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**ORGANOMETALLIC AND COORDINATION CHEMISTRY OF THE MAIN GROUP
AND RARE EARTH ELEMENTS**

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**Thesis presented for the degree of
Doctor of Science of James Cook University
February, 2006**

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SUMMARY

This thesis presents a series of publications relating predominantly to the organometallic, organoamido and coordination chemistry of the main group and rare earth elements as well as some supramolecular chemistry involving crown ethers and oxonium ions. Investigations have concentrated on new synthetic approaches to rare earth and main group organoamido, organometallic and aryloxo compounds and their characterisation. The chemistry of crown ethers has been thoroughly explored, particular with relevance to that involving oxonium ions and a wide variety of metal ion. Supramolecular research has mainly involved studies of hydrogen bonded species in the solid state. Particular emphasis on the characterization has involved X-ray crystallography and the structural elucidation of the compounds in the solid. Systematic studies of rare earth, bismuth and HX salts of amines have been also performed.

This thesis contains no material which has been submitted for a degree in any University by the author or other person, except where due reference is made in the text.

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February 22, 2006

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I wish to thank all who have been connected with the work involved in this thesis, particularly all my collaborators, but most importantly my PhD supervisor Prof. Colin Raston, my Postdoctoral supervisors, Prof. Jerry Atwood, Prof. Allan White and Prof. Glen Deacon and my other collaborators (Prof. Cameron Jones, Dr Marcus Cole, Dr Jonathan Steed, Prof. Ulrich Kynast and Prof. Eva-Marie Hey-Hawkins) with whom I have shared a very fruitful and successful number of years of research. My hard toiling PhD, Honours, undergraduate and exchange students have made most of the work in this thesis possible and without their contributions little of it would have been accomplished. Much of this work has been funded by the Australian Research Council, the Leverhulme Trust, UK and the DAAD, Germany and I am very grateful for the continued support. Finally I would like to acknowledge The University of Western Australia, The University of Alabama, The University of Missouri and Monash University for employment and support and I would particularly like to acknowledge James Cook University for giving me a start to my academic career and their support while I was working in Townsville.

PREFACE

Table of Collaborators

Comments on Collaborative Studies

Collaborators and Research Students (in chronological order)*

<i>Collaborator</i>	<i>Years</i>	<i>Publications</i> [#]
Prof. Colin L Raston (University of W.A.) <i>PhD Supervisor</i>	1984-1988	1,2,3,4,5,6,7,8,9, 10,12,18,24,27, 29,144,149
Dr Brian W. Skelton (University of W.A.)	1986-2006	1,2,3,4,9,12,29, 31,32,33,37,38, 39,40,41,42,46, 58,61,62,63,64, 65,66,88,114,135 141,145,149,160, 171,189,193,195, 196,197,198,199
Prof. Allan H. White (University of W.A.)	1986-2006	1,2,3,4,6,7,8,9, 10,12,27,29,31, 32,33,37,38,39, 40,41,42,46,58, 61,62,63,64,65, 66,88,114,135, 141,145,149,160, 171,189,193,195, 196,197,198,199

<i>Collaborator</i>	<i>Years</i>	<i>Publications</i> [#]
Prof. Cameron Jones (Cardiff University)	1996-2006	10,27,35,48,68, 82,84,87,92,93, 94,95,97,98,101, 102,106,109,115, 116,127,128,133, 139,154,155,161, 176,177,178,186, 191,192,200
Dr Michael G. Gardiner (University of Tasmania)	1992-2006	12,27,173
Prof. Jerry L. Atwood (University of Missouri)	1992-1994	13,14,15,16,17, 18,19,20,21,22, 23, 24,25,28,30, 34,44,51,56,74, 81
Dr Jonathan W. Steed (Durham University)	1994-2006	18,45,50,53,57, 59,67,69,90,96, 98,99,102,109, 130,140
Prof. Glen B. Deacon (Monash University)	1996-2006	31,32,33,37,46, 48,53,55,58,66, 83,88,100,108, 114,117,131,142, 145,148,153,156, 158,167,168,169, 171,174,179,180, 181,187,188,189, 190,192,194

<i>Collaborator</i>	<i>Years</i>	<i>Publications</i> [#]
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Prof. F. Richard Keene (James Cook University)	1997-2006	36,55,75,76,78, 107,185
Ms Sarah J. Belfield (James Cook University) <i>BSc Student</i>	1998	43
Dr Matthew K. Smith (James Cook University) <i>PhD Student</i>	1999-2002	43,75,87,90,99, 105,111,113,121, 122,124,125,146, 150,166
Prof. Ulrich H. Kynast (Fachhochschule Münster)	1997-2006	44,85,129,137
Dr Craig M. Forsyth (Monash University) <i>Postdoctoral Fellow</i>	2004-2006	46,52,58,66,83, 114,158,167,189, 192
Ms Susan M Lynch (James Cook University) <i>BSc Student</i>	1997	49
Prof. Rüdiger Mews (University of Bremen)	1998-2006	55,174
Prof. Jana Hodacova (Prague, Czech Republic)	1998-2001	70,138
Ms Kym R. Fewings (James Cook University) <i>Honours Student</i>	1998	72,96
<i>Collaborator</i>	<i>Years</i>	<i>Publications[#]</i>

Dr Marcus L. Cole ¹ (James Cook/Monash University) <i>Postdoctoral Fellow</i>	2001-2004	93,101,102,110, 112,116,118,119, 120,125,126,127, 132,136,141,151, 155,159,161,162, 163,168,169,172, 173,175,176,178, 180
Mr. Lance M. Louis (James Cook University) <i>Honours Student</i>	1999	73,105,112,118, 119,197
Prof. Eva-Marie Hey-Hawkins (University of Leipzig)	1997-2006	77,80,108,110, 119,120,127,146, 152,157,164,165
Assoc. Prof. Bruce F. Bowden (James Cook University)	1997-2001	79
Dr Neil A. Smithies ¹ (James Cook University)	1998	82,84,94,97,109, 127,133,139,161
Mr Stuart G. Leary (Monash University) <i>PhD Student</i>	2001-2006	84,86,94,97,109, 127,133,139,161
Mr Stephan Brück ² (James Cook University)	1998	85
Dr Matthias Hilder ² (James Cook/Monash University) <i>PhD Student</i>	2001-2004	85,137,146,194
Dr Ryan C. Thomas ¹ (James Cook University)	1999	87,98
<i>Collaborator</i>	<i>Years</i>	<i>Publications[#]</i>

Prof. Leone Spiccia (Monash University)	1998-2006	60,89,103
Prof. Len F. Lindoy (University of Sydney)	1999	104
Dr David J. Evans (Monash University) <i>PhD Student</i>	2002-2005	110,112,113,117, 120,121,125,145, 174
Dr Rita Harika (Monash University) <i>PhD Student</i>	2000-2002	114,145,158
Mr Jens Baldamus ³ (Monash University)	2001	108,110,119,120, 127
Ms Christiane Berghof ³ (Monash University)	2001	110,119,120
Prof. W Roy Jackson (Monash University)	2001-2006	133
Ms Ulrike Helmstedt ³ (James Cook University)	1999	127
Ms Franziska Lange ³ (Monash University)	2001	127
Dr Steven E Bottle (QUT)	1998-2000	134
Dr Thilo Hahn ³ (James Cook University)	2000	146
Prof. Maria Forsyth (Monash University)	2001-2006	148,187,188
Dr Marc Kloth ¹ (Monash University)	2003	154,176,186,191
Dr Aaron J. Davies ¹ (Monash University)	2004	155,178
<i>Collaborator</i>	<i>Years</i>	<i>Publications[#]</i>

Dr Rene T. Boere (Lethbridge University)	2004-2006	159,162
Ms Kristina Konstas (Monash University)	2003-2006	168,169
Dr Kathryn M. Proctor (Monash University) <i>PhD Student</i>	2002-2005	175,180,191
Dr Andreas Stasch (Cardiff/Monash University) <i>Postdoctoral Fellow</i>	2004-2006	176,177,191,200
Dr Philip C. Andrews (Monash University)	2001-2006	186
Dr Markus Brym ¹ (Cardiff University)	2003	186
Mr Graeme J. Moxey (Monash University) <i>PhD Student</i>	2005-present	188

* There have also been a significant number of minor collaborators, who have principally been undergraduate students or students of my collaborative partners. However, in some cases collaborators have been other principal scientists who have helped in collection and interpretation of spectroscopic data. While these have not been included in this list, they are all acknowledged for their contributions and their names have been included as authors on all publications where they have made any contribution (see list of publications). Where exchange students, Honours or PhD students have contributed to publications, the results presented in these papers were reported in their respective PhD, Diploma or Honours theses.

