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37th International Conference on Coordination Chemistry

PGMs PROMINENT IN A WIDE RANGE OF RESEARCH AND APPLICATIONS

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The 2006 International Conference on Coordination Chemistry (ICCC) took place, for the first time, on African soil, between the 13th and 18th August 2006 in the beautiful city of Cape Town, South Africa (1). Following on from the successful conferences in Merida (2004), Heidelberg (2002) and Edinburgh (2000), this event attracted over 600 delegates from approximately 60 countries around the world and involved 287 scheduled oral presentations and over 330 poster presentations. Abstracts of all the oral and poster presentations were edited by D. J. Robinson (one of the present reviewers) and I. M. Robinson, and published in hard copy and electronic versions (2). The page numbers given in brackets in this article refer to the relevant page number in these publications. Leading international researchers were invited to give a total of 8 Plenary and 49 Keynote lectures. The conference was structured in terms of six themes, presented in parallel sessions. The themes were as follows:

- Metals in Biology and Medicine
- Metals in Materials, Nano-Structures and Devices
- Metals in Catalysis and Industry
- Metals in Self Assembly and Supramolecular Systems
- Metal Complexes in Solution: Structure, Mechanism and Ligand Design
- Precious Metals, Photochemistry and Computational Chemistry.

There were many contributions involving the chemistry of the platinum group metals (pgms) throughout all of the themes. It would therefore be impossible here to provide anything more than a flavour of the diverse chemistry presented in each area.

Plenary Presentations

The excellent plenary presentations given, by world leaders in their fields, straddled the themes of the conference. Of particular note was the final plenary lecture presented by Robert H. Grubbs, the Atkins Professor of Chemistry at the California Institute of Technology, U.S.A., and co-winner of the 2005 Nobel Prize in Chemistry. The 2005 Nobel Prize in Chemistry was shared by Yves Chauvin, Robert H. Grubbs and Richard R. Schrock, for the development of the metathesis method in organic synthesis (3). In this lecture Professor Grubbs described the early development of the now famous first and second generation Grubbs' catalysts, and the more recent applications of these ruthenium catalysts in the synthesis of a wide variety of valuable chemicals and polymers. The other plenary lectures, by Professors Amilra Prasanna de Silva (Queen's University Belfast, U.K.), Peter J. Sadler (University of Edinburgh, U.K.), Helder M. Marques (University of the Witwatersrand, South Africa), Tobin J. Marks (Northwestern University, U.S.A.), Rudi van Eldik (University of Erlangen-Nürnberg, Germany) and Omar Yaghi (University of California, U.S.A.), similarly covered extensive and equally important areas; it was apparent that in these, coordination chemistry is alive and thriving.

Metals in Biology and Medicine

A significant number of contributions concerned alternative pgm-containing complexes (particularly of platinum and palladium) with potential anticancer activity. Ligands included L-ascorbic acid (p. 39), bidentate oxalate groups (p. 42), 1,1′-bis(diphenylphosphine)ferrocene and derivatives (p. 304), cyanoxime ligands (p. 314), branch-chained esters (p. 331), amine and dicarboxylate ligands (p. 333) and hydantoin derivatives (p. 369). New insights into possible *in vivo* reactions (p. 39) and the mechanism by which these platinum complexes may act were reported (p. 40), including kinetic studies (p. 527), consideration of both DNA and RNA as possible targets (p. 41), thermogravimetric behaviour (p. 338), chemically triggering the *cis*/*trans* isomerisation of anticancer platinum drugs (p. 372) and the synthesis of model calyx[*n*]arene complexes (p. 258). Novel photoactivation of several octahedral *cis* and *trans* diamino diazo platinum(IV) complexes was reported to lead to novel reactions including those which may prove applicable to killing cancer cells (pp. 2, 62).

