-Tetraazacyclododecane- 1, 4, 7, 10- tetraacetic acid), DTPA (Diethylenetriaminepentaacetic acid) or NTA (Nitrilo-triacetic acid). Since the lanthanide ion is shielded by the chelate moieties attached to the PNA- probe, a sensitizer is prevented to form a luminescent complex. Upon addition of complementary DNA the PNA- lanthanide- ring opens and the sensitizer can coordinate the metal ion. The so- formed complex can be detected selectively by time-resolved measurements (**Fig.2**).



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PM39

Cyclodextrin [2]- and [3]-Pseudorotaxanes: A Synthetic and Equilibrium Study

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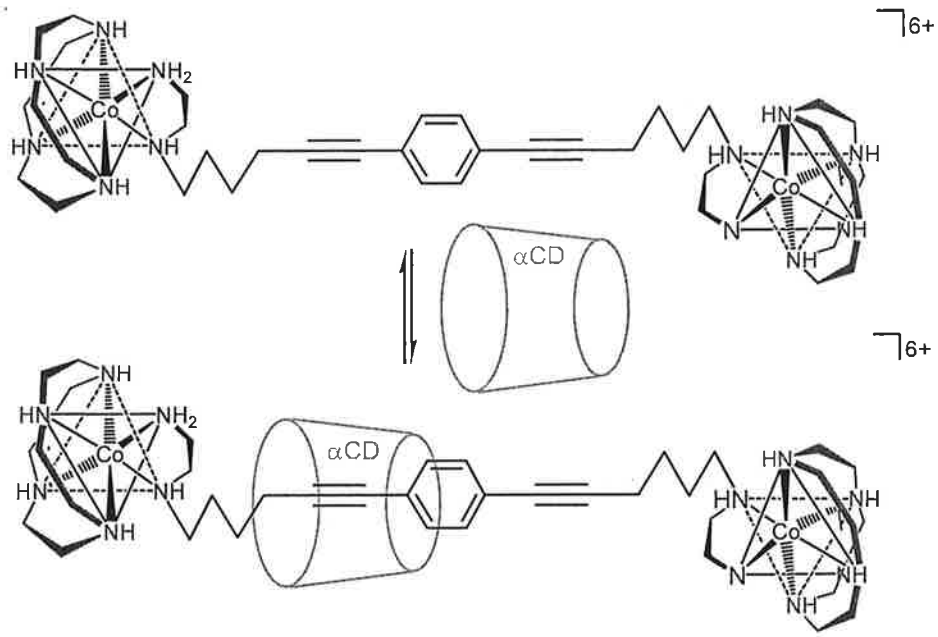
[2]-Pseudorotaxanes are host-guest complexes consisting of a guest, or axle, sometimes with quite bulky end groups, which threads through a cyclic host. They are often sufficiently labile to allow the guest to thread into and dethread from the host in solution as shown below also. This process is referred to as "slippage" mechanism and is a convenient route to [2]-pseudorotaxanes in solution. The same [2]-pseudorotaxanes may also be synthesised by attachment of the end groups to the axle after it threads the cyclic host. This is referred to as a "self-assembly" mechanism. Analogous [3]-pseudorotaxanes are formed when a second cyclic host threaded by the axle. In this study α-cyclodextrin and β-cyclodextrin, αCD and βCD, act as the cyclic hosts and the axle end groups are cobalt(III) complexes as exemplified in the slippage formation of the αCD [2]-pseudorotaxane shown below. The two synthetic pathways and associated equilibria for the [2]- and [3]-pseudorotaxanes will be comparing and their characterization by UV-vis, 1D and 2D ^{1}H NMR will be discussed.



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PM40

The effect of metal composition on ruthenium-platinum colloids as catalysts for the hydrogenation of phenylacetylene

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The manufacture of styrene is an important industrial process, and is generally achieved by dehydrogenation of ethylbenzene.[1] However this reaction may produce phenylacetylene as a byproduct (see Figure 1), which in levels above 10ppm can poison polymerisation catalysts used in subsequent reactions.[2] As a result, hydrogenation catalysts are often used to reduce phenylacetylene to styrene.

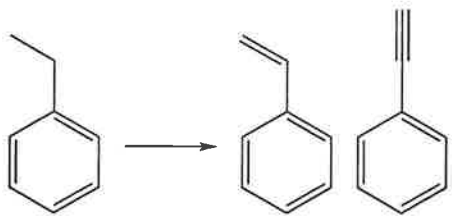

Fig. 1: The dehydrogenation of ethylbenzene to form styrene and phenylacetylene

Ruthenium-platinum nanoclusters have already been shown to be highly active heterogeneous catalysts when placed in mesoporous supports such as silica.[3] However, due to the discrete nature of cluster synthesis, it is generally difficult to perform a systematic study of the effects of metal composition on catalytic activity. In this study, a series of ruthenium-platinum bimetallic colloids was produced to mimic active bimetallic clusters. Immobilization onto high surface area silica with pore size of approximately 60Å was followed by thermal treatment to produce active catalysts. Performance of these catalysts in hydrogenation of phenylacetylene to styrene and ethylbenzene will be studied and reported.

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PM41

Heteroleptic Dipyrrin/BipyridineComplexes of Ruthenium(II)

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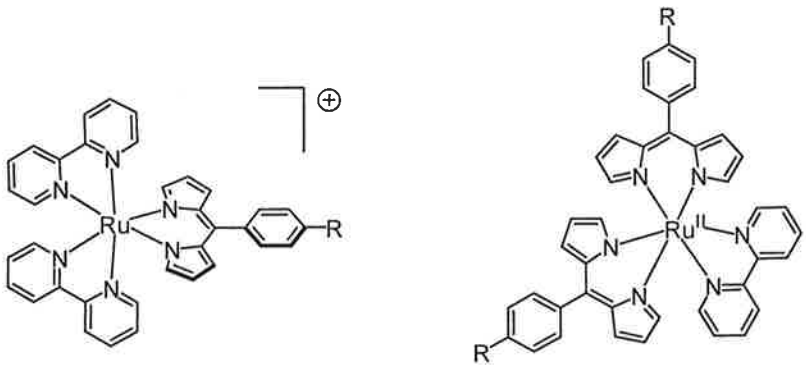
The coordination chemistry of dipyrrinato ligands, first studied several decades ago, is undergoing a rapid resurgence.[1,2] Dipyrrinato ligands possess a conjugated π system akin to porphyrins, which endows their complexes with useful optical properties. As compounds which incorporate dipyrrins are often deeply colored and can display intense photoluminescence (particularly BF_2 complexes or BODIPYs[3]), they hold promise as functional components of light harvesting and/or energy transfer systems.

Although dipyrrinato complexes of many transition metal ions have been reported, ruthenium does not feature on this list. Ruthenium(II) complexes are generally stable, diamagnetic, and kinetically inert, and have justifiably received great attention for their unparalled photophysical properties. As ruthenium-dipyrrinato complexes could conceivably combine the spectroscopic attributes of the dipyrrinato ligands with the photophysical properties of ruthenium(II), we have targeted the synthesis of mixed (heteroleleptic) dipyrrinato/2,2'-bipyridine (bipy) complexes of ruthenium(II). The presentation will detail the spectroscopic characterization of these complexes (including resonance Raman) and their application as dyes in dye-sensitized solar cells.



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PM42

Osmabenzene ring substitution reactions through attack by nucleophiles

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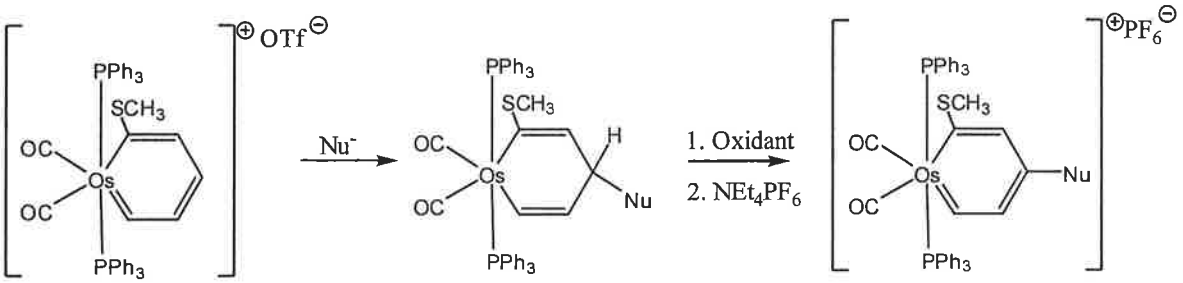
Selective substitution of ring carbon atoms could provide an important route to novel functionalized metallabenzenes. Although there are a few examples of electrophilic aromatic substitution reactions in the literature[1,2], nucleophilic substitution reactions on metallabenzenes have not yet been reported. We now present examples of nucleophilic attack on a cationic osmabenzene[3] (Scheme 1). The attack by a nucleophile results in a neutral osmacyclohexadiene which can then be oxidised to give a new γ-substituted osmabenzene. This transformation can be carried out with a range of different nucleophiles and the properties of the resulting products will be presented.