See Publication List

1. Exchange student from Cardiff University
2. Exchange student from Fachhochschule Münster
3. Exchange student from University of Leipzig

Comments on Collaborative Studies

A considerable number of publications have arisen from the result of my research students (see Table). I also consider that collaborations with others in the organometallic field, or other specialist areas to be of the utmost importance. Therefore, I collaborate widely with many other chemists. The role of these collaborators is commented here.

The collaboration with Prof. Colin Raston commenced when I was a PhD student in his laboratory at the University of Western Australia. Research papers that were published as part of my PhD thesis (see publication list 1-6) have been included in this thesis for completeness. *However, they are not to be included in the evaluation of the candidate.* Other work involving Prof. Raston was a spin-off from the PhD research is included in this thesis as the work was performed during a period of Research Officer for Prof. Raston at Griffith University 1988-89. Collaborations with Prof. Allan White and Dr. Brian Skelton have been predominantly through the use of their skills in X-ray crystallography, however, a short stint as a Research Fellow with Prof. White at University of Western Australia in 1995 was extremely productive and this collaboration has extended to the present. My involvement was in the synthesis of many compounds in the structural systematic studies of rare earth, bismuth and group 13 coordination compounds as well as solid state interactions of HX salts of amines. A two-year Postdoctoral Fellowship was undertaken with Prof. Jerry Atwood at the University of Alabama and Missouri and this was the start of a fruitful collaboration. During this time I learnt the art of X-ray crystallography and used this form of characterization on a large series of liquid clathrates involving crown ethers and oxonium ions. This collaboration extended several years after my Postdoctoral Fellowship. Since late 1995 a strong collaboration has been held with Prof. Glen Deacon at Monash University. This started when I was a Postdoctoral Fellow in his group and has continued since gaining a lectureship at James Cook University in 1997, then at Monash University since 2001. During this time, our collaboration has been a strong partnership involving new synthetic approaches to rare earth organometallics, organoamides and aryloxo complexes. The collaboration has been recognized by the Australian Research Council in the award of two ARC Large/Discovery Grants since 2000 with Prof. Deacon, both as a co-Chief Investigator. Other strong collaborations have been held with Prof. Ulrich Kynast (FH Münster), Prof. Eva-Marie Hey-Hawkins (Leipzig), Prof. Rüdiger Mews and Prof. Cameron Jones (Cardiff) mostly through the exchange of undergraduate and postgraduate students. In all, I have had greater than 20 students from these three groups spend approximately six months each in my laboratory and have had several of my students spend time overseas. Additionally, the collaboration with Prof. Jones has attracted significant funding from the Leverhulme Trust (UK) for the employment of a Postdoctoral Fellow (Dr Andreas Stasch). This project centers on the formation of group 13 hydride species that have traditionally been unstable,

and has generated many new results. Other collaborations have been held with other colleagues (Prof. Len Lindoy, Prof. Jana Hodacova, A/Prof. Bruce Bowden, Dr Steven Bottle, Dr Michael Gardiner, Prof. Roy Jackson and Prof. Richard Keene) where my major involvement has been on a crystallographic basis providing structural information for my colleagues. The collaboration with Prof Keene has been particularly prolific with structural studies on his $[\text{Ru}(\text{bidentate})_3]^{2+}$ species. These compounds are notorious as providing poorly diffracting species and we were able to generate a large amount of information.

INTRODUCTION

Statement of Research Record and Contribution to Organometallic and Inorganic Chemistry

Details of Research Output

1. Statement of Research Record and Contribution to Organometallic and Inorganic Chemistry

Since entering Academia, my research has evolved around a multidisciplinary approach in many aspects of inorganic, organometallic, supramolecular and structural chemistry. The research is primarily fundamental in nature, but several applied projects are involved. My major research achievements are summarised below:

Major successful research efforts that continue to flourish involve the wide-ranging areas:

- Main group organometallic and organoamido chemistry
- Organolanthanoid chemistry
- Oxonium Ion chemistry
- Supramolecular chemistry involving crown ethers and hydrated metal ions

Major research highlights include:

- Continued significant contributions to main group organometallic chemistry (59 refereed publications), lanthanoid chemistry (42 refereed papers) and supramolecular chemistry predominantly involving hydrogen bonded species (> 40 refereed journal articles).
- Acquisition of major research infrastructure; successful RIEFP Grant for a Bruker AXS SMART 1000 X-ray diffractometer at James Cook University and a successful ARC LIEF Grant for acquisition of Bruker X8 APEX CCD X-ray diffractometer (purchase price \$629,000)
- A publication cited by *Angewandte Chemie* as a "Hot Paper" [60]. This journal is one of the leading chemistry journals and nomination of this article shows the merit of the work.
- Publications in *Chemical Communications* [168] and *Dalton Transactions* [174] cited as "Hot Papers"
- Invitations to present seminars at seven major international meetings (85th Canadian Society for Chemistry, Vancouver 2002, XVIth Workshop on Rare Earth Chemistry, Berlin Dec. 2003, XVIIth Workshop on Rare Earth Chemistry, Bayreuth Dec. 2004, IV Razuvaev Lectures, Nizhny Novgorod-Perm-Nizhny Novgorod, Russia, 3-11 September 2005, Invitations to present at two symposia at
- Invitations to speak at 25 international and domestic Universities and Institutions
- Recipient of the Qld Young Tall Poppy Award in 2001 for outstanding research ability
- Recipient of three prestigious DAAD Guest Professorships at University of Leipzig (1998-99, 2000-01 and 2002)
- Elected Fellow of the Royal Australian Chemical Institute in 2002. I have also been heavily involved in the Royal Australian Chemical Institute for the past nine years, holding the following positions; Secretary, RACI Inorganic Division; Interim Chairman, RACI Inorganic Division;

Secretary, RACI North Queensland Section; North Queensland Representative of the RACI Inorganic Chemistry Group (Qld); Committee Member, RACI North Queensland Section.

➤ In 2002, I was elected to the International and Editorial Board for New Journal of Chemistry that is being developed as the flagship journal for the Royal Society of Chemistry.

➤ I have been a registered referee on many international journal boards and have refereed articles for a large number of journals including Chemical Communications, JCS Dalton Transactions, JCS Perkin Transactions 2, New Journal of Chemistry, Polyhedron, Inorganic Chemistry Communications, Journal of Coordination Chemistry, Australian Journal of Chemistry, Proceedings of the National Academy of Sciences (US), Angewandte Chemie, Chemistry – A European Journal, and European Journal of Inorganic Chemistry.

➤ Since 2002, I have been on the Instrument Advisory Board, *Australian Nuclear Science & Technology Organisation*

Testament to my ability to bring projects from initiation to being much more developed is my research output.

➤ Since 1997, (first year in Academia) I have published 189 (with another 11 accepted for publication and in press) papers in refereed journals.

➤ I (or my research students) have presented in excess of 70 posters/lectures at local and international conferences.

➤ I have obtained strong financial support, both internally (ARC Small, Monash Postgraduate Research and Teaching Fellowships Scheme, Centre for Green Chemistry) and externally (ARC Large/Discovery Grants, ARC RIEFP) to fund research projects.

- | | |
|--|----------------|
| ➤ Total funding in 1997-2006 period | \$4.08 million |
| ➤ Funding for fundamental projects | \$2.39 million |
| ➤ Funding for infrastructure | \$1.63 million |
| ➤ Others, e.g. travel grants, visiting professorships. | \$0.06 million |

Currently I hold two ARC Discovery grants (one as Chief CI with G.B. Deacon and one with co-CI P.C. Andrews) and two Leverhulme Trust (UK) Grants (one with C. Jones and one with J.W. Steed).

Important collaborations have been developed both locally and internationally. This allows access to expertise and facilities not available within Monash as well as contributing my own expertise to other research groups. Additionally, international collaborations allow for exchange of students between research groups during their PhD. From our collaborations, many publications have arisen, and help to contribute greatly to the “internationalisation of Universities in Australia”. Currently, active collaborations exist within the School of Chemistry, Materials Science, CSIRO

for Forestry Products, Universities of Cardiff, Leipzig, Muenster, Bremen, Prague and King's College.

I have had strong interest in researchers at all levels to work in my research group. Currently I supervise 4 postdoctoral fellows, eight PhD students, five exchange students from Germany and one Honours student. Completed students include six PhD students (average completion in 3.25 years,) and nine honours students. I have also supervised 22 exchange students from the UK, Germany and Poland.