Studies of the synthesis, characterisation and biochemical activity of several new half-sandwich arene complexes of ruthenium and osmium were described (pp. 2, 35, 371). Complexes of ruthenium-containing polyaminocarboxylate (p. 38), thiosemicarbazone and isoniazide (p. 48), oxine and azole ligands (p. 325), photoactivated polypyridine ligands (p. 33) and substituted chelating quinolinquinones (p. 368) were also reported. DNA binding studies of ruthenium complexes of polypyridines (pp. 326, 346), crown ethers and bridging polypyridilic ligands (p. 349) were discussed, including the formation of ruthenium 'molecular dots' to capture DNA strands (p. 89). Ruthenium nitrides were prepared and studied as models of biologically relevant intermediates (p. 215).

Several new polytopic metal complexes (including rhodium, palladium and platinum) possessing 2,6-di-*tert*-butylphenol pendant groups were found to be active for electron transfer and possible use in the prevention of xenobiotic-induced oxidative stress in organisms (p. 65). Similarly, fundamental studies (p. 534) and interesting activity including greater cytotoxicity of a number of new derivatives of titanocene or titanium organometallics including those coordinated to ruthenocene ligands (pp. 30, 31) were reported.

Metals in Materials, Nano-Structures and Devices

A number of interesting mixed metal and mixed-valence, halide-bridged complexes were prepared with nickel and palladium, and studied photochemically as model complexes (p. 72); and ruthenium-containing novel chromophore quenchers of rhenium(I) were also reported (p. 377). In related work, the absorption of ruthenium(II) photosensitisers was subject to a theoretical analysis (p. 414). The self-assembled monolayer of peptide-linked ruthenium polypyridyl complexes was probed by surface-enhanced resonance Raman spectroscopy (SERRS) (p. 383). The photoinduced energy transfer within ruthenium polypyridyl dyads was discussed (p. 614). The synthesis and characterisation of several new ruthenium(II) complexes with bidentate diimine and imine-phosphino ligands was addressed (pp. 401, 618); also the 'ship-in-a-bottle' synthesis of related polypyridyl complexes within the zeolite matrix (p. 410). A potential novel application of substituted pyridyl organoiridium complexes in light emitting diodes (LEDs) was presented (p. 388).

The use of coordination complexes as precursors to the preparation of pgm-containing nanoparticles was the theme of several papers. Palladium 'quantum dots' were prepared from palladium aroyl(seleno)urea precursors (p. 93), and ruthenium olefin complexes were used to produce ruthenium nanoparticles (p. 105).

A series of half-sandwich ruthenium, iridium and palladium complexes (p. 109) and novel η^2-bound fullerene palladium and platinum complexes of ruthenocene were also described (p. 90). A new series of highly conducting thin films of gold nanoparticles have been prepared, with ruthenium complexes acting as the links between particles (p. 92).

The interesting liquid crystal properties of *ortho*-metalated imine complexes of platinum(II) and palladium(II) (p. 380) and ferrocene-containing β-diketone complexes of rhodium were reported (p. 129). Ruthenium and osmium bipyridine complexes have been used to prepare mesoporous silicates using sol-gel synthesis (p. 68).

Metals in Catalysis and Industry

A significant number of presentations described the use of Grubbs' (ruthenium) catalysts, and metathesis and unsymmetrical variation of the ligand structures (p. 597). Interesting uses of the metathesis reaction include coupling within the coordination sphere to synthesise caged palladium and rhodium diphosphine complexes (p. 114), and alkenyl bridged iron complexes (p. 564). Related ring-closing reactions were used to prepare pallada- (p. 436), platina- (p. 146) and rhoda-cycloalkanes (p. 426), and thermal decomposition of these complexes was reported (p. 450).