Scheme 3. Reaction scheme for nucleophilic attack on a cationic osmabenzene

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PM43

A Tale of Two Helices: Enantiomeric Resolution of a Metallosupramolecular Helicate Using DNA-Affinity Chromatography

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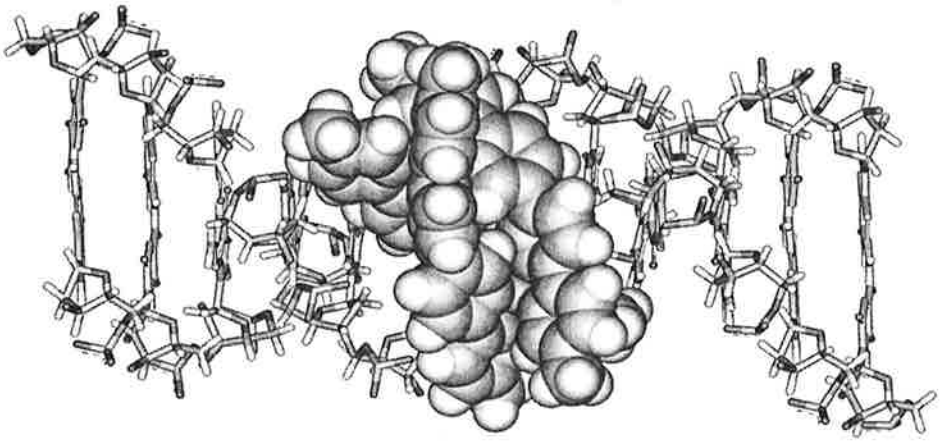
The inherent homochirality of natural biological systems necessitates careful consideration of stereochemistry in the effective design of bioactive molecules. DNA – a right-handed helix in its predominant native state – has demonstrated considerable enantioselectivity in its interactions with transition metal complexes.[1] Such chiral discrimination has recently been exploited in the chromatographic separation/resolution of polypyridylruthenium(II) complexes.[2]

Herein we report on the highly efficient resolution of a $[Ru_2(\mathbf{L})_3]^{4+}$ triple helicate (**L** = 5,5‴-dimethyl-2,2′:5′,5″:2″,2‴-quaterpyridine) into its *P* (ΔΔ) and *M* (ΛΛ) enantiomers using DNA-affinity chromatography employing a variety of different DNA sequences and secondary structures. While AT-rich DNA was found to affect the most efficient resolution, GC-rich duplexes, as well as bulge- and hairpin-containing sequences, still yielded satisfactory separations. In all instances the right-handed *P* helicate was more strongly retained by the chromatographic medium than was the left-handed *M* enantiomer. This enantioselectivity was confirmed by means of equilibrium dialysis experiments.



Acknowledgements: We thank the Australian Research Council for financial support.

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PM44

The influence of 2,9-dimethyl-1,10-phenanthroline upon oxidation and crystal packing within supramolecular copper amine phosphonates

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The versatile phosphonic acid ($RPO(OH)_2$) has the capacity to provide up to three oxygen atoms in coordination with metals, and an ability to form exceptionally strong hydrogen bonds. Yet in crystal engineering the phosphonate group is somewhat understudied despite its potential to form interesting supramolecular networks. The engineering of such arrays, specifically by interaction with aromatic amines, may produce novel materials with possible practical applications such as ion exchange, intercalation, catalysis, light harvesting and magnetic devices.[1]

The synthesis and crystal structure of three new copper(I) and copper(II) supramolecular amine and amine phosphonate complexes is reported.[2] Using a derivative of the phen ligand, 2,9-dimethyl-1,10-phenanthroline (dmp) in reaction with Cu(I), **(fig 1)** it was possible to control and prevent oxidation of the Cu(I) centre due the crowding effect provided by the substituted methyl groups. This was not possible for the phen analogue. Addition of phenylphosphonic acid to the $[Cu^{(I)}(dmp)_2]Cl$ (1) complex yielded two alternative structures. *In-situ* addition of the acid resulted in red block crystals **(fig 2)** that form isolated Cu(I) complexes intercalated between extended H bonded phenylphosphonate chains of the acid/anion (2). Whereas isolation of (1) prior to the addition of the acid (*stepwise* process) produced a green needle-like Cu(II) complex $[Cu^{(II)}(dmp)_2.(H_2O)_2.C_6H_5PO_2(OH)]$ (3). However, on addition of an excess of dmp to the *stepwise* process the equilibrium was forced towards the product (3). Luminescence was observed in both (1) and (3), the addition of the acid providing a 5-fold enhancement in intensity.

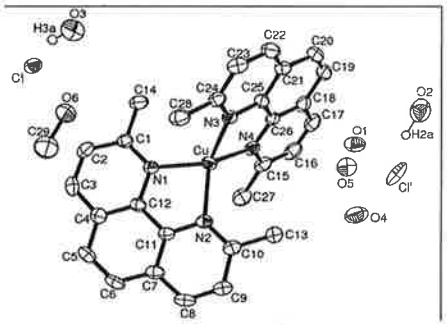

Fig. 1: 4-coordinate tetrahedral complex, $[Cu^{(I)}(dmp)_2]Cl.\ MeOH.\ 5H_2O$ (1)

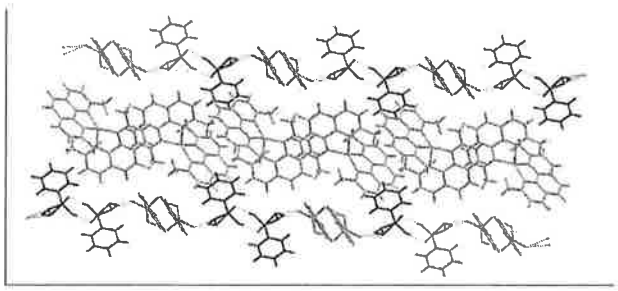

Fig. 2: packing of the $[Cu^{(I)}(dmp)_2].[C_6H_5PO_3H_2.C_6H_5PO_3H]$ (3) The H bonded acid/anion chains interact with the $[Cu^{(I)}(dmp)_2]^+$ cations by EF pi-pi stacking.

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PM45

Puckered crevice for long and large substrates in esterase family

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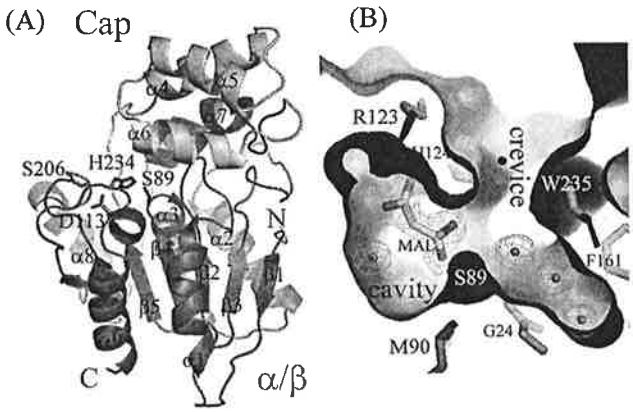
Esterases are one of the most common enzymes and are involved in diverse cellular functions. ybfF protein from *E. coli* (Ec_ybfF) belongs to the esterase family for the large substrates, palmitoyl-CoA and malonyl-CoA, that are important cellular intermediates for energy conversion and biomolecular synthesis. To obtain molecular information on ybfF esterase, which is found in a wide range of microorganisms, we elucidated the crystal structures of Ec_ybfF in complexes with small molecules at resolutions of 1.1 and 1.68 Å, respectively. The structure of Ec_ybfF is composed of a globular α/β hydrolase domain with a three helical bundle cap, which is linked by a kinked helix to the α/β hydrolase domain. It contains a catalytic tetrad of Ser-His-Asp-Ser with the first Ser acting as a nucleophile. The unique spatial arrangement and orientation of the helical cap with respect to the α/β hydrolase domain forms a substrate binding crevice for large substrates. The helical cap is also directly involved in catalysis by providing a substrate anchor, viz. the conserved residues of Arg123 and Tyr208. The high resolution structure of Ec_ybfF shows that the inserted helical bundle structure and its spatial orientation with respect to the α/β hydrolase domain is critical for creating a large inner-space and constituting a specific active site, thereby providing the broad substrate spectrum toward large biomolecules. [1]



Acknowledgements:
This work was partially supported by a CNU Specialization Grant funded by Chonnam National University and partially supported by grants from the Korea Science and Engineering Foundation (KOSEF) (No. R01-2006-000-10743-0) and from the BioGreen 21 Program (20070401034007) of the Rural Development Administration, Republic of Korea.

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PM46

For large substrates, a protein of small molecular weight adopts highly flexible structure at the active site

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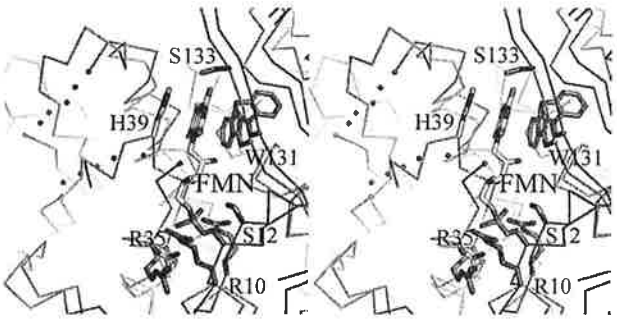
Nitroreductases (NTR) are enzymes that reduce hazardous nitroaromatic compounds and are of special interest due to their potential use in bioremediation and their activation of prodrugs in directed anticancer therapies. We elucidated the crystal structures of ydjA from *E. coli* (Ec_ydjA), one of the smallest nitroreductases, in an FMN-bound and a cofactor-free form. The α+β mixed monomeric Ec_ydjA forms a homodimeric structure through the interactions of the long central helices and the extended regions at both termini. Two FMN molecules are bound at the dimeric interface. The absence of the internal 30 amino acids in Ec_ydjA, which form two helices and restrict the cofactor and substrate binding in other NTR family members, creates a wider and more flexible active site. Unlike the bent FMN ring structures present in most NTR complexes known, the flavin system in the Ec_ydjA structure maintains a flat ring conformation, which is sandwiched by a Trp and a His residue from both monomers. Analysis of our Ec_ydjA structure explains its specificity for larger substrates and provides structural information for the rational design of novel prodrugs to reduce the nitrogen-containing hazardous molecules. [1]



Acknowledgements:

This work was partially supported by a Chonnam National University (CNU) Specialization Grant funded by CNU, by CNU Special Grant for Administration No. 2007-0250, and by grants from the Korea Science and Engineering Foundation (No. R01-2006-000-10743-0) and from the BioGreen 21 Program (20070401034007) of the Rural Development Administration, Republic of Korea.

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PM47

Ionic liquid-based absorbents for the removal of alkynes from isoprene

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The light olefins, such as ethylene, propylene, and isoprene play an essential role in various chemical synthesis and industrial processes. The removal of alkynes, such as 2-butyne and isopropenyl acetylene (IPA), from cracked naphtha is the highest cost and energy consuming process in the petrochemical industry. The selective hydrogenation by precious metal catalysts was tried, but this also suffered from several drawbacks such as using expensive catalysts and poor selectivity. Recently, the development of effective absorbent of alkyness using metals such as silver, nickel, and cupper are reported but they still do not show good performance. Herein, we report the development of selective absorbents using ionic liquids containing metal ions and the investigation of absorption performance.