2. Details of Research Output

Research interests involve many aspects of inorganic and organometallic chemistry of the main group and lanthanoid elements, in particular organometallic and macrocyclic complexes. These complexes have relevance to such areas as catalysis, new materials and organic syntheses. There is a strong emphasis on synthetic methods and structural studies which involve a range of spectroscopic and structural techniques, in particular X-ray crystallography. Much of this research involves collaborative links with colleagues both within and external to the department.

In addition, research is also being conducted into supramolecular architectures involving crown ethers. Supramolecular chemistry involves exploration into the weaker interactions (ie non-covalent) in chemistry, namely hydrogen bonding, π -stacking, dipole-dipole and arene interactions. We have been looking into the hydrogen bonding networks arising from crown ether hydrogen bond acceptors and hydrated metal ions as hydrogen bond donors.

Each research subject is discussed in more detail below (references are given in the publication list):

The publications presented in this thesis are conveniently subdivided into their relevant areas of research and can be cross-referenced as follows (see publication list for paper numbers):

(i) *Main group organometallic and organoamido chemistry* (1, 2, 3, 4, 5, 7, 8, 9,10, 12, 27, 35, 48, 66, 68, 82, 83, 84, 86, 92, 93, 94, 95, 97, 98, 101, 102, 106, 109, 110, 112, 115, 118, 119, 120, 125, 126, 127, 128, 132, 133, 139, 147, 154, 155, 157, 159, 162, 163, 164, 165, 169, 175, 176, 177, 186, 190, 191, 200).

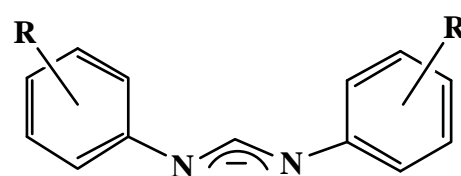
(ii) *Rare Earth Chemistry* (31, 32, 33, 37, 46, 52, 55, 58, 61, 62, 63, 64, 65, 85, 88, 113, 114, 117, 121, 124, 129, 136, 137, 142, 143, 145, 146, 148, 150, 156, 158, 167, 168, 171, 172, 173, 174, 179, 180, 187, 188, 189).

(iii) *Oxonium Ion chemistry* (review 1, 14, 15, 20, 21, 22, 25, 30, 34, 44, 50, 51,74, 81).

(iv) *Supramolecular chemistry involving crown ethers and hydrated metal ions and X-ray Crystallographic studies*: combined due to the great importance of X-ray work in supramolecular chemistry (**13**, 16, 17, 18, 19, 23, 26, 28, 29, **36**, **38**, 39, 40, 41, 42, 43, 45, 47, 53, **54**, 56, 57, 59, 60, 67, 69, **70**, 71, 72, 73, **75**, **76**, **77**, **78**, **79**, **80**, 87, **89**, 90, **91**, 96, 99, 100, 103, **104**, 105, **107**, 108, 111, 116, 122, **123**, 130, 131, **134**, 135, **138**, 140, 141, 144, 149, 151, **152**, 153, 160, 161, 166, 170, 181, 185, 193, 195, 196, 197, 198, 199). Publications in bold refer to those where the contribution was mainly of a crystallographic input, although facilitation into preparing the manuscripts for publication was given.

2.1 Main group organometallic and organoamido chemistry

Transition metal complexes of the formamidines (**1**) have been studied extensively for a number of years. These studies have shown a variety of structural variations that arise upon complexation of the metal, and interesting metal-metal bonded species have been isolated. These ligands have only recently been used by us in main group as previously they were considered too air- and/or moisture-sensitive to study. This chemistry has uncovered some exciting new structural themes [110,112,118-120,124,127,132,155,159,162,163,176,177,178,200]. In this project, we prepare a range of formamidines with various substituents and investigate the structural and reactivity changes which can be imparted by these modifications.



(1)

Variation of the substituents and their position on the aromatic rings can provide differing steric bulk about the metal centres and will therefore result in differing structural chemistry and reactivity. The ligands we have available have Me, Et, Prⁱ, F substitution at the 2 and/or 6 position on the arene.

Recently I received an invite from the *Chemical Communications* to write a Feature Article of my research in their journal. This review is currently in its formative stages. I have also been asked by *Australian Journal of Chemistry* to write a review on aspects of main group organoamido chemistry.

In chemistry involving related ligands, we have made significant recent contributions to the literature. With the 2-(trimethylsilylamino)-6-methylpyridine ligand we have uncovered some novel chemistry with the main group elements Li [84,97,132] aluminium [94], silicon and tin [109], the transition elements titanium and zirconium [139] and lanthanoid elements [127]. With 8-(trimethylsilyl)aminoquinoline we have also reported some novel structures and reactivity in lithium complexes [82].

2.2 Rare Earth Chemistry

Formamidinate chemistry: Significant success has been achieved in several areas of lanthanoid research including organolanthanoid, coordination chemistry and luminescent properties.

Sterically hindered formamidinates show enormous structural variety in coordination to alkali metals and appear sufficiently bulky to have a Cp-replacement role in organolanthanoid chemistry [110,112,118-120,124,127, 132, 136]. Their characterisation provides a range of reagents to prepare homoleptic lanthanoid formamidinates by metathesis, from which a wide variation in bonding types have been recently found [136]. Further success using these complexes to afford new lanthanoid(II) and (III) species have led to landmark papers in Chemical Communications [168,172].

Luminescence studies: This research involves a systematic study of the structural/luminescence relationships in complexes involving lanthanoids bound to carboxylate ligands. We have shown that compounds with very long lifetimes and luminescent intensity can be produced from this study [85,129,137]. There are obvious potential applications in novel electro-optical devices such as organic light emitting diodes (OLEDs), components in solar cells, sensors, and luminescent immunoassays.

Recent research performed in collaboration with Prof. G.B. Deacon

Pyrazolate chemistry: 3,5-diphenylpyrazole (Ph₂pzH) has been found to react with scandium metal giving the homoleptic [Sc₂(Ph₂pz)₆], which exhibits the new pyrazolate coordination mode μ - η^2 : η^1 [114]. The synthesis opens the way for a wide-ranging study of reactions of Ph₂pzH with lanthanoid metals, and illustrates the way in which homoleptic complexes provide a basis for novel coordination modes. Redox transmetalation/ligand exchange in pyridine has provided the first (unexpected) example of unidentate (N) coordination of a pyrazolate to a large lanthanoid in [Nd(η^2 -Me₂pz)(η^1 -Me₂pz)(Me₂pzH)₂(py)] (Me₂pz = 3,5-dimethylpyrazolate).

Near naked cations. Exploration of possible syntheses of near naked lanthanoid cations has led to ether-lanthanoid halide complexes which advance understanding of their structures [117,174]. The reactions also show that Ln³⁺ can compete with Al³⁺ for coordination of Cl⁻, a result with implications for commercial bimetallic Nd/Al catalyst systems. Earlier research showed that preparation of acetonitrile “near naked” lanthanoid metal centers were able to be synthesized by several methods [55]. More recently we have used crown ethers in this area of chemistry to stabilize small clusters involving Gd₄F₇ fragments.

Phenolate chemistry: The first homoleptic anionic aryloxolanthanoid complexes were prepared and structurally characterized using the sterically hindered 2,6-diphenylphenolate ligand (Odpp⁻) [32]. Using a high temperature metal-based synthesis involving lanthanoid metal and HOdpp or 2,6-dibenzylphenol, novel solvent-free homoleptic complexes of ytterbium and europium (and the closely related group 2 elements, calcium, strontium and barium) could be prepared which all had

novel Ln- π -arene interactions to satisfy the coordinatively unsaturated metal centers [58, 83,180]. Additionally, by using redox/transmetallation/ligand exchange reactions novel low coordinate lanthanoid(II) and (III) aryloxide complexes can be prepared in high yields [33,189]. We are currently preparing an invited *Dalton Perspective* of our contributions to this area of research.

Lanthanoid halide chemistry: High yielding reactions to prepare anhydrous thf-solvated lanthanoid halides have been developed. Thus, treatment of lanthanoid metal with an organic halide in a donor solvent (L) can generate $\text{LnCl}_3(\text{L})_n$, $\text{LnBr}_3(\text{L})_n$ or $\text{LnI}_3(\text{L})_n$ [37,88]. These compounds are very useful starting materials in the synthesis of organolanthanoid reagents, but also show a very rich structural series [37,88,117].