Further insights into the mechanism of the palladium-catalysed Stille and Heck reactions were described (pp. 116, 148). Interesting polymers were prepared using palladium-catalysed cyclopolymerisation and copolymerisation reactions (p. 133). Extensive use of NMR spectroscopy and a computational density functional theory (DFT) study have shed light on the mechanism of the palladium-catalysed alkyne hydrogenation rection (p. 159). A new cationic palladium dimer was reported to be a catalyst for the Suzuki coupling reaction under mild conditions (p. 427). Novel 'daisy-chain' polymers were successfully prepared using palladium(0)-catalysed couplings as the key carbon–carbon bond forming reactions (p. 202).

The synthesis, characterisation and intermolecular interactions of potential new rhodium hydroformylation catalysts were presented (pp. 125, 430). Rhodium-catalysed asymmetric hydrogenation of itaconic acid derivatives was described as a route to pharmaceutically interesting products (p. 155).

Other non-ruthenium carbene and carbene-like fractions continue to attract research attention from a number of research groups (pp. 149, 443). For example, novel palladium carbenes have been prepared using novel silver and mercury reagents (p. 419) and using carbene transmetalation (p. 425), sometimes employing *N*-heterocyclic carbenes (p. 271).

A number of new bimetallic complexes have been designed and synthesised to mimic enzymes, and tested for both catalytic and biological activity (p. 122). A number of unsubstituted and phosphite substituted ruthenium and osmium carbonyl clusters were described (pp. 154, 439, 449), as were some trinuclear rhodium (p. 156) and tetranuclear ruthenium (p. 437) catalyst precursors for asymmetric hydrogenation. The novel use of a platinum-catalysed cycloisomerisation of camphor-derived bisalkynes was reported to produce tetracyclic cyclopentenone derivatives (p. 124). Derivatives with a $\{Pt_2S_2\}$ core have been developed for organosulfur synthesis and dehalogenation of persistent organic pollutants (p. 130), with the same core (and the selenium analogue) being useful in the synthesis of larger multimetallic complexes (p. 558). Several papers described further development of the use of dendrimer supports for 'heterogenising' homogeneous catalysts, including cyclopentadienyl ruthenium fractions (p. 138).

Osmium complexes continue to be prepared as potential models of catalytic intermediates for more reactive catalysts, including osmabenzofuran and osmabenzene complexes (p. 140) as models of active metal sulfide sites (p. 611). New tools are emerging for the improved elucidation of catalytic reaction mechanisms, including matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) (p. 118) and *in situ* NMR spectroscopy including high-pressure methods (pp. 123, 143, 151, 444). Similarly, systematic spectroscopic studies improved characterisation techniques towards further understanding of the nature of bonding and backbonding in a number of pgm complexes (pp. 120, 429) and the role of varying solvent properties (p. 448).

The effect of varying tertiary phosphine substituents upon the solution and solid-state behaviour of rhodium(I) complexes was reported (p. 420). While many catalysts depend on a *cis*-bidentate ligand to arrange the complex geometry, a specific ligand (SPANphos) has been designed, modelled and synthesised to bind *trans* to square planar, in an attempt to modify the action of conventional palladium, platinum and rhodium catalysts (p. 111). Indeed, an increasing number of presentations featured theoretical and fundamental studies of catalysts and catalytic reactions. Examples included platinum(II) and palladium(II) catalysts (p. 432), rhodium hydroformylation reactions (p. 113), hydroxide assisted palladium catalyst activation (p. 134) and photocatalysed ruthenium degradation of pesticides attached to titanium oxide particles (p. 612).

Metals in Self Assembly and Supramolecular Systems

A number of new substituted terpyridine ligands and their square planar platinum(II) complexes have been used as metallotectons for the assembly of heterometallic macrocyclic complexes (p. 193), and their interaction with aromatic molecules was reported (p. 489). Novel mixed-valence platinum(II)-platinum(IV) one-dimensional systems were reportedly assembled in a host-guest configuration (p. 472), and molecular magnets and molecular conductors containing platinum(II) centres were reported (p. 490). Magnetic properties of one-dimensional Pt_6Rh_2 systems were reported (p. 508).