PM48

Synthesis and Application of Photoactive Gold Modified TiO2

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In this study we focus on the synergic effect between gold nanoparticle and TiO_2 in photoactive applications including the photocatalytic decomposition of 1,4-dioxane and the fabrication of solar cells. Gold nanoparticle supported TiO_2 was synthesized by DP method followed by leaching in order to maximize surface plasmon absorption. We found that the surface plasmon absorption is not a function of gold amount on the TiO_2, but it reveals maximum absorption for the particular gold coverage, which may be more related to surface structure of gold nanoparticle. Self-assembled monolayer using organosulfur compounds were applied to the film of gold modified TiO_2 in order to fuctionalize two different function groups for fabrication of the quantum dot solar cell. The structures have been characterized by infrared (IR) spectroscopy.

PM49

Synthesis and Characterization of Palladium complexes of a large macrocyclic ligand

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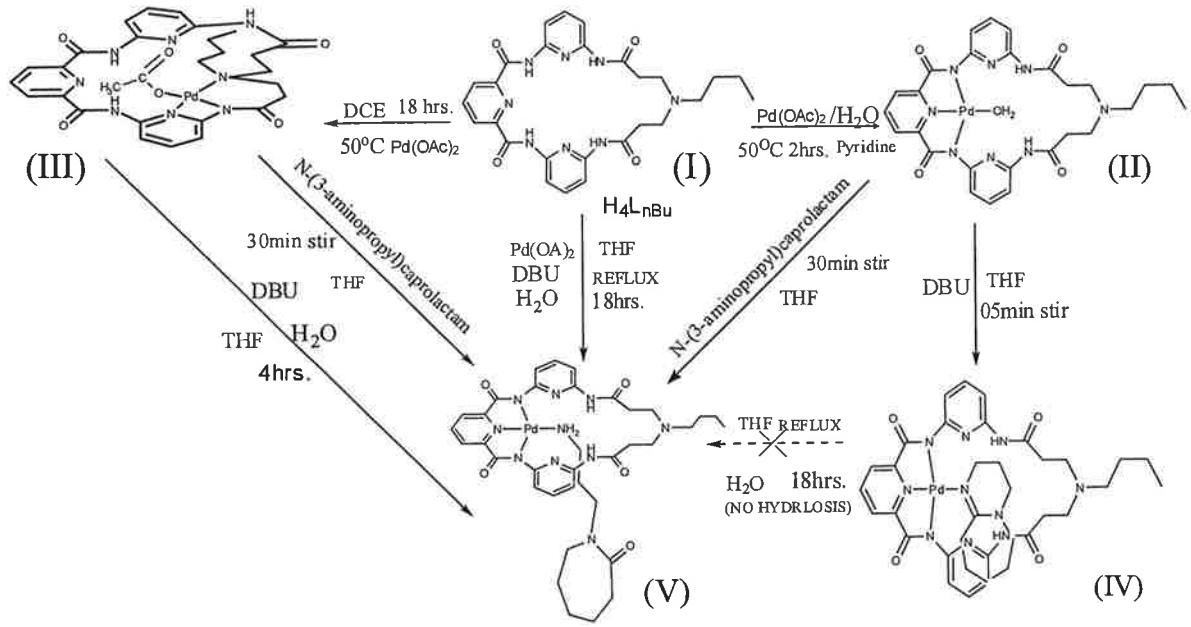
Macrocyclic ligands that are capable of coordinating and holding in close proximity two or more metal ions in such a way that bound substrate molecules can be activated both through interactions with the metal centres and strategically placed functional groups on the ligand backbone have attracted a great deal of attention. Metal complexes of this type are expected to display new and unusual catalytic activity for reactions involving industrially important compounds.[1]

The new amide- and pyridine- containing macrocyclic ligand H_4L_{nBu} (**I**) that contain two potential coordination pockets has been synthesized. Palladium can be coordinated in the head or tail region of **I** to give complex **II** or **III** depending on the conditions employed. Water can be displaced from **II** by DBU and N-(3-aminopropyl)caprolactam to form **IV** and **V**. Alternately **V** can be made directly from **III** by hydrolysis of DBU in THF for 4 hours. Further information about these complexes and the reactions they undergo will be presented.



Scheme A: Reactivity of macrocycle (**I**) and its palladium complexes (**II-IV**)

Acknowledgements:

Higher Education Commision Of Pakistan (HEC)

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PM50

Formation and Reactions of Iridabenzenes with Sulfur Functions

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Metallabenzenes are analogues of benzene, where one CH unit has been replaced by a metal atom and its ancillary ligands (see **Figure 1**).[1] Recently our research group reported[2] the synthesis of a stable iridabenzene (**1**) derived from the neutral iridacyclopentadiene complex **2b** (see **Scheme 1**).

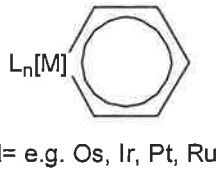
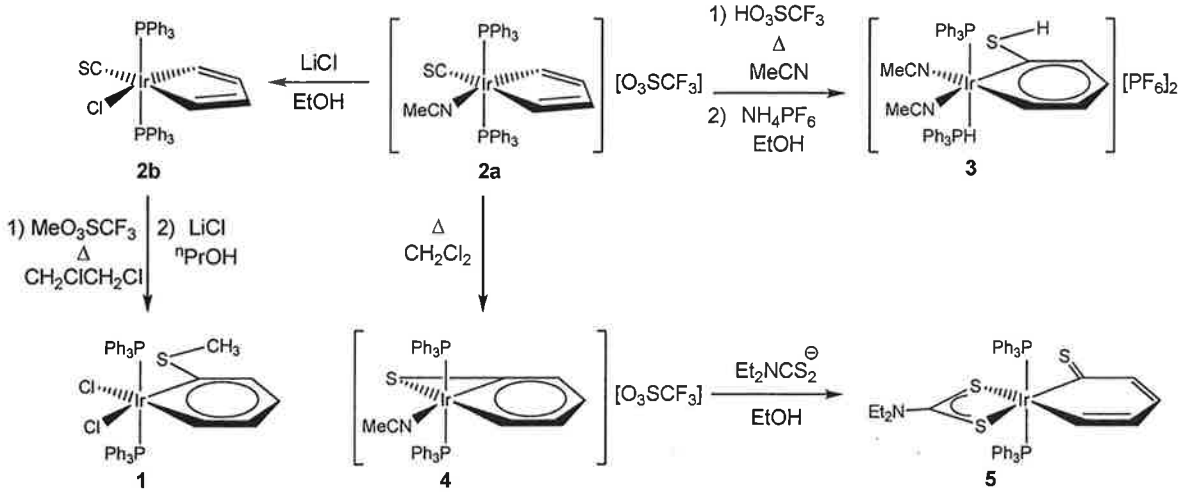


Figure 4

In this work, isolation of the cationic iridacyclopentadiene **2a** has lead to the formation of several new iridabenzenes (see **Scheme 1**). Reaction of **2a** with triflic acid using acetonitrile as solvent generates the green di-cationic iridabenzene (**3**), which contains a thiol functional group. By gently heating a solution of **2a**, migratory insertion of the thiocarbonyl ligand into an adjacent iridium-carbon bond occurs to give the brown iridabenzene (**4**), where the sulfur atom is π-bound to iridium. In a related reaction, diethyldithiocarbamate binds to **4** in a bidentate fashion. This ligand displaces the π-bound sulfur, and the orange iridacyclohexadienethione (**5**) is formed. While **3** and **4** are expected to display aromatic properties, **5** is not. Details of the bonding and chemistry of these new metalla-aromatic compounds will be presented.



Scheme 1

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PM51

Synthetic nucleases for the identification of DNA-recognition sites of DNA-binding proteins

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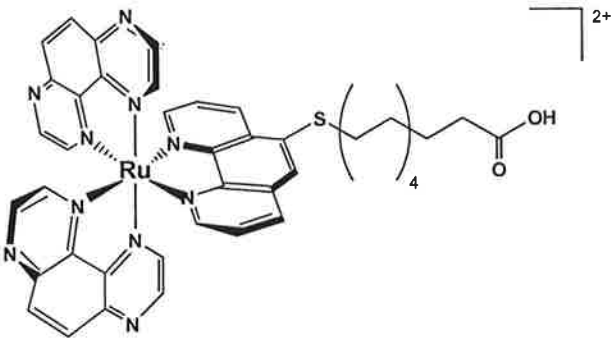
There are currently no methods available which can easily characterise specific DNA-recognition sites of putative DNA-binding molecules: our program aims to develop techniques to identify and characterise protein:DNA interactions in a genome-wide approach. At the same time, the use of synthetic nucleases will also provide a particularly useful means to study known DNA-binding proteins for the discovery of weaker secondary DNA-recognition sites which probably have a significant role in the complicated processes that occur within a cell.

Our first approach has been to link a synthetic DNA-cleaving catalyst to a given DNA-binding domain (DBD), based on the hypothesis that if a molecule with nuclease activity is colliding and interacting through its DBD with a DNA molecule of known length and sequence for long enough, it will result in cleavage of the DNA in close proximity to the site of interaction. The single-strand cleavage of the sugar-phosphate backbone of duplex DNA ("nicking") can be accomplished by a range of compounds - including polypyridylruthenium complexes. Such species can function as nucleases that have relatively weak and non-specific binding, but provide efficient single-strand photocleavage.[1,2]

This paper will report the synthesis of our first target ruthenium centre $[Ru(tap)_2(phen')]^{2+}$ {where tap = 1,4,5,8-tetraazaphenanthrene; phen' = a functionalised derivative of 1,10-phenanthroline which allows covalent linkage to the DNA-binding domain (DBD)}, and of its attachment to a DBD.