2.3 Oxonium Ion chemistry

In the textbook definition of an acid, the oxonium ion, H_3O^+ is commonly given as the form in which the hydrated proton (ie. $\text{H}^+\cdot\text{H}_2\text{O}$) exists. This has been the common interpretation since the early 1900s, but little was known of the structural nature of this species until the late 1950s, and even as late as the 1990s only a handful of structural determinations in the solid-state had been performed. I was involved in an intense research project with Prof. Jerry Atwood to determine a method to isolate the oxonium ion H_3O^+ , but also higher oligomers of the hydrated series $(\text{H}^+)_n\cdot\text{H}_2\text{O}$ (where $n = 1, 2, 3$). Using a supramolecular approach where crown ethers of varying intermolecular diameter and symmetry, were used as hydrogen bond acceptors and in acidic conditions, advances to the knowledge of this chemistry were made. Thus, we were able to expand the number of known H_3O^+ containing complexes from 10 to 26 [14,15,20,21,25,30,34,44] as well as identifying new H_5O_2^+ [22,34,51,81], H_7O_3^+ [50,74,81] and H_9O_4^+ [74] species. A large review has been written covering all aspects of this work [reviews 1].

2.4 Supramolecular chemistry involving crown ethers and hydrated metal ions

Supramolecular chemistry involves exploration into the weaker interactions (ie non-covalent) in chemistry, namely hydrogen bonding, π -stacking, dipole-dipole and arene interactions. Supramolecular architectures involving crown ethers and hydrated metal ions are held together in three-dimensional arrays by crown ether hydrogen bond acceptors and hydrated metal ions as hydrogen bond donors. Significant contributions into crystal engineering, new structural motifs and packing arrays have been determined in published works [45,49,53,57,59,60,71,87,90,96,99,103,105,121,122,130,166].

One of these papers, *Angew. Chem., Int. Ed. Engl.*, **1999**, 38, 2224-2226.[60] was cited by *Angewandte Chemie* as a "Hot Paper". This journal is one of the leading chemistry journals and nomination of this article shows the merit of the work. This work led to the isolation of an oxo-bridged iron(III) binuclear aqua ion whose structure had been the subject of intense debate in the

literature.

2.5 Some Significant Publications

60. Supramolecular Complexation of Polynuclear Aqua Ions: Crystallization, Structure and Electronic Properties of a Crown Ether Adduct of the μ -oxo Bridged Iron(III) Aqua Dimer.
P C Junk, B J McCool, B Moubaraki, K S Murray and L Spiccia' *Angew. Chem., Int. Ed. Engl.*, **1999**, 38, 2224-2226.

This paper was cited by Angewandte Chemie as a HOT PAPER for that particular edition.

102. Ether and Crown Ether Adduct Complexes of Sodium and Potassium Cyclopentadienide and Methylcyclopentadienide – Molecular Structures of $[\text{Na}(\text{dme})\text{Cp}]_{\infty}$, $[\text{K}(\text{dme})_{0.5}\text{Cp}]_{\infty}$, $[\text{Na}(15\text{-Crown-5})\text{Cp}]$, $[\text{Na}(18\text{-Crown-6})\text{Cp}^{\text{Me}}]$ and the " Naked Cp⁻ " Complex $[\text{K}(15\text{-Crown-5})_2][\text{Cp}]$.
ML Cole, C Jones and PC. Junk, *J. Chem. Soc., Dalton Trans.*, 2002, 896-905.

This publication was one of the highest accessed articles from Dalton Transactions in March 2002. It is a seminal piece of Organometallic Chemistry that all chemists in this discipline have shown interest in.

132. Pyridyl donor induced 1,3-silyl migration in metal complexes of the guanidine $\text{CyHNC}\{\text{N}(\text{SiMe}_3)\text{Py}\}\text{NCy}$, $\text{Py} = 2\text{-(6-MeC}_5\text{H}_3\text{N)}$.

M. L. Cole and P.C. Junk, *Dalton Trans.*, **2003**, 2109-11.

This paper showed a very unusual 1,3 silyl and hydrogen migration induced by a pyridyl group. It has shown a lot of interest in recent seminars and we are exploring further research in this new area.

125. Structural studies of N,N'-di(ortho-fluorophenyl)formamidinate group 1 metallations

ML Cole, DJ Evans, PC Junk and MK Smith, *Chem. Euro. J.*, 2003, **9**, 415-24.

The activation of C-F bonds has been an area of active research, and the compounds isolated in this paper showed this phenomenon. The fact that it was published in the high impact factor Chemistry a European Journal is testament to its appeal in the chemistry community.

168. Steric Engineering of C-F Activation with Lanthanoid Formamidinates

ML Cole, GB Deacon, PC Junk and K Konstas, *Chem. Comm.*, **2005**, 1581-3.

This paper was cited by Chemical Communications as a HOT PAPER for that particular edition

174. Stabilising small clusters: synthesis and characterisation of thermolabile $[\text{Gd}_4\text{F}_7(15\text{-crown-5})_4][\text{AsF}_6]_5 \cdot 6\text{SO}_2$

GB Deacon, DJ Evans, P C Junk, E Lork, R Mews, and B Žemara, *Dalton Trans.*, **2005**, 2237 - 2238.

This paper was cited by Dalton Transactions as a HOT PAPER for that particular edition

Other significant publications include:

Two papers (*J. Chem. Soc., Dalton Trans.*, **2002**, 896-905, *J. Chem. Soc., Dalton Trans.*, **2002**, 2185-93) were amongst the top ten accessed articles from the web from the online version of *Dalton Transactions*; testament to the topical nature of the work.

CURRICULUM VITAE

NAME: Peter Courtney Junk

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TELEPHONE: +61 (03) 9905 4570

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EMAIL: peter.junk@sci.monash.edu.au

DATE OF BIRTH: 12th May, 1962

NATIONALITY: Australian

ACADEMIC BACKGROUND

1985 - 1988 Doctor of Philosophy in Organometallic Chemistry, Department of Physical and Inorganic Chemistry, University of Western Australia. Thesis entitled "*Studies of Amido- and Alkyl- s and p Block Element Chemistry*". Supervisor: Professor C L Raston

1984 Honours in Physical and Inorganic Chemistry (1st Class)
Supervisor: Professor C L Raston

1980 - 1982 Bachelor of Science, University of Western Australia, with a double major in Physical and Inorganic, Organic Chemistry.

1975 - 1979 John Forrest Senior High School, Perth, WA

1968 - 1974 Hillcrest Primary School, Perth, WA

PRIZES/SCHOLARSHIPS/FELLOWSHIPS:

March 2003 - April 2003 Ecka Granules Visiting Lectureship, University of Tasmania.

June 2002 – July 2002 DAAD Guest Professorship (C4 level), University of Leipzig.

April 2001 Queensland Young Tall Poppy Award - Australian Institute of Political Science

December 2000 - April 2001 DAAD Guest Professorship (C3 level), University of Leipzig.

December 1998 - April 1999 DAAD Guest Professorship (C3 level), University of Leipzig.

1985 - 1988 Commonwealth Postgraduate Scholarship for PhD program.

1984 CSR prize for the top Honours student, Department of Physical and Inorganic Chemistry, the University of Western Australia.

EMPLOYMENT HISTORY:

2005-2006 Acting Head of School (occasional), School of Chemistry, Monash University

August 2005 Acting Dean of Science, Monash University, Victoria, Australia.

Nov 2003 – present Associate Professor in Inorganic Chemistry (*accelerated promotion*), Department of Chemistry, Monash University, Clayton, Victoria, Australia

January 2003 – present	Associate Dean External, Faculty of Science, Monash University, 25% basis.
July 2001 – Nov 2003	Senior Lecturer in Inorganic Chemistry, Department of Chemistry, Monash University, Clayton, Victoria, Australia
Jan 2000 - July 2001	Senior Lecturer in Inorganic Chemistry (<i>accelerated promotion</i>), Department of Chemistry, James Cook University, Townsville, Queensland, Australia
Jan 1997 - Dec 1999	Lecturer in Inorganic Chemistry, Department of Chemistry, James Cook University, Townsville, Queensland, Australia
Dec 1995 - Jan 1997	Research Fellow, Department of Chemistry, Monash University, Clayton, Victoria, Australia <i>Supervisor: Professor Glen B Deacon</i>
May 1995 - Dec 1995	Research Officer, Department of Chemistry, University of Western Australia, Nedlands, Western Australia <i>Supervisors: Associate Professor Allan H White and Professor David L Kepert</i>
Nov 1994 - Mar 1995	Research Fellow, Institut de Biologie et Chimie des Proteines, CNRS, Lyon, France
Nov 1992 - Nov 1994	Postdoctoral Associate, Department of Chemistry, University of Alabama, Tuscaloosa, Alabama, USA, and Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri, USA <i>Supervisor: Professor Jerry L Atwood</i>
Aug 1989 - Oct 1992	Research Chemist, the Department of Research and Development, Ampol Petroleum Company, Lytton, Qld. <i>Supervisors: Dr Allan J Clark and Dr Laurie D Palmer</i>
Apr 1988 - Aug 1989	Senior Research Assistant, the Division of Science and Technology, Griffith University, Nathan, Qld. <i>Supervisor: Professor Colin L Raston</i>
Mar 1983 - Jul 1983	Laboratory Assistant, The University of Western Australia in the School of Chemistry.
Dec 1982 - Feb 1983	Vacation employment as a Laboratory Assistant with the State Energy Commission of Western Australia, East Perth Power Station. <i>Supervisor: Dr Roman Mandyczewski</i>