The photochemical properties of ruthenium pyridyl (p. 609), bipyridyl, polypyridyl (p. 623) and phenanthroline complexes continue to attract attention, including in the areas of supramolecular assemblies (p. 168), porphyrin complexes (p. 467) and kinetically locked molecular architectures (p. 174). Similar bipyridyl complexes have been found to aggregate with ruthenium cyano complexes with significant hydrogen bonding (p. 198). The electronic properties of cyano bridged polymetallic complexes were reported, including those of several with a Fe_2Ru nucleus (pp. 452, 471), and others with more complex Ru_5 networks of ethynylpyridine bridges (p. 470). The interaction of ruthenium and osmium luminophores with cyclodextrins, and consequent electronic communication properties were reported (p. 176).

A range of rhodium and ruthenium organometallics have been used as building blocks in co-deposition reactions, yielding extended hybrid networks using metal–π–arene and π–π–arene interactions (p. 115). Polymeric rhodium pyrazine complexes were used to form novel single-crystal hosts for reversible CO_2 and O_2 adsorption, both of which have been studied by X-ray diffraction methods (p. 451, 506).

Platinum(II) complexes have been incorporated to improve the sensitivity of cobalt(II)-based quartz crystal microbalance gas sensors (p. 175), while other fluorophore containing molecules have been designed as sensors for palladium(II) (p. 584). Some new fluorosulfur (p. 462) and SNS and SCS (p. 620) pincer ligands were reported to be useful in preparing mononuclear and binuclear palladium complexes.

Metal Complexes in Solution: Structure, Mechanism and Ligand Design

The development and testing on behalf of PolyMet Mining Corp of the PLATSOL™ process for treatment of precious metal concentrates were described (p. 210). Alternative potential extractants for pgm recovery were presented; these involve polyamine containing ion exchangers (p. 613) or functionalised guanadinium groups (p. 619). Other early steps in the computational (p. 283) and experimental (p. 274) design of potential new extractants for pgm chloro anions were reported.

A range of new palladium(II) pyrazolyl (p. 250) and pyrazolate (p. 280) complexes, and reaction kinetics of several platinum(II) and palladium(II) amine (p. 550) and polyamine (p. 579) complexes in aqueous systems were reported. Novel bimetallic complexes containing platinum were prepared by the coordination of isothiazolin-3-one (p. 554). A range of dialkyl ureas and thiocarbamic acid esters (p. 530), unsymmetrical thioureas (p. 568) and silsesquioxanes (p. 566) have been coordinated to palladium(II) and platinum(II) fragments to produce coordination compounds with interesting properties (p. 594, 607). Similarly novel selenium functionalised dodecaborane complexes of platinum(II) were reported (p. 546). The insertion reactions of selected platinum complexes were described (p. 551).

The kinetics of selected oxidative addition reactions of platinum(II) complexes were reported (p. 587) and the cycloaddition of nitrones with palladium or platinum nitriles was studied experimentally and theoretically (p. 598). Interesting properties of heterometallic complexes containing platinum or rhodium and a zirconocene fraction were presented (p. 219). ^{195}Pt NMR spectroscopy (p. 281, 602) continues to be an increasingly useful and user-friendly probe into the speciation (p. 608) and coordination chemistry of platinum, and the study of its chloro anion extraction (p. 276).

Improved elucidation of the speciation of the rhodium chloro (p. 538, 539) and basic osmium (p. 565) systems was reported, using capillary zone electrophoresis, potentiometry and computational methods. Kinetic and computational studies of rhodium thiophene (p. 532) or phosphine (p. 536) β-diketonato complexes and the anomalous behaviour of cobalt(III) and rhodium(III) multidentate amine complexes were described (p. 240).