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PM52

Ruthenium-NHC Complexes Immobilized on MCF:

Application to Catalytic Ring-Closing Metathesis

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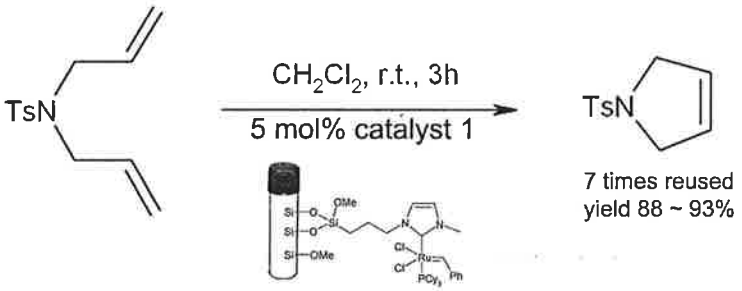
Diverse organometallic systems are used as useful catalysts in countless organic reactions, including the C-C bond formation.[1] For example, a ring-closing metathesis (RCM) catalyzed by Grubbs catalysts has been used for construction of diverse cyclic organic compounds.[2] The series of Grubbs catalysts have many advantages as catalytic compounds such as facile control of their chemical properties. However, to be applied as industrial catalysts, the catalysts should be heterogenized. In literature, various ways to immobilize Grubbs catalysts have been suggested. [3] We herein report on the development of an excellent heterogeneous catalyst for RCM by immobilizing a modified Grubbs catalyst on mesoporous silica. Mesoporous and structurally uniform materials, including MCM, SBA, KIT and MCF, have been applied to the diverse heterogeneous catalytic systems. In this study, siliceous mesostructured cellular foam (MCF) was chosen as a solid support, which have a large surface area of 700 ~ 1005 m^2/g and a pore volume within the range of 1.4 ~ 2.3 cm^3/g. We developed heterogeneous Ru-NHC catalysts by immobilization of Grubbs catalysts on the MCF-type mesoporous silica through a modification of the NHC ligand. Starting from NHC ligand, a facile three-step reaction gave the supported catalyst which is a robust, stable, and easy to reuse. In addition to the advantages discussed above, the developed catalyst was highly effective for the intramolecular RCM reaction and could be reused at least seven times without any loss of its catalytic activities. Moreover, research is being conducted to further develop our RCM catalysts system for application to enantioselective catalysis.



Acknowledgements: This work was supported by Pusan National University Research Grant, 2008.

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PM53

Novel transformations of the germyl ligand in tri-*p*-tolyl germyl complexes of ruthenium.

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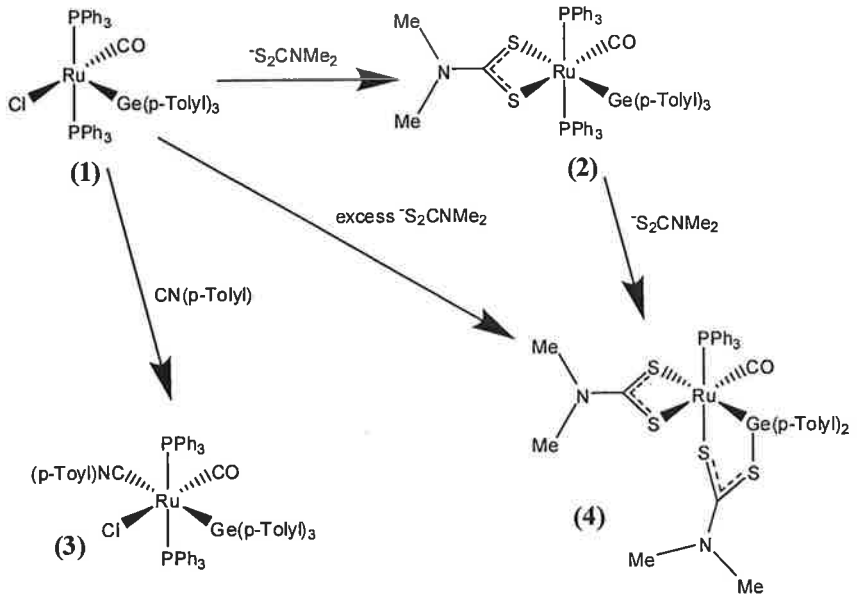
Ruthenium germyl complexes have been shown to be effective germylation catalysts for alkenes[1] and alkynes,[2] however there has been relatively limited research into the chemistry of the germyl ligand compared to the silyl and stannyl analogues.[3] Therefore we report a study into the coordinatively unsaturated tri-*p*-tolylgermyl complex $Ru(Ge(p\text{-tolyl})_3)Cl(CO)(PPh_3)_2$ (**1**) which is formed through reaction between $Ru(Ph)Cl(CO)(PPh_3)_2$ and $HGe(p\text{-tolyl})_3$ in benzene heated under reflux. Treatment of **1** with sodium dimethyldithiocarbamate or CN(*p*-tolyl) yields the coordinatively saturated complexes $Ru(Ge(p\text{-tolyl})_3)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**2**) or $Ru(Ge(p\text{-tolyl})_3)(CN(p\text{-tolyl}))Cl(CO)(PPh_3)_2$ (**3**), respectively. Surprisingly when **1** is treated with excess sodium dimethyldithiocarbamate one of the *p*-tolyl substituents on germanium is displaced and the product, $Ru(Ge\{p\text{-tolyl}\}_2SC\{NMe_2\}S)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**4**), has a dithiocarbamate ligand bridging the ruthenium and germanium atoms. Related reactions which also result in the loss of one of the p-tolyl groups on germanium will be presented.



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PM54

Zno Nanowires with Pt Adsorption Using a Photochemical Reduction Mechanism

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In this study, the growth of high density single-crystalline ZnO nanowires on patterned ZnO:Ga/SiO_2/Si templates was reported. We also adsorbed Pt nanoparticles onto nanowire surfaces. Figures 1(a) and 1(b) show enlarged SEM photographs of the ZnO nanowires grown on SiO_2 spacers without and with Pt adsorption, respectively. In contrast to the unstained ZnO nanowires (i.e., pure ZnO nanowires) shown in figure 1(a), it can be seen that nano-sized particles were adhered on the surfaces of the nanowires shown in figure 1(b). Figure 1(c) shows EDX spectrum measured from surface of the stained ZnO nanowire. It can be seen that we observed a clear Pt peak while no Cl-related signal was found. Such a result indicates that we have adsorbed Pt nano-particles onto the nanowire surfaces (i.e., ZnO nanowires with Pt)[1,2,3]. It should be noted that the C signal shown in figure 1(c) is related to the contamination during sample preparation while the Si signal should originate from the substrates.

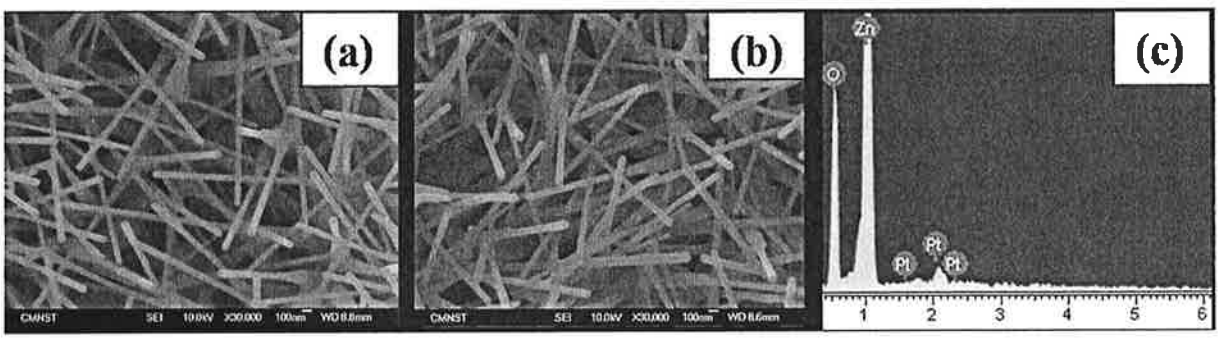

Figure 1 Enlarged SEM photographs of the ZnO nanowires grown on the SiO_2 spacer regions (a) without and (b) with Pt adsorption. (c) EDX spectrum measured from the surface of the stained ZnO nanowires.

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PM55

Relaxation dynamics of $Cr(acac)_3$ probed by ultrafast IR and UV/Vis spectroscopy

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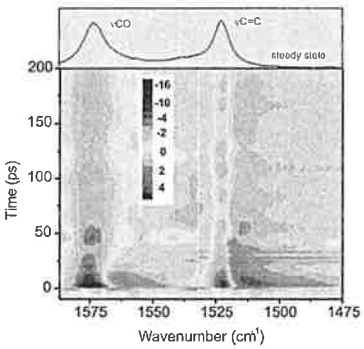
A wide range of Cr(III) complexes have been studied in the past as a way to tackle the photochemistry and photophysics of transition metal complexes. [1-3]. Despite of this exhaustive investigation, Cr(III) photophysics continues as a hot topic.[4] The essentials of the photophysics can be understood in terms of three levels: the $^4A_2$ ground state and the lowest excited quartet ($^4T_2$) and doublet (^2E). The role of the quartet and doublet states in Cr(III) photoreactions, as well as the relevance of ground state intermediates and back-intersystem crossing in the doublet reactivity (i.e, $^2E \rightarrow {}^4T_2 \rightarrow$ products) is still under debate.[3]

Recently, femtosecond time-resolved electronic absorption spectroscopy has been used to probe the excited state dynamics of $Cr(acac)_3$.[4] The transient signal observed upon both $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4LMCT$ excitation was assigned to absorption of the ^2E state. The results where interpreted as a very fast $^4T_2/{}^4LMCT \rightarrow {}^2E$ conversion (i.e, prompt intersystem crossing) with rates exceeding 10^{13} s^{-1}, thus suggesting that intersystem crossing is faster than both vibrational relaxation and internal conversion. However, time-resolved experiments have failed to observe ground state and $^4T_2$ state transient signals. A severe spectral overlap between ground and excited state absorptions is one of the factors preventing the observation of ground state recovery dynamics by transient electronic absorption spectroscopy. Without this information; it is not possible to unambiguously access the relevance of the ^2E state in the photophysics of the $Cr(acac)_3$ complex.

In this poster we discuss the data obtained using femtosecond IR and UV/Vis spectroscopy to probe the relaxation dynamics of $Cr(acac)_3$ upon excitation to different electronic state surfaces.[5] Vibrational relaxation alone was also probed by transient IR spectroscopy upon excitation of pure vibrational transitions in the mid-IR region, at 6700-6300 nm. The data reported represents a significant contribution to the understanding of the photophysics of this complex. In particular, we are presenting the first direct observation of bleach recovery kinetics.



Acknowledgements:

E.M. acknowledges a Marie Currie Intra-European Fellowship from European Commission.

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For experimental details, see E. M. S. Maçôas , R. Kananavicius, P. Myllyperkiö, M. Pettersson, H. Kunttu, *J. Phys. Chem. A*, **2007**, *111*, 2054.