TEACHING EXPERIENCE:

July 2005 – October 2006	CHM3922, Understanding Chemical Reactions, Monash University
July 2003-July 2004	CHM3942 Synthesis of Bioactive Molecules, Monash University.
March – April 2003	Honours Lecture Course on X-ray Crystallography, University of Tasmania
March 2003-March 2005	CHM4001, Honours Lecture Course on Organometallic Chemistry.
August – September 2002	CHM1022 Chemistry at Monash University
June - July 2002	Organometallic Chemistry for 6 th year students at University of Leipzig.
June - July 2002	Bioinorganic Chemistry as part of the Graduiertenkolleg at University of Leipzig.
May 2002-04	Spectroscopy for CHM3911, Monash University
March 2002	CHM4001 Honours Lecture Course on Nobel Prize Winners
August 2001 - October 2006	Formulation Chemistry for Formulation Science Students at Monash University.

July 2001 - October 2006	BND 1022 Food Chemistry for Biomedical Science Students at Monash University.
January 2001 - March 2001	Bioinorganic Chemistry as part of the Graduiertenkolleg at University of Leipzig.
Dec 2000 - March 2001	Coordination Chemistry for 6 th Semester Students at University of Leipzig
October 1999/2000	Lecturer for PC1005 Chemistry for Pharmacy Students at James Cook University.
January 1999 - March 1999	Bioinorganic Chemistry as part of the Graduiertenkolleg at University of Leipzig.
Dec 1998 - March 1999	Coordination Chemistry for 6 th Semester Students at University of Leipzig
July 1997 - November 2000	Lecturer for SC1301 Introductory Chemistry for Primary School Teachers at James Cook University
July 1997 - November 2000	Lecturer for 2nd year Inorganic Chemistry (CH2022) at James Cook University
March 1997 - May 2001	Lecturer for BM1011 Introductory Chemistry for Nursing Science at James Cook University
March 1997 - May 2001	Lecturer for 3rd year Advanced Inorganic Chemistry (CH3072) at James Cook University
March 1997 - May 2001	Lecturer for 3rd year Inorganic Chemistry (CH3022) at James Cook University
October 1995	Lecturer of Chemistry 120 Course on Descriptive Inorganic Chemistry in the School of Chemistry, University of Western Australia
July 1995 - Nov 1995	Laboratory Demonstrator to Second Year Physical and Organic Chemistry in the School of Chemistry, University of Western Australia
Aug 1993 - Dec 1993	Lecturer for the Freshman Chemistry Course at the University of Alabama, Tuscaloosa, Alabama, USA
Feb 1988 - Jul 1989	Laboratory Demonstrator to First and Second Year Undergraduate students in the Division of Science and Technology, Griffith University, Qld.
Feb 1984 - Oct 1987	Laboratory Demonstrator to First, Second and Third Year Undergraduate students in the School of Chemistry, University of Western Australia.

COORDINATION OF SUBJECTS

2001-2005	Chief Examiner, 3 rd Year Chemistry, Monash University
2001-2005	3 rd Year Coordinator, School of Chemistry, Monash University
2001-present	Subject Coordinator, BND1022, CHM2962, School of Chemistry, Monash University.
1-0	Honours Coordinator, Chemistry, James Cook University
1-0	3 rd Year Coordinator, Chemistry, James Cook University
1-0	Subject Coordinator CH3022, Chemistry, James Cook University
1-0	Subject Coordinator CH2022, Chemistry, James Cook University
1997-2001	Subject Coordinator BM1022, Chemistry, James Cook University

COMMITTEES

2006- present	Chair, Body Corporate, Leicester Gardens, Carlton, Vic.
2003-present	Associate Member, Centre for Fundamental and Applied Main Group Chemistry, see http://www.cf.ac.uk/chemy/cfamgc/
2004-2005	Open Day Director, Clayton Campus, Monash University
2003 – 2005	Europe Steering Committee, Monash University
2003 – 2005	North America Steering Committee, Monash University
2003 – 2005	North Asia Steering Committee, Monash University
2003– 2005	South Asia Steering Committee, Monash University
2003 – 2005	South-East Asia Steering Committee, Monash University
2004	Advisory Committee, International Symposium on Macrocyclic Chemistry, July 2004, Cairns.
2003-04	Organizing Committee OZOM2, Conference on Organometallic Chemistry, Adelaide January 11-14 2004.
2003-2005	Chair of the Science Faculty's Marketing Advisory Group, Monash University
2003-2005	Member of the Vice-Chancellor's International Group, Monash University
2003-2005	Member of the International Recruitment Group, Monash University
2003-2005	Member of Dean's Advisory Committee, Monash University
2003-2005	Member of India Interest Group, Monash University
2003-2005	Member of China Interest Group, Monash University
2002-2005	Member of Monash Abroad Steering Committee, Monash University
2002- present	Committee Member, Body Corporate, Leicester Gardens, Carlton, Vic.
2002 – present	Instrument Advisory Team, ANSTO, Lucas Heights
2002-03	Organising Committee for IC'03, Inorganic Divisional Conference of the RACI.
2002 – present	Major Instruments Facility Academic Leader, X-ray Facility, School of Chemistry, Monash University
2001 – 2005	Education Committee, School of Chemistry, Monash University
2000	Research Committee, Faculty of Science & Engineering, James Cook University
1997 – 2001	Staff member for JCU Chemical Society, James Cook University
1997	Established JCU Chemical Society, James Cook University

SUCCESSFUL RESEARCH GRANTS:

July 2005	Leverhulme Trust Research Project Grant, "Probing hydrogen activation and elimination by neutron diffraction" with Dr Jonathan Steed (Durham) and Prof Len Barbour (Stellenbosch), \$260,000 (100,000 pounds sterling)
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November 2004	ARC LIEF Scheme, "Enhanced X-Ray Analysis and Characterisation Facility", \$1,250,000 (ARC contribution \$650,000, VICS contribution, \$250,000, Monash contribution, \$200,000, RMIT contribution \$150,000)
November 2004	ARC Discovery Grants Scheme "Development of non-iodinated, non ionic, water-soluble metal based compounds for clinical administration as radiographic contrast media" with Dr Phil Andrews, Prof M. Silberstein and Dr S. Midgley, \$300,000 .
October 2003	ARC Discovery Grants Scheme "Frontiers in synthetic and structural rare earth chemistry" with Prof GB Deacon, \$900,000
July 2003	Leverhulme Trust International Academic Exchange Grant, "The stabilization and application of novel group 13 carbene analogues" with Prof. Cameron Jones, Cardiff University, \$190,000 (72,371 pounds sterling)
October 2002	Postgraduate Research & Teaching Fellowship, Monash University, \$10,000
March 2002	Postgraduate Research Scholarship, Centre for Green Chemistry, Monash University, \$84,000
November 2001	Monash and King's College SEED Funding " Neutron Diffraction Studies on Water", \$5,500 , with Dr JW Steed (King's College)
October 2001	ARC Discovery Grants Scheme " Studies of Group 15 complexes of the Lanthanoids and Group 2 metals-An unexploited field of research", \$212,118
December 2000	JCU Merit Research Grants Scheme "Heterobimetallic complexes of the group 13 and 15 elements with the lanthanoids", \$16,000
November 2000	ARC Large Grants Scheme "New horizons in rare earth chemistry" with Profs GB Deacon and AH White, \$236,000
December 1999	ARC Small Grants Scheme "N-functionalised amidolanthanoid chemistry", \$14,100
December 1998	ARC Small Grants Scheme "Nitrogen-functionalised metal and metalloid amide chemistry", \$21,000
December 1998	ARC-RIEFP "Single crystal X-ray structure determination of small molecules" \$190,000, plus contributions from JCU (\$128,000) and Bruker/Siemens (\$62,000). Total: \$380,000.
December 1997	JCU Merit Research Grants Scheme "Sterically demanding group 2 organometallic complexes", \$5,000
November 1997	ARC Large Grants Scheme "Lanthanoid Aza-Crown Ether Chemistry". \$141,000.
April 1997	RIBG Seed Funding "Lanthanoid Aza-crown ether chemistry", \$3690
December 1996	ARC Small Grants Scheme "Metallation of aza-crown ethers as precursors to lanthanide macrocyclic complexes", \$5,000 - declined
December 1995	Australian Research Council Project "Studies of some nitrogen-base adducts of the Group 13 and lanthanide salts", \$19,319 - declined.