The coordination modes of amino functionalised dithiocarboxylate ligands to rhodium(I) centres have been studied computationally (p. 235), while similar ruthenium(II) complexes were studied electronically and described by DFT methods as molecular multielectron reservoirs (p. 236). 'Ruthenium trichloride' continues to be a convenient starting material for the synthesis, *via* assisted ligation, of a range of ruthenium complexes (p. 553) including di-*S*,*S*-2-propionate ligands which are potential antitumour reagents (p. 592).

Possible intermediates in pgm-catalysed alcohol oxidation reactions include oxyl radicals. One such ruthenium complex was prepared and studied for its relevance in such a reaction (p. 254).

Precious Metals, Photochemistry and Computational Chemistry

The increasing use of high-level thermodynamic and quantum chemistry methods, in particular DFT, even for molecules with heavy metal centres, was well illustrated (p. 260). The fundamental role of water in the speciation and stabilisation of ion pairs involving pgm chloro anions was reported (p. 595). The active role of water in possible reaction mechanisms has been studied in the pH selective C=C *versus* C=O reduction reaction of α,β-unsaturated aldehydes (p. 150).

Novel di- and trinuclear platinum-thalium compounds with unsupported metal–metal bond(s) were described (p. 279). The spectroscopic and electrochemical properties of several benzimidazole platinum(IV) compounds were described (p. 278). A number of novel tetrapalladium complexes with bridging silylene and germylene ligands were reported (p. 272), and the energy transfer properties of coordination polymers containing platinum and lanthanide units were described (p. 621).

In addition to those mentioned above, many other presentations considered the coordination of pgms (particularly ruthenium) to photoactive ligand components and the properties of the subsequently formed mononuclear (pp. 257, 263, 264), dinuclear (p. 265) and polynuclear (p. 265, 267) complexes. Ligand variations in novel diruthenium paddlewheel complexes and the effect of variations on the Ru–Ru bond were discussed (p. 277).

Concluding Remarks

Due to the size of the conference, the running of parallel themes and the extent to which pgms featured through many of the sessions, the reviewers were unable to attend all the relevant presentations. However, it was clear that the coordination chemistry of the pgms is in a healthy state, in terms of both worldwide development and application. Worthy of note was that the 37th ICCC was timed and located close to a number of related conferences, including the Cape Organometallic Symposium, the International Symposium on Homogeneous Catalysis and the Structural Chemistry Indaba. Many visitors could therefore justify the long distances travelled by attendance at two or more events.

Feedback received from delegates both during and after this conference showed general agreement that this 37th ICCC upheld the tradition of the series for well organised events. The reviewers look forward to the 38th ICCC, scheduled for Jerusalem, Israel, from the 20th to 25th July 2008 (4).

References

1 ICCC37, 37th International Conference of Coordination Chemistry, Cape Town, South Africa, http://webhost.sun.ac.za/pgm_group/

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3 V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2005, **50**, (1), 35

4 ICCC38, 38th International Conference of Coordination Chemistry, http://www.kenes.com/iccc38/

The Reviewers

David John Robinson is currently the manager responsible for sustainable development within Anglo Research and is based in Johannesburg, South Africa. He has been active in both fundamental and applied pgm chemistry research, and in particular, the development of improved separation technologies over a 15 year career with Anglo Platinum. He has been involved directly in their production at the modern precious metals refinery near Rustenburg, South Africa. His interests include developing improved industry–academia research collaborations and the application of improved fundamental knowledge to the solution of real refining problems.

Malcolm Arendse is currently a lead research scientist in the refining research group at Anglo Research in Johannesburg. He started his career as a lecturer at the University of the Western Cape, South Africa, in 1986. After completing a Ph.D. in Inorganic Chemistry at the University of Missouri-St. Louis, U.S.A., he joined Anglo Platinum in 2003. His research interests and activities have been in the areas of pgm refining, separation, speciation and catalysis.

Musical entertainment for the Banquet at the 37th International Conference on Coordination Chemistry. A wide selection of photographs of the Conference is available at the website (1)