PM56

Synthesis and fluorescence studies on macrocyclic derivatives bearing aminophenylbenzothiazole functionalities: Identification of a potential "OFF-ON-OFF" fluorescent sensor probe for zinc ions.

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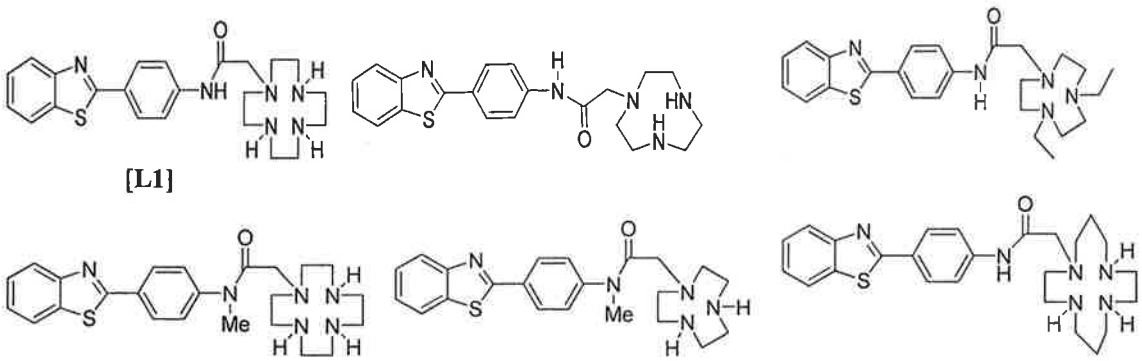
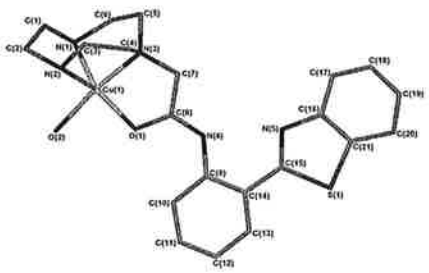
Departments of Neurology[1] and Chemistry[2], Monash University, Clayton, Australia- 3618.

The development of fluorescent sensors for applications that include the detection of metal ions and biomolecules is attracting much attention [1-3]. With these applications in mind we have prepared several photo-responsive benzothiazole derivatives bearing macrocyclic derivatives capable of binding strongly to transition metal ions. The two macrocyclic ligands are 1,4,7-triazacyclononane (tacn) and 1,4,7,10-tetrazacyclododecane (cyclen), have been converted into benzothiazole derivatives, a selection of which are shown in the Figure.



[L1]

The ligands were found to be fluorescent and when irradiated at 300 nm, an emission centered at 394 nm was observed. This fluorescence was quenched by the addition of Cu^{2+} and Zn^{2+}, while Fe^{3+} was found to have a little influence even at relatively high concentration. The addition of Zn^{2+} to **(L1)** was found to result in some unusual behaviour. The initial addition of Zn^{2+} caused a strong enhancement of the fluorescent intensity, which reached a maximum when 1.0 equivalent of Zn^{2+} had been added. Further addition of Zn^{2+} resulted in a drop in the fluorescent intensity and a change in the fluorescence spectrum, which may be attributed to the interaction between the excess of Zn^{2+} ions with the benzothiazole group (Zn....S or ...N interactions). We have obtained an Off-On-Off response which may be exploited in sensor development. We will also report investigations with other macrocycle-benzothiazole derivatives.



X-ray crystal structure of mono aminophenyl benzothiazole –copper-cyclen complex

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PM57

Enhanced Anion selectivity and strength of binding by the incorporation of neutral H-bond donors

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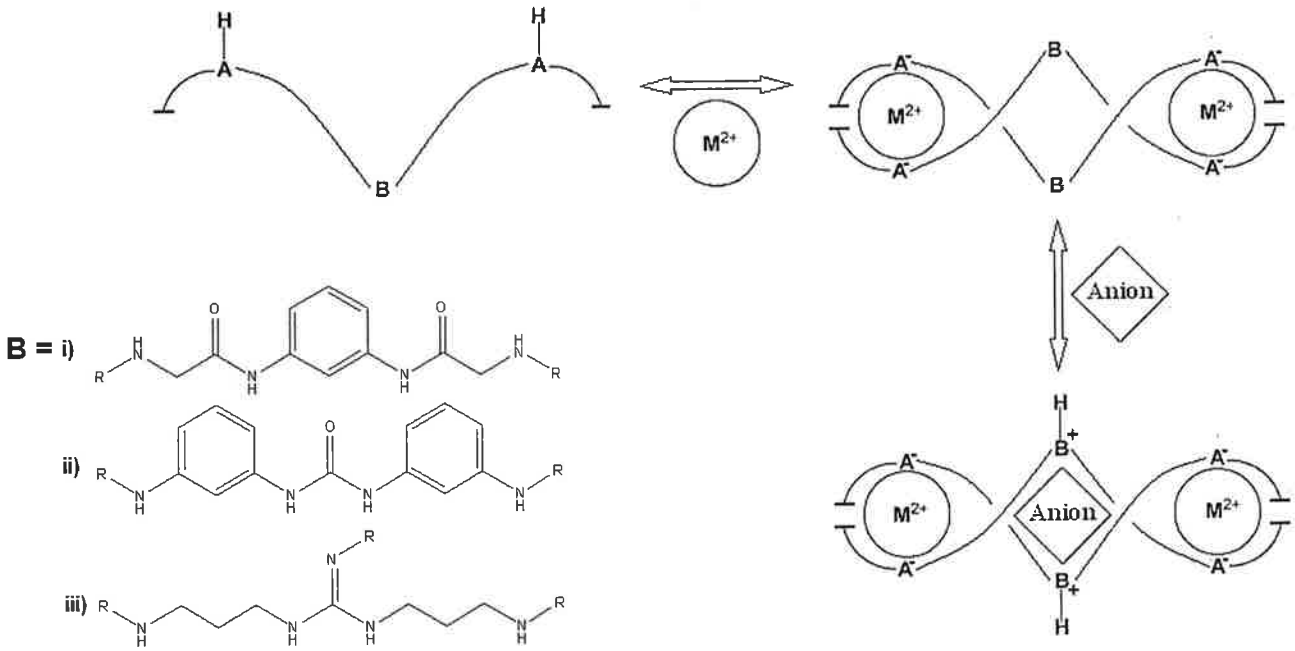
The field of anion recognition is an exciting and ever expanding area of research. There are now many examples of transition metal complexes that have been shown to encapsulate anions but few of these show significant selectively.[1] A possible solution to this situation is to modify and refine the anion binding site by the addition of neutral anion binding donors. Current complexes within our group are capable of binding anions but lack selectivity.[2] It is hoped that by introducing neutral amide donors into the linked metal coordination sites, enhanced selectivity may also result. Potential neutral amide donors to be incorporated are acetamide, urea and guanadinium functionalized ligands. [3, 4] Progress towards these new ligands will be discussed.



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PM58

Structures and Reactions of New Osmium Polyhydride Complexes

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Transition metal polyhydrides are a class of compounds that are able to undergo a range of useful organometallic reactions such as alkene and carbonyl hydrogenation and cleavage of sp^2 and sp^3 C-H bonds. This research involved the synthesis of new polyhydride complexes derived from the known compound $[OsH_6(PPh^iPr_2)_2]$.[1] Deprotonation of the parent polyhydride gave the anionic complex $[OsH_5(PPh^iPr_2)_2]^-$. This complex acted as a hydride transfer catalyst, catalysing the formation of methane from methyl iodide and potassium hydride, shown in Figure 1.

Protonation of the parent polyhydride led to the formation of a bimetallic cationic complex $[Os_2H_7(PPh^iPr_2)_4]^+$. A second

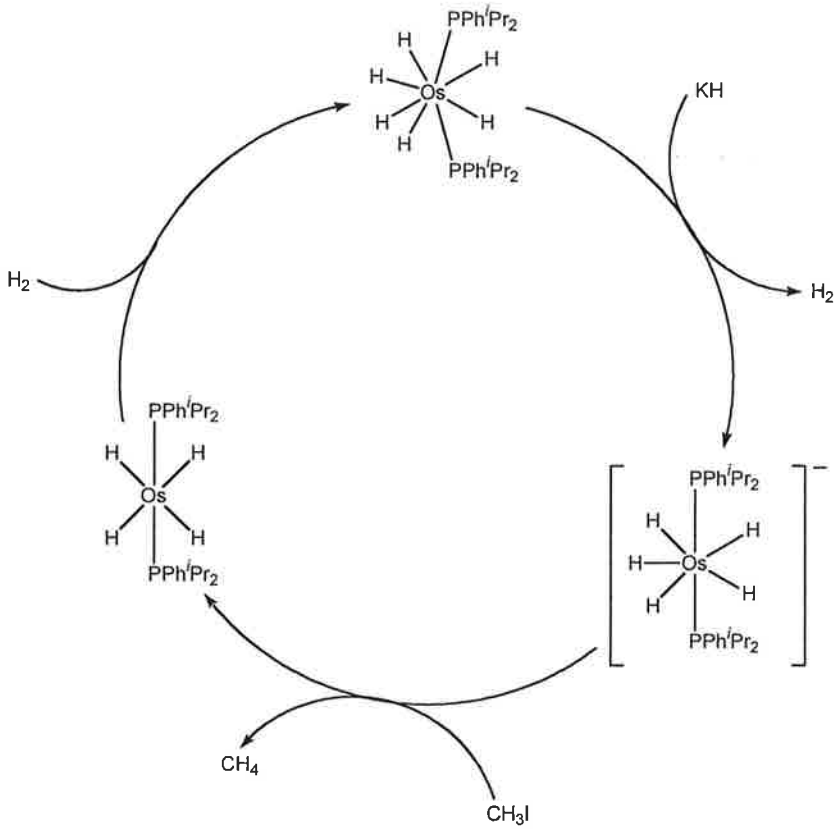

Figure 1

bimetallic polyhydride, $[Os_2H_6(PPh^iPr_2)_4]$ was generated from this complex, of which an X-ray crystal structure was obtained. Alteration of the charge on the metal centre alters the reactivity of $[OsH_6(PPh^iPr_2)_2]$, enabling both discrete mononuclear catalysis and cooperative polymetallic binding.