OTHER GRANTS:

June 2005	Monash University Travel grant, \$1200
August 2004	Participant in ARC Network for " <i>Molecular and Materials Structure Network</i> ", \$1,500,000 , funded by ARC.

June 2004	Monash University Travel grant, \$1200
December 2003	Travel grant funded by the Ian Potter Foundation for travel from Melbourne to Germany, \$1,500 .
December 2003	Travel grant funded by the Corday-Morgan Memorial Fund (RSC) for travel from Leipzig to London and Cardiff, \$500 .
December 2003	Monash University Travel grant, \$800 .
June 2002	ILL Travel Grants for Neutron Diffraction time in Grenoble €500
June 2002	DAAD Guest Professorship, University of Leipzig, €6,000
December 2000	DAAD Guest Professorship, University of Leipzig, DM18,100
December 2000	Travel grant funded by the Corday-Morgan Memorial Fund (RSC) for travel from Leipzig to London and Cardiff, \$1,000 .
December 1998	DAAD Guest Professorship, University of Leipzig, DM 17,000
December 1998	Travel grant funded by the Corday-Morgan Memorial Fund (RSC) for travel from Leipzig to London and Cardiff, \$1,250 .
February 1995	Travel grant funded by the British Council (Paris) to travel from Lyon (France) to Swansea (Wales) to establish collaborative research links with Dr Cameron Jones at the University of Wales (Swansea), \$1,500 .

PROFESSIONAL CONSULTANCY

"Evaluation of Liquid Clathrate Complexes as Applied to Explosive Products and Systems"

Consultancy with ICI Explosives on the above project was conducted between July 1997 and end 1997. The project was funded by ICI Explosives to the value of **\$10,000**. A progress/final report was sent to ICI at end 1997.

Continuing professional witness consultancies with local solicitors in a variety of cases.

MEMBERSHIP OF PROFESSIONAL BODIES:

2002	Elected, Fellow of the Royal Australian Chemical Institute
2000 - present	National Secretary, RACI Inorganic Division
1998 – 2001	Secretary, RACI North Queensland Section
1998 - present	Member of the Society of Crystallographers in Australia
1997 - 2001	North Qld Representative of the RACI Inorganic Chemistry Group (Qld)
1997 - 2001	Committee Member, RACI North Queensland Section
1982 - present	Member of the Royal Australian Chemical Institute

EDITORIAL & ADVISORY BOARDS:

2002 - present	International Advisory and Editorial Board for <i>New Journal of Chemistry</i>
2002 - present	Instrument Advisory Board, <i>Australian Nuclear Science & Technology Organisation</i>

REFEREEING FOR JOURNALS:

Refereed journal articles for the following Chemistry Journals:

Acta Crystallographica C
 Angewandte Chemie Int. Ed. Engl.
 Australian Journal of Chemistry
 Canadian Journal of Chemistry
 Chemical Communications
 Chemistry: A European Journal
 Cryst. Eng. Comm.
 European Journal of Inorganic Chemistry
 European Journal of Organic Chemistry
 Heteroatom Chemistry
 Inorganic Chemistry Communications
 Journal of Coordination Chemistry
 Journal of Crystal Growth & Design
 Journal of Chemical Crystallography
 Journal of the Chemical Society, Dalton Transactions
 Journal of Organometallic Chemistry
 Main Group Chemistry
 Metals and Alloys
 New Journal of Chemistry
 Organic and Biomolecular Chemistry
 Polyhedron
 Proceedings of the National Academy of Sciences
 Supramolecular Chemistry

REFEREEING OF THESES:

(i) Refereed PhD theses for the following institutions:

University of Western Australia
 University of Queensland
 University of Leipzig (x3)
 Annamalai University, India

(ii) Refereed Masters theses for the following institutions:

Monash University

(iii) Refereed numerous Honours theses at the following institutions:

James Cook University
 Monash University

REFEREEING OF RESEARCH GRANTS:

1-0	Evaluation of ARC Large and Discovery Grants
1998-2001	Evaluation of ARC Small Grants, James Cook University, Curtin University and Monash University

SUPERVISION OF RESEARCH:

As at February 2006

Supervised six PhD students to completion (average completion time = 3.2 yrs).
 Supervised 10 Honours students to completion.
 Supervising four Postdoctoral Fellows, 10 PhD students and one Honours student.
 Supervised 24 international visiting students on Occupational Trainee Programs

PUBLICATION LIST

Reviews:

1. Structural aspects of oxonium ion/crown ether complexes.
PC Junk, *Rev. Inorg. Chem.*, **2001**, *21*, 93-124.

Refereed Journal Articles:

1. Highly hindered amido-lithium and -magnesium complexes: crystal structures of $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2(\text{thf})\}_2]$ and $[\text{MgBu}^s\{\mu\text{-N}(\text{SiMe}_3)_2\}_2]$ (thf = tetrahydrofuran). (*Maxwell J. O'Connor special edition*)
L M Engelhardt, B S Jolly, P C Junk, C L Raston, B W Skelton and A H White, *Aust. J. Chem.*, **1986**, *39*, 1337-45.
2. Complexes of (Phenazine)⁻ and (phenazine)²⁻ with magnesium(II): Syntheses of $[\text{Mg}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{thf})_3]$, $[\text{Mg}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{thf})_2]$, and $[\text{Mg}_2\text{Br}_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{thf})_6]\cdot[\text{MgBr}_2(\text{thf})_4]$ (thf = tetrahydrofuran) (X-ray authenticated).
P C Junk, C L Raston, B W Skelton and A H White, *J. Chem. Soc., Chem. Commun.*, **1987**, 1162-64.
The contents of this paper was cited in *Chemistry and Industry*, **21 December 1987**.
3. Main group-conjugated organic anion chemistry. 1. Synthesis of magnesium anthracene, silylated anthracenes, or fluoranthene tetrahydrofuran and tertiary amine complexes and of magnesium cyclooctatetraene; X-ray structure of $[\text{MgL}(\text{TMEDA})]\cdot[\text{MgL}(\text{THF})_2]$ (L = 9,10-bis(trimethylsilyl)anthracene).
T Alonso, S Harvey, P C Junk, C L Raston, B W Skelton and A H White, *Organometallics*, **1987**, *6*, 2110-16.
4. Syntheses and structural studies of [2-(6-methyl)pyridyl]- and (8-quinolyl)- trimethylsilylamido-lithium complexes.
L M Engelhardt, G E Jacobsen, P C Junk, C L Raston, B W Skelton and A H White, *J. Chem. Soc., Dalton Trans.*, **1988**, 1011-20.
5. Main group-conjugated organic anion chemistry. 3. Application of 'magnesium-anthracene' compounds in the synthesis of Grignard reagents.
S Harvey, P C Junk, C L Raston and G Salem, *J. Org. Chem.*, **1988**, *53*, 3134-40.
6. Metal vapour syntheses of Bis{1,3-bis(trimethylsilyl)-cyclopentadienyl}-calcium, -strontium and -barium compounds; X-ray structures of $[\text{M}\{\eta\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_3)_2\}_2(\text{thf})]$, M = Ca, Sr. L M Engelhardt, P C Junk, C L Raston and A H White, *J. Chem. Soc., Chem. Commun.*, **1988**, 1500-1.
7. Calcium, strontium and barium cyclooctatetraenediyl complexes: synthesis of a stable phosphacyclopropane (structurally authenticated).
D S Hutchings, P C Junk, W C Patalinghug, C L Raston and A H White, *J. Chem. Soc. Chem. Commun.*, **1989**, 973-4.
8. N-functionalized amino-aluminium and -boron complexes: Intramolecular aromatic nitrogen-assisted formation of aminoboranes.
L M Engelhardt, G E Jacobsen, P C Junk, C L Raston and A H White, *J. Chem. Soc., Chem. Commun.*, **1990**, 89-91.
9. Hypervalent silicon via thermolysis of a cadmium amide: Thermally stable magnesium and zinc amides $[\text{ML}_2]$, L = N(8-quinolyl)(SiMe₃).
L M Engelhardt, P C Junk, W C Patalinghug, R E Sue, C L Raston, B W Skelton and A H White, *J. Chem. Soc., Chem. Commun.*, **1991**, 930-32.
10. Alkylation of (As, Sb, Bi)Cl₃: Formation of $[(\text{As}, \text{Sb}, \text{Bi})\text{RCl}_2]$, (E)- $[\text{BiR}(\text{CH}_2\text{CH}=\text{C}(\text{SiMe}_3)(\text{C}_5\text{H}_4\text{N}-2)]$ and 2- $\text{CH}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N}-5\text{-R}$ [R = C(SiMe₃)₂C₅H₄N-2'].
C Jones, L M Engelhardt, P C Junk, D S Hutchings, W C Patalinghug, C L Raston and A H White, *J. Chem. Soc., Chem. Commun.*, **1991**, 1560-62.