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PM59

Synthesis, Photophysical Properties, and Photocatalytic Activities of Tris(2,2'-bipyridine)ruthenium(II) Derivatives Tethered to Peptide Residues with Viologen Moieties

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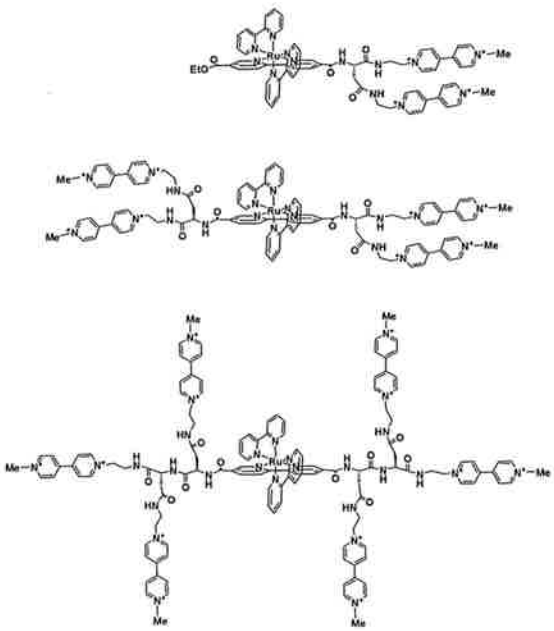
Interests over many years have concentrated on photochemical reduction of water into molecular hydrogen based on a three component system consisting of $Ru(bpy)_3^{2+}$ (photosensitizer), methylviologen (electron relay), and a Pt(II)-based molecular catalyst (H_2-evolving catalyst), in the presence of a sacrificial electron donor (EDTA).[1,2] Photo-hydrogen-evolving molecular devices involving more than two components out of the above-mentioned three components have also been developed in our group.[2] In this study, the title dyads (**RuMV2, RuMV4, RuMV6**; see below) have been synthesized, where the main purpose has been to achieve long-lived and high-yield charge separated (CS) states. Their photophysical properties as well as their use in photochemical H_2 production from water have also examined in detail.

RuMV2, RuMV4, RuMV6 were found to be very weak emittors due to the extremely rapid intramolecular electron transfer quenching after the formation of the so-called ^{3}MLCT excited state of the $Ru(bpy)_3^{2+}$-derived unit. The rate constants were estimated as 8.3×10^{10} s^{-1} for **RuMV2**, 1.2×10^{10} s^{-1} for **RuMV4**, and 2.3×10^{10} s^{-1} for **RuMV6**. More importantly, the lifetimes of their CS state (10 ns, **RuMV2**; 20 ns, **RuMV4**; 21 ns, **RuMV6**) were found to be quite long compared with those reported for such dyads. Such a long lifetime was only achieved for the dyad devopled by Turro et al (21 ns).[3] The quantum yield of the CS state varies in the order of **RuMV4** (0.92) > **RuMV2** (0.81) > **RuMV6** (0.64).



Scheme 1. Structure of the molecule used in this study.

On the other hand, photochemical hydrogen production from water using the two component system consisting of one of the present dyads and a Pt(II)-based catalyst (*cis*-$PtCl_2(NH_3)_2$)[1,2] was investigated. The total amount of H_2 evolved after 3 h of photoirradiation was 3.0×10^{-3} ml for **RuMV2**, 5.1×10^{-2} ml for **RuMV4**, and 1.0×10^{-2} ml for **RuMV6**, demonstrating that the overall efficiency well correlates with the quantum yield of the CS state (*vide supra*).

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PM60

X-ray diffraction study of bisphosphonate metal complexes: Mg, Sr and Ba complexes of (dichloromethylene)bisphosphonic acid P,P'-dibenzoyl anhydride

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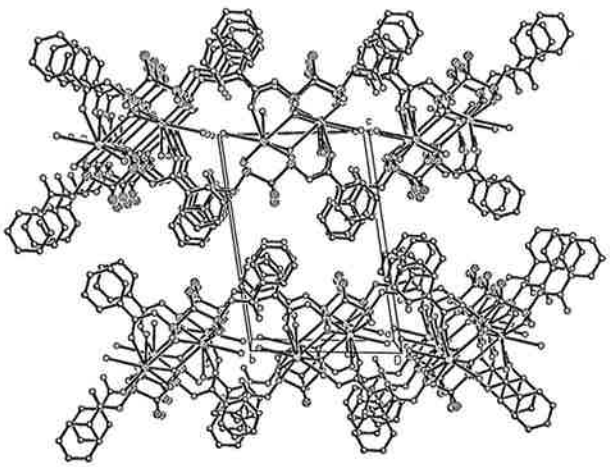
Bisphosphonates (BPs) have important pharmaceutical applications. One of the best known methylenebisphosphonate is disodium dichloromethylenebisphosphonate tetrahydrate, clodronate, which is used to inhibit the bone resorption. These compounds are highly hydrophilic and polar due to their ionization and therefore their lipophilicity is very low, and they are poorly absorbed by humans (bioavailability < 3%).[1] The research on improved prodrugs of clodronate have resulted in derivatives of clodronic acid and the investigation of their metal complexes is an interesting extension of this work. Metal phosphonates have also resulted in many interesting structures and applications in the field of solid state chemistry, for example in sorption, catalysis and ion exchange.[2-3]

The first alkaline earth metal complexes of a dibenzoyl derivative of clodronic acid were prepared and characterised by X-ray crystallography, elemental analysis and infrared spectroscopy. The complexes were $[Mg\{[Cl_2C(PO_2O(C(O)C_6H_5))_2](H_2O)_5\}\cdot H_2O]$ **(1)**, $[Sr_2\{[Cl_2C(PO_2O(C(O)C_6H_5))_2]_2(H_2O)_9\}\cdot H_2O]_n$ **(2)** and $[Ba\{Cl_2C(PO_2O(C(O)C_6H_5))_2\}(H_2O)_2]_n$ **(3)**. The monomeric units of **1** and the polymeric chains of **2** and **3** form 2D layer-like structures through intermolecular hydrogen bonds. The $Cl_2C(PO_2O(C(O)C_6H_5))_2^{2-}$ ligand acts as a bridging and chelating ligand, forming six- and eight-membered chelate rings with metal atoms. In addition, the previously determined[3] polymeric calcium complex of clodronate, $[Ca_2\{Cl_2C(PO_3)_2\}(H_2O)_6\cdot 4.5H_2O]_n$ **(4)**, was synthesised by hydrolysis method from the dibenzoyl derivative of clodronic acid.



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PM61

Highly sensitive ZnO nanowire ammonia sensor with Pt adsorption

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We report the growth of high-density single crystalline ZnO nanowires on patterned ZnO:Ga/SiO_2/Si templates, Pt adsorption on nanowire surfaces and the fabrication of ZnO nanowire-based ammonia gas sensors. Figure 1 shows detector responses of the ZnO nanowire-based ammonia gas sensors measured at 300°C. During these measurements, 1000 ppm ammonia gas was introduced into a sealed chamber and we measured the resistivity of the sensor both in air (Ra) and in the presence of ammonia gas (Rb). To quantify the sensor performance, we define the response of our sensor as [((Ra − Rb)/Ra) × 100%]. With this definition, it can be seen that the sensor response was 36% for the ZnO nanowires with Pt. In contrast, sensor response was only around 24% for the pure ZnO nanowires. In other words, we can indeed significantly enhance the sensitivity of ammonia gas by the adsorption of Pt nano-particles on ZnO nanowire surface.

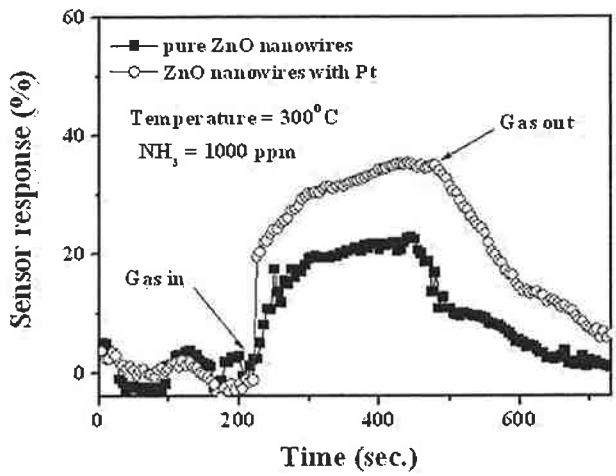

Figure 1 Detector responses of the ZnO nanowire-based ammonia gas sensors measured at 300°C.

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PM62

Novel *Si,P* Hybrid Ligands

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A major objective of modern organometallic chemistry is the design of ligands with steric and electronic properties that will strongly influence the metal centre in a desirable manner. However, silyl-metal complexes remain relatively unexplored in this area of chemistry, partly because metal-silicon bonds tend to undergo facile cleavage. This can be greatly retarded by the chelate effect, and a number of (phosphinoalkyl)silyl (*Si,P*) ligands have been developed on this basis.[1]

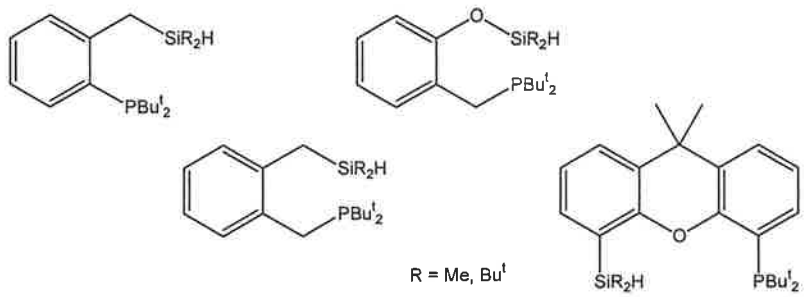

Figure 1: New *Si,P* hybrid ligands

Heterodentate *Si,P* functionalities can be combined with other ligand features to produce potentially very valuable ligands for use in homogeneous catalysis. Herein we report the synthesis of new wide bite angle *Si,P* hybrid ligands of the type shown in Figure 1. Preliminary results of complexation studies of these ligands with transition metals will also be discussed (Figure 2).