11. Refining assessment of syncrudes from NEDO/BCLV coal liquefaction.
P C Junk, L D Palmer, J Walker and M B Winn, *NERD+D Program Project No. 1114*, September **1991**.
12. A triplet biradical organocalcium species derived from partial oxygen quenching of a substituted cyclopentadienyl calcium compound.
M G Gardiner, G R Hanson, P C Junk, C L Raston, B W Skelton and A H White, *J. Chem. Soc., Chem. Commun.*, **1992**, 1154-56.
13. Synthesis and characterisation of symmetric and asymmetric oxo-bridged trinuclear chromium benzoate complexes: Crystal and molecular structure of $[\text{Cr}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})]\text{ClO}_4$.
A Harton, M K Nagi, M M Glass, P C Junk, J L Atwood and J B Vincent, *Inorg. Chim. Acta*, **1994**, 217, 171-79.
14. Synthesis and X-ray structure of $[\text{H}_3\text{O}^+.18\text{-crown-6}][\text{Br-Br-Br}]$; A compound containing both H_3O^+ and a linear and symmetrical Br_3^- ion crystallized from aromatic solution.
J L Atwood, P C Junk, M T May and K D Robinson, *J. Chem. Cryst.*, **1994**, 24, 243-5.
15. Synthesis and X-ray structures of $[\text{H}_3\text{O}^+.18\text{-crown-6}]_n[\text{MCl}_4^{n-}]$; (M = Fe, n = 1; M = Co, n = 2); Compounds with form liquid clathrates with aromatic solutions.
P C Junk and J L Atwood, *J. Chem. Cryst.*, **1994**, 24, 247-50.
16. On the crystal structure of hexathia-18-crown-6.
P C Junk and J L Atwood, *Supramol. Chem.*, **1994**, 3, 241-2.
17. Structure of p-tert-butylcalix[5]arene.ethylacetate. A polymeric array of neighbour-included calixarenes.
J L Atwood, R K Juneja, P C Junk and K D Robinson, *J. Chem. Cryst.*, **1994**, 24, 573-76.
18. A ball and socket nano-structure: New supramolecular chemistry based on cyclotrimeratrylene.
J W Steed, P C Junk, J L Atwood, M J Barnes, C L Raston and R S Burkhalter, *J. Am. Chem. Soc.*, **1994**, 116, 10346-7.
19. Cationic, neutral and anionic organoaluminum species in $[\text{AlMe}_2.18\text{-crown-6.AlMe}_2\text{X}][\text{AlMeX}_3]$, (X = Cl, I).
J L Atwood, S G Bott, S Harvey and P C Junk, *Organometallics*, **1994**, 13, 4151-2.
20. Liquid clathrate media containing transition metal halocarbonyl anions; formation and crystal structures of $[\text{K}^+.18\text{-crown-6}][\text{Cr}(\text{CO})_5\text{Cl}]$, $[\text{H}_3\text{O}^+.18\text{-crown-6}][\text{W}(\text{CO})_5\text{Cl}]$, $[\text{H}_3\text{O}^+.18\text{-crown-6}][\text{W}(\text{CO})_4\text{Cl}_3]$, and $[\text{H}_2\text{O-bis-aza-18-crown-6.}(\text{H}^+)_2][\text{W}(\text{CO})_4\text{Cl}_3]_2$.
J L Atwood, S G Bott, P C Junk and M T May, *J. Organomet. Chem.*, **1995**, 487, 7-15.
21. Synthesis and X-ray structure of $[\text{H}_3\text{O}^+.18\text{-crown-6}][\text{I}_7^-]$; a liquid clathrate containing a new infinite saw-horse configuration of $[\text{I}_7^-]$.
P C Junk, L R MacGillivray, M T May, K D Robinson and J L Atwood, *Inorg. Chem.*, **1995**, 34, 5395-6.
22. Synthesis and X-ray structure of $(\text{H}_5\text{O}_2^+.21\text{-crown-7})(\text{WOCl}_5^-)$; a complex in which the 21-crown-7 molecule adopts a rigid, bowl-like conformation.
P C Junk and J L Atwood, *J. Chem. Soc., Chem. Commun.*, **1995**, 1551-2.
23. Structure of the p-sulfonatocalix[4]arene complex with tetramethylammonium ions, $[\text{NMe}_4]_5[\text{p-sulfonatocalix[4]arene}.4\text{H}_2\text{O}]$.
J L Atwood, L J Barbour, P C Junk and G W Orr, *Supramol. Chem.*, **1995**, 5, 105-8.
24. Zinc dimerisation of p-but-calix[4]arene.
J L Atwood, P C Junk, S M Lawrence and C L Raston, *Supramol. Chem.*, **1996**, 7, 15-17.
25. Anionic coordination complexes of Mo and W which crystallize from liquid clathrate media with oxonium ion-crown ether cations.
J L Atwood, S G Bott, P C Junk and M T May, *J. Coord. Chem.*, **1996**, 37, 89-105.
26. Solubilities of the cyclodextrins in the presence of transition metal salts.
M Eddouadi, A W Coleman and P C Junk, *J. Incl. Phenom. Mol. Recogn.*, **1996**, 26, 133-51.

27. Monomeric, N-functionalised amido complexes of aluminium: Synthesis of $[\text{AlCl}\{\text{NR}(8\text{-C}_6\text{H}_6\text{N})\}_2]$, R = H or SiMe_3 , and $[\text{Al}\{\text{N}(2\text{-C}_5\text{H}_4\text{N})(2\text{-C}_5\text{H}_4\text{N})\}_3]$
L M Engelhardt, M G Gardiner, C Jones, P C Junk, C L Raston and A H White, *J. Chem. Soc., Dalton Trans.*, **1996**, 3053-57.
28. X-ray structure of the water soluble adeninium p-sulfonatoCalix(4)arene which displays cationic and anionic bilayers.
J L Atwood, L J Barbour, E S Dawson, P C Junk and J F Kienzle, *Supramol. Chem.*, **1996**, 7, 271-4.
29. Unidentate nitrogen base adducts of aluminium trichloride.
L M Engelhardt, P C Junk, C L Raston, B W Skelton and A H White, *J. Chem. Soc., Dalton Trans.*, **1996**, 3297-3301.
30. New, Simple Coordination compounds of Cr, Mo and W from liquid clathrate media.
J L Atwood, P C Junk, M T May and K D Robinson, *J. Coord. Chem.*, **1996**, 40, 247.
31. A tetranuclear neodymium cage which tightly binds sodium carbonate molecules.
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190. The effective electron transfer distance in dinuclear ruthenium complexes containing the unsymmetrical bridging ligand 3,5-bis(2-pyridyl)-1,2,4-triazolate
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194. The Structural Systematics of Protonation of Some Important Nitrogen-base Ligands. II[‡] Some Univalent Anion Salts of Singly Protonated Bis(2-pyridyl)amine
PC Junk, L Wei-Min, LI Semenova, BW. Skelton, and AH White, *Z. Anorg. Allg. Chem.*, **2006**, 632, 1303-1311.
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PC Junk, Y Kim, BW Skelton, and AH White, *Z. Anorg. Allg. Chem.*, **2006**, 632, 1340-1350.
198. X-ray structural characterization of diethylether solvated lithium iodide derived from a metathesis reaction
M Brym, C Jones, PC. Junk and M Kloth, *Z. Anorg. Allg. Chem.*, **2006**, 632, 1402-1404.
199. Synthesis and structural characterisation of lithium and sodium 2,6-dibenzylphenolate complexes
ML Cole, PC Junk, KM Proctor, JL Scott and CR Strauss, *Dalton Trans.*, **2006**, 3338-3349.
200. Synthesis and structural characterisation of heavy alkaline earth N,N'-Bis(aryl)formamidinate complexes
ML Cole, GB Deacon, CM Forsyth, K Konstas and PC Junk, *Dalton Trans.*, **2006**, 3360-3367.
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INVITED LECTURES:

1. Magnesium anthracene chemistry, Dept of Chemistry, James Cook University, Townsville, Qld, July **1989**.
2. Oxonium ion/crown ether complexes derived from liquid clathrate media, University of Missouri-Columbia, Columbia, Mo, USA, October **1994**.
3. Oxonium ion/crown ether chemistry. Department of Chemistry, University of Western Australia, September **1995**.
4. Acids, crowns and clathrates. Department of Chemistry, Monash University, March **1996**.
5. Calixarene Chemistry. Dept of Chemistry, James Cook University, Townsville, Qld, July **1997**.
6. Aryloxolanthanoid Chemistry, Dept of Chemistry, University of Leipzig, Germany, February, **1999**.
7. Arene interactions in Aryloxolanthanoid Chemistry, Dept of Chemistry, King's College, London, February **1999**.
8. Arene Interactions in Lanthanoid and Main Group Chemistry, Dept of Chemistry, University of Wales, Cardiff, February **1999**.
1997. Aryloxolanthanoid Chemistry, Dept of Chemistry, University of Miami, USA, March **1999**.
10. University life in Australia, Dept of Chemistry, University of Leipzig, Germany, December, **2000**.
1997. Some recent developments in metal amido chemistry, Dept of Chemistry, University of Leipzig, Germany, January, **2001**.
1998. Organometallic Chemistry in Australia, Dept of Chemistry, Fachhochschule Muenster, Germany, February, **2001**.
1999. Novel main group metal amido chemistry, Dept of Chemistry, University of Bremen, Germany, March, **2001**.
14. Some recent developments in metal amido chemistry, Dept of Chemistry, Melbourne University, March, **2002**.
15. Recent excursions in metal amido chemistry, Dept of Chemistry, University of Leipzig, Germany, June **2002**.
16. Metal-based syntheses and structural characterisation of lanthanoid organometallic complexes, Institut Max von Laue – Paul Langevin, Grenoble, France, July **2002**.
17. New directions in main group and lanthanoid amido chemistry, School of Chemistry, University of Tasmania, March, **2003**.
18. New directions in main group and lanthanoid amido chemistry, Research School of Chemistry, Australian National University, July, **2003**.
19. New directions in main group and lanthanoid amido chemistry, School of Chemistry, National University of Singapore, October, **2003**.
20. Novel new main group and lanthanoid amido chemistry, Dept of Chemistry, University of Leipzig, Germany, Dec. **2003**.
21. Novel new main group and lanthanoid amido chemistry, Dept of Chemistry, University of Bremen, Germany, Dec. **2003**.
22. New frontiers in synthetic and structural lanthanoid and group 2 chemistry, Dept of Chemistry, University of Leipzig, Germany, Dec. **2004**.
23. New frontiers in synthetic and structural lanthanoid and group 2 chemistry, Dept of Chemistry, FreieUniversitaet Berlin, Germany, Dec. **2004**.

24. Advancement of metal-based syntheses as major routes to highly reactive rare earth compounds, Dept of Chemistry, University of Wales, Cardiff, September **2005**.
25. Advancement of metal-based syntheses as major routes to highly reactive rare earth compounds, Dept of Chemistry, Syracuse University, September **2005**.

CONFERENCE PRESENTATIONS (ORAL):

1. Fuel Oil Flashpoint, Chief Petroleum Chemist's Conference, Bowral, NSW, Australia, March **1992**.
2. A Convenient synthesis of anhydrous lanthanoid chlorides and their use in the formation of novel organolanthanoid complexes.
Presented at the "*RACI Inorganic Group Queensland Regional Symposium*", Rockhampton, 10-11 July **1997**.
3. Organolanthanoid Chemistry
"*RACI - North Queensland Section Meeting*", Townsville, 16-17 August, **1997**.
4. Single crystal X-ray diffraction using a SMART CCD diffractometer.
Presented at "*RACI Central Qld Branch Meeting*", Rockhampton, 29 July **2000**.
5. Metal-Based Syntheses of Rare Earth Organoamides and Aryloxides, 85th Canadian Society for Chemistry (CSC) Conference and Exhibition, Vancouver, Canada, June 1-5, **2002**. *Invited speaker*.
6. Novel new chemistry involving organoamidolanthanoids, *Tage der Seltenen Erden*, Berlin, December, **2003**.
7. New rare earth chemistry of N-donor chelating ligands, *Tage der Seltenen Erden*, Bayreuth, Germany, December, **2004**.
8. Advancement of metal-based syntheses as major routes to highly reactive rare earth compounds, *From Molecules Towards Materials, IV Razuvaev Lectures*, Nizhny Novgorod-Perm-Nizhny Novgorod, Russia, 3-11 September **2005**. *Invited Keynote Speaker*.

CONFERENCE PRESENTATIONS (POSTERS):

1. The utility of magnesium (anthracene) (THF)_{3-n} (TMEDA)_n, n = 0 or 1 in the synthesis of Grignard reagents. S Harvey, PC Junk, CL Raston and G Salem. Presented at *XIIIth International Conference on Organometallic Chemistry*", Vienna, September 8 - 13, **1985**.
2. Lithium and magnesium sterically hindered amide and alkoxide complexes. LM Engelhardt, GE Jacobsen, PC Junk, BH Newton, CL Raston and AH White. Presented at "*Conference of the RACI Inorganic Division*", Melbourne, January 28-31, **1986**.
3. Magnesium(anthracene) complexes: Their utility in the synthesis of Grignard reagents. S Harvey, PC Junk, CL Raston and G Salem. Presented at "*Conference of the RACI Inorganic Division*", Melbourne, January 28-31, **1986**.
4. Magnesium(anthracene) complexes: Their utility in the synthesis of Grignard reagents. S Harvey, PC Junk, CL Raston and G Salem. Presented at "*Ninth National Conference of the Royal Australian Chemical Institute Division of Organic Chemistry*", Adelaide, May 11-15, **1986**.
5. Conjugated aromatic anion - magnesium chemistry. S Harvey, PC Junk, CL Raston, BW Skelton and AH White. Presented at "*The 14th National Conference of the Inorganic Division of the Royal Australian Chemical Institute*", Sydney, 24-28 August **1987**.
6. Subvalent aluminium chemistry. LM Engelhardt, MJ Henderson, PC Junk, UH Kynast, CL Raston and H White. Presented at "*The 14th National Conference of the Inorganic Division of the Royal Australian Chemical Institute*", Sydney, 24-28 August **1987**.
7. Calcium, strontium and barium 1,3-bis(trimethylsilyl)cyclopentadienyl, and cyclo-octatetraenediyl chemistry.

- PC Junk, CL Raston, BW Skelton and AH White. Presented at "*International Coordination Chemistry Conference*", Broadbeach, Qld, Australia, 3-8 July, **1989**.
8. New coordination compounds derived from liquid clathrates.
PC Junk, MT May, KD Robinson and JL Atwood. Presented at the "*American Chemical Society, 49th Southwest Regional Meeting*", Austin, Texas, 24-27 October, **1993**.
 9. Oxonium ion/crown ether complexes derived from liquid clathrate media.
PC Junk and JL Atwood. Presented at the "*15th International Symposium on Macrocyclic Chemistry*", Lawrence, Kansas, USA, 12-17 June, **1994**.
 10. Crown ether-oxonium ion complexes derived from liquid clathrate media.
PC Junk and JL Atwood. Presented at the "*8th International Symposium on Molecular Recognition and Inclusion*", Ottawa, Canada, 31 July - 5 August, **1994**.
 11. A convenient, high-yielding synthesis of anhydrous lanthanoid chlorides
GB Deacon, T Feng, PC Junk, BW Skelton and AH White. Presented at "*XVIIth International Conference on Organometallic Chemistry*" Brisbane, 7-12 July, **1996**.
 12. Bidentate nitrogen base adducts of bismuth(III) nitrate
LJ Barbour, SJ Belfield, PC Junk and MK Smith. Presented at "*Conference of the RACI Inorganic Division*", Wollongong, February 1-5, **1998**.
 114. Novel β -diketonato Ligands in Rare Earth Chemistry
M Hilder, PC Junk, and UH Kynast. Presented at "*IIRACIC*", Canberra, February 6-11, **2000**
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