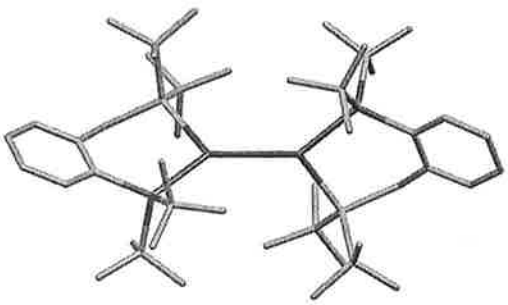

Figure 2: A platinum dimer with *Si,P* hybrid ligands

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PM63

Mössbauer and X-ray Single Crystal Determination of Microscopic EFG and MSD Tensors in Ferrous High Spin Salts

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Ferrous ammonium sulphate hexahydrate ($FeSO_4(NH_4)_2SO_4.6H_2O$) or FAS and ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) or FCL are two simple classic inorganic compounds, both containing two iron atoms in a monoclinic unit cell. The Fe^{2+} ions occupy sites of triclinic point group symmetry (C_1), with experiment yielding only a macroscopic (superimposed) electric field gradient (EFG) by the observed $\bar{1}$ (= C_i) Laue symmetry.[1] We are undertaking more precise measurements than previously reported to resolve the microscopic contributions to the single observed Mössbauer quadrupole doublet from the two symmetry related sites for both FAS and FCL. Experimentally, we constructed a single-circle goniometer, where a doubly polished single crystal of a known plane, ($\bar{2}$ 01) for FAS is mounted at 45° with respect to the γ-beam, and on rotation, effectively passing the beam through a cone of polar and azimuthal angles. With thickness and polarization corrections to the thin crystal limit, we run simulations with reduced intensity ratios and our x-ray mean-square-displacement (MSD) data transformed to arbitrary co-ordinates and previously reported or guess macroscopic EFG data using the MOSREF program[2], until convergence. For FAS we provide an unambiguous solution to the "ambiguous" monoclinic case of a manifold of microscopic EFG solutions, and believe this is the first reported determination of microscopic EFG's for the monoclinic case where the Fe^{2+} do not sit on a C_2 axis.[3] Mössbauer derived MSD and Mössbauer-Lamb factors are in this instance ~50% larger than room temperature x-ray and Debye-Waller factors, consistent with sodium nitroprusside (SNP) determinations by Housely *et al.*[4] Results for FCL are still tentative.

Acknowledgements:

Acknowledgments to University of Canterbury, Department of Chemistry, Mechanical workshop for construction of the goniometer setup, Prof. Ward Robinson for x-ray structure determinations and useful discussions, and Mr Rob Spiers, Geology Department, for crystal polishing assistance. We also acknowledge Dr Catherine McCammon for spectrum fittings and transmission-integral thickness corrections using the program NORMOS. JNB acknowledges financial support of a TEC Top Achiever scholarship and WCT acknowledges part financial support from the NZ Superannuation Fund.

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PM64

Green oxidation technologies: Immobilization of Fe-TAML catalysts.

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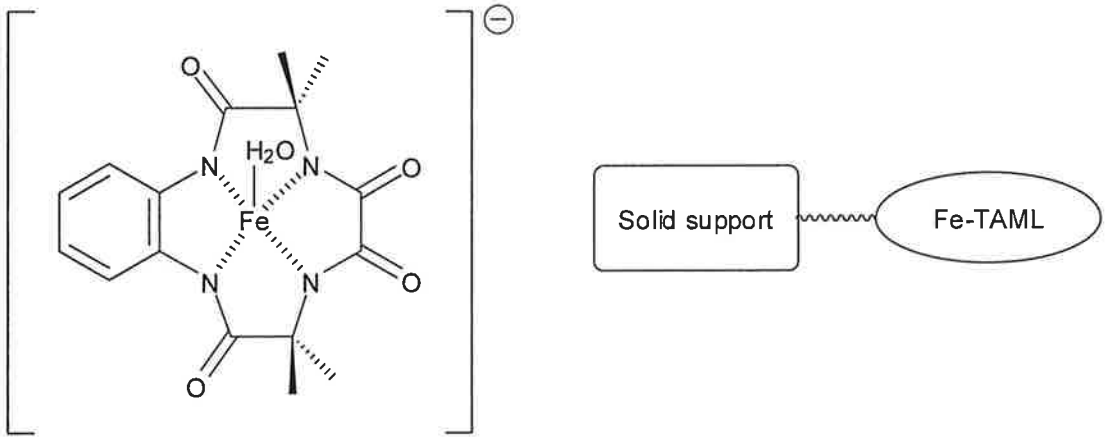
Every year, the New Zealand pulp and paper industry generate approximately 400,000 tonnes of solubilised lignin. This material is mainly burned to produce energy, but it can be put to a better use. Studies have shown that numerous fine chemicals such as vanillin can be obtained by direct selective oxidation of soluble lignin using oxygen.[1] However, because of the high cost, inefficiency or toxicity of the required oxidants, none has been used in industrial production.

Fe-TAML's (see figure 1)[2] are water soluble, iron based compounds that catalyse oxidation by hydrogen peroxide and oxygen, and are still active at sub-micromolar concentrations. The oxidizing strength of these catalysts can be modified by functionalisation of the aromatic ring. Fe-TAML's anchored to a solid support could form the basis of an efficient, as well as environmentally benign, lignin oxidative process. We will present the result of our studies into the functionalisation and the immobilisation of these systems and their use as oxidation catalysts.



An example of an Fe-TAML complex

Immobilized Fe-TAML

Figure 1

Acknowledgements:

University of Auckland, Faculty of Science, Post Doctoral Fellowship.

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PM65

Influence of Terminal OH Groups on the Metal Complexes of Pyrimidine-Hydrazone Strands

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A new pyrimidine hydrazone ligand strand has been prepared which contains terminal hydroxymethyl arms. Metal complexes were prepared with Pb(II), Ag(I) and Cu(II) salts to investigate the binding of the ligand strand and the influence the terminal arms had on the structure and organization of the metal complexes formed. X-ray structural analysis revealed that metal coordination extended the molecular strand into a linear shape or grid shape depending on the metal-to-ligand ratio. The uncoiling of these ligand strands on binding to metal ions has also been reported by others.[1] However, the inclusion of the hydroxymethyl arms in these new ligands has led to a number of unusual structures such as linear complexes, dimers, distorted grids and isomeric complexes.

The new pyrimidine hydrazone ligand and a variety of its complexes will be presented. The influence of the hydroxylmethyl arms on the complexes and their extended structures will be analyzed and discussed.

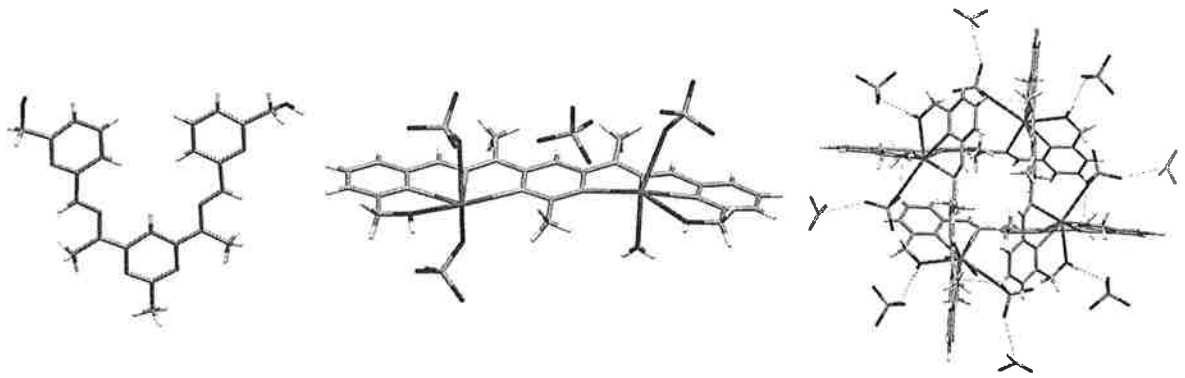

Figure showing the ligand with terminal OH groups, the linear and grid complexes formed with Pb(II). In all these examples the OH groups are bound to the Pb(II) ions.

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PM66

Synthesis and Characterisation of Novel Bismuth β-diketonate Precursors

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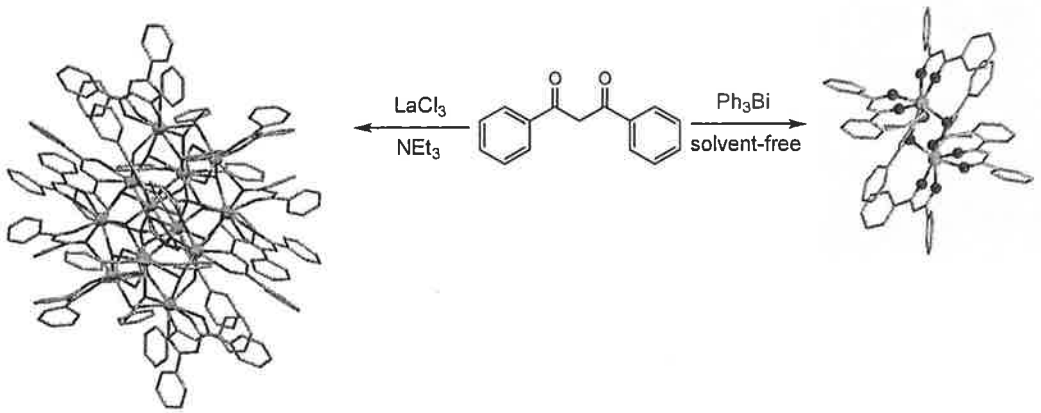
The chemistry of bismuth has received a great deal of attention in the last decade due to the vast number of applications of Bi compounds, ranging from medicinal chemistry[1] to high T_c superconductors.[2] However, often encountered issues in Bi chemistry include: i) the formation of highly insoluble, hence poorly characterised, products; ii) a tendency toward hydrolysis with concomitant formation of polynuclear clusters with variable Bi_xO_y cores. We have recently investigated in our group the reactivity of rare earth trivalent cations with β-diketonate in order to obtain polynuclear lanthanoid hydroxo-clusters.[3] We have also dedicated part of our research to the preparation of Bi precursors using fluorinated alcohol ligands.[4] As an extension to these previous works, we have decided to explore the chemistry of trivalent Bi with β-diketones, using triarylbismuthine (e.g. triphenyl and tritolylbismuth) or bismuth silylamide (e.g. bismuth tris(bistrimethylsilyl amide)) as starting material. An overview of the obtained compounds and a correlation to the analogous chemistry of the rare earths elements is here presented.



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The authors would like to acknowledge the Australian Research Council and Bayer Schering Pharma for the funding provided.

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PM67

The Effect of Ancillary Ligands on the Behaviour of Alkoxybenzimidazolin-2-ylidene-Palladium Complexes as Pre-Catalysts

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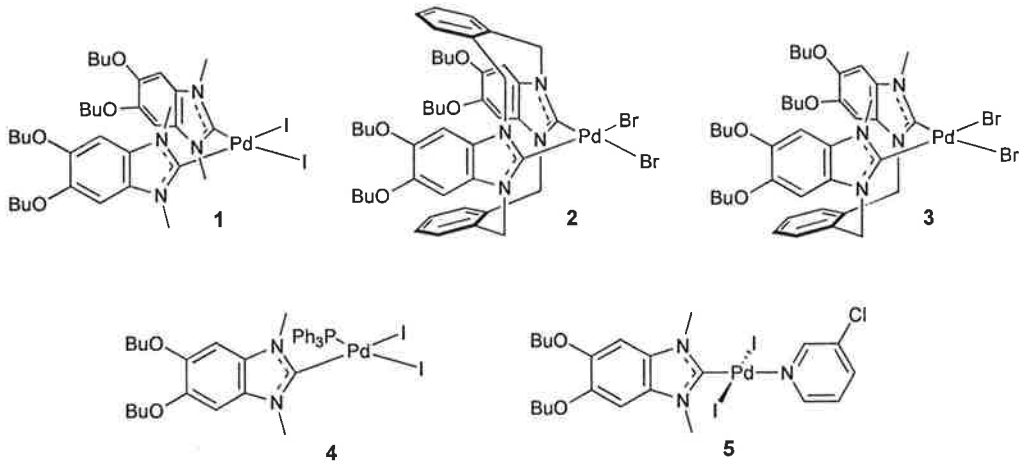
We are interested in investigating how structural differences affect the properties and catalytic activity of a series of palladium *N*-heterocyclic carbene (NHC) complexes.[1] We have synthesised complexes of the type $Pd(NHC)_2X_2$ (both chelating and non-chelating), $Pd(NHC)(pyridyl)X_2$, and $Pd(NHC)(phosphine)X_2$ (**1-5**). To minimise any steric effects, NHCs that impart minimal steric bulk around the metal centre have been used, ensuring that ligand type (NHC *vs* pyridyl *vs* phosphine) is the primary factor responsible for any observed differences in catalytic activity.

We have focused on NHCs based on 5,6-dibutoxybenzimidazole and 4,7-dibutoxybenzimidazole. The butoxy groups increase the solubility of the complexes in common organic solvents, but may also increase the electron density at the metal centre. The complexes exhibited moderate activity in the Mizoroki-Heck and Suzuki-Miyaura coupling reactions, with subtle differences in activity between complex types being observed.



Acknowledgements:

We thank the Australian Research Council for a Discovery Grant (to M.V.B. and A.H.W.) and the Gleddon Trust for a Robert and Maude Gleddon Postgraduate Scholarship (to P.V.S.), and Curtin University of Technology for a Research and Teaching Fellowship (to D.H.B.).

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PM68

Supramolecular Assembly Using Amino Acid Schiff Bases

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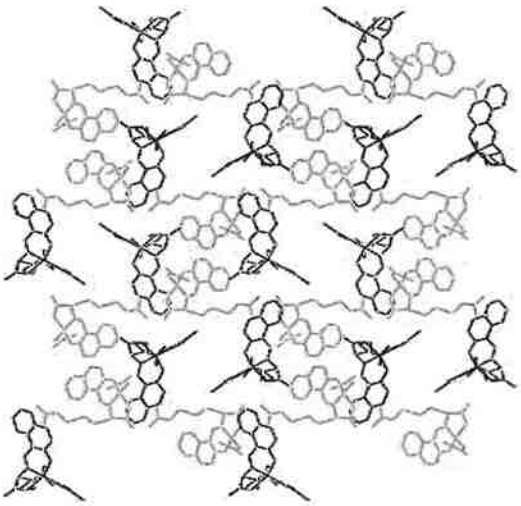
Self-assembly is interesting both for its biological relevance, and because it is a new approach to complex structures that are difficult or impossible to prepare by traditional techniques. Molecular assemblies are controlled by symmetry, topology and chemical bonding of the building blocks, natural building blocks such as amino acids have been extensively pursued for decades. [1] There have been considerable efforts directed at the development of amino acid Schiff base complexes due to their anti-inflammatory, anti-ulcer, anti-convulsant and anti-cancer properties. Guanidinium group on arginine has demonstrated its malleability as a building block in charge-assisted hydrogen-bonded network,[2] and arginine Schiff bases were found to be potent thrombin inhibitor.[3] We aim to construct synthetic supramolecular architectures using amphiphilic amino acid derivative as bioligands and metal ions with biological importance or catalytic properties. Simultaneously employing various non-covalent interactions, including hydrogen bonding, π-π stacking, solvophobic and electrostatic interactions, will contribute to the stabilization of the structures.



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We thank Ms. Geok Kheng Tan for technical assistance. This research is supported by the National University of Singapore (R-143-050-288-101).

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PM69

New Platinum(II) and Platinum(0) Complexes of Bulky Iminophosphine ligands

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The design of new ligands for promoting high reactivity and selectivity in homogeneous catalysis is a field of ongoing research. Recently there has been significant interest in polydentate ligands with both hard and soft donor atoms. Iminophosphines have proven interesting due to the combination of the soft phosphorus and hard nitrogen donor atoms. This has meant that the ligands display versatile coordination behaviour and are potentially hemilable.[1]

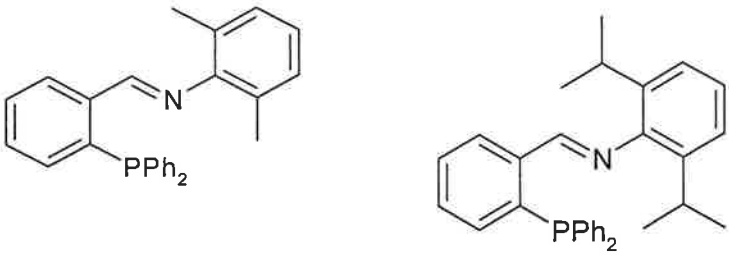

Figure 1

Here we report the synthesis of previously unexplored platinum(II) and platinum(0) complexes containing the ligands shown in Figure 1. A different reactivity pattern was observed when the ligands were reacted with Pt(II) and Pt(0). When the ligands reacted with a Pt(II) precursor the iminophosphines behaved as bidentate ligands, coordinating to the platinum through both the phosphorus and nitrogen. In contrast, when the ligands were reacted with a Pt(0) precursor they acted as monodentate phosphorus ligands. This illustrates the ability of these iminophosphine ligands to act as bidentate or monodentate ligands.

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PM70

Towards metal helicates: polystranded ligands containing multiple amino acids

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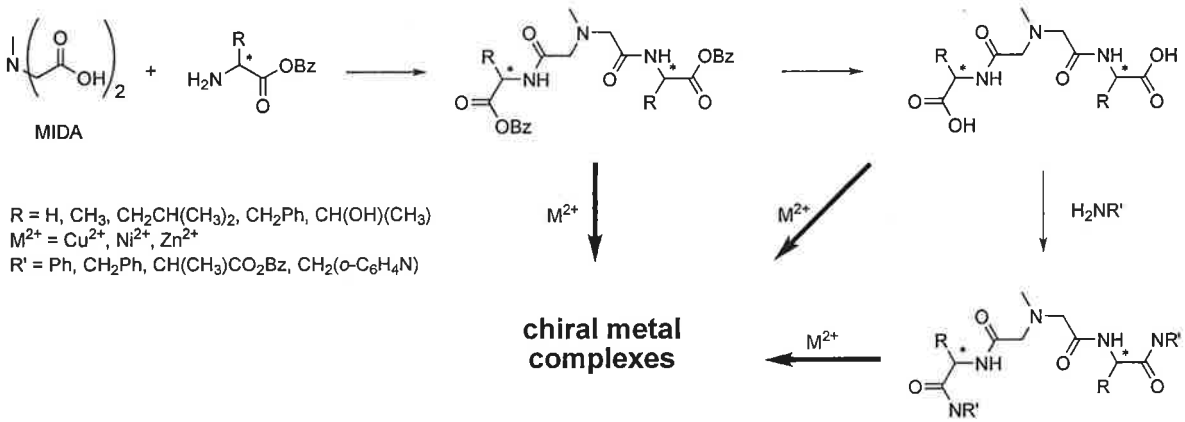
We have recently developed a robust synthetic route to a small library of amino acid-containing compounds with the potential to be used as ligands.[1] The cores of these ligands are either nitrilotriacetic acid (NTA) or methyliminodiacetic acid (MIDA, shown in Scheme 1). Amino acids that have been used to explore the versatility of the amide coupling route include C-protected glycine, alanine, phenylalanine, leucine, aspartic acid and threonine. After deprotection, a number of different substituents have been incorporated onto each arm as shown in Scheme 1. The three strand compounds based on NTA cores bear C_3 symmetry, while those with two strands (MIDA core, shown in Scheme 1) have C_1 symmetry.



Scheme 1. Synthesis of new chiral ligands bearing amino acid substituents based on MIDA core

Metal binding to the double stranded compounds is expected to involve the apical tertiary amine and either the carboxylate groups of the free acids or, in the cases of copper(II) and nickel(II), deprotonation of the amide to form a pseudo square planar coordination environment. Several of these complexes have been prepared and their synthesis and characterisation will be presented. The mechanism of complexation has been studied using potentiometric titrations. Recent results incorporating a second amino acid or metal binding site onto the arms will also be presented.[2] Our goal is to investigate whether the compounds will form metal helicates, and whether the chirality of the amino acid will determine the twist of the helicate.

Acknowledgements:

MS thanks UQ for a Post-doctoral Fellowship, during which this work was started. JK thanks UniChe for a Summer Vacation Scholarship. MS and DMS thank the QUT School of Physical and Chemical Sciences for funding.

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