

# Liversidge Research Lecture

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INORGANIC CHEMISTRY: FRONTIERS AND FUTURE

I. G. DANCE



The Royal Society of New South Wales



**Ian Gordon Dance**

### IAN GORDON DANCE 1940 -

**Ian Gordon Dance** was born on 8 September 1940 in Maitland, N.S.W. After secondary education at Homebush Boys' High School he studied at the University of Sydney where he was awarded the Union Carbide Major Scholarship for Chemistry in 1960, and graduated B.Sc. (1st class Hons.) with the University medal for Inorganic Chemistry in 1961. In 1962 he worked as an Analytical Chemist at the N.S.W. Department of Mines, then he returned to the University of Sydney to carry out research on the crystal structure of chromium trichloride hexahydrate under the supervision of Dr. Hans Freeman (later Professor), and graduated M.Sc. in 1963. He then proceeded to the University of Manchester as a British Commonwealth Scholar where he worked with Professor Jack Lewis (later Sir Jack, and then Lord Lewis) on coordination chemistry, and graduated Ph.D. in 1966. During 1966-1967 he was a Research Associate with Professor R.H. Holm at the University of Wisconsin, USA, and subsequently (1967-1968), at Massachusetts Institute of Technology, USA. For the period 1968-1974 he was Assistant Professor of Chemistry at the University of Wisconsin, Madison, USA where he worked on metal dithiolene complexes and their electron transfer and coordinative reactivity. In 1975 he took up an appointment as Lecturer in Chemistry at the University of New South Wales where he was promoted to Senior Lecturer in 1976, to Associate Professor in 1981, and to Professor of Inorganic Chemistry in 1986; for the period 1990-1993 he was Head of School. Upon taking up his appointment at the University of New South Wales he commenced investigations of metal thiolate complexes of the type  $[M_x(SR)_y]^z$ . This programme led to the discovery of many unexpected and unprecedented compounds; much of the laboratory work was carried out by Ian Dance himself. In the 1980s he and his group moved into research on metal chalcogenide clusters including macromolecular clusters of the general type  $[E_wM_x(E'R)_y]^z$ , where E,E' = S,Se,Te. His work in this area led him to predict three potentially infinite series of high symmetry structures for these compounds. In connection with this programme he became interested in the application of multinuclear NMR spectroscopy in inorganic and organometallic research. The characterisation of solution equilibria by NMR led to controlled, rational syntheses of homoleptic metal polychalcogenide compounds. He also developed the use of mass spectroscopy and, more specifically, the use of laser desorption Fourier Transform Ion Cyclotron Resonance mass spectroscopy in investigations of metal clusters. His synthetic interests include the area of homoleptic metal polychalcogenide chemistry. His other research interests include inclusion phenomena; gas phase inorganic chemistry - and the use of density functional calculations; metallocarbohedrenes and metal-carbon clusters; molecular modelling and computational chemistry; operative mechanisms of nitrogenase and hydrogenase enzymes; and supramolecular inorganic chemistry. Current research has three major components: supramolecular inorganic chemistry, including prediction of crystal packing; experimental and theoretical aspects of unprecedented inorganic molecules; and theoretical aspects of metalloenzymes.

Ian Dance has been very active in University and extracurricular affairs in both teaching and research. His extracurricular activities in teaching include membership of the Science Examination Committee, and Convenor of the Chemistry Sub-Committee, NSW Board of Senior School Studies, 1979-1980; co-organiser and Project Supervisor, Summer School for secondary Science Students, University of New South Wales, 1976-78. In connection with research he was a member of the Chemistry Sub-Panel of the

Australian Research Council, 1995-97; a member of the editorial boards of *Polyhedron* (1986-98), *Australian Journal of Chemistry* (1994--), *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* (1995--), *New Journal of Chemistry* (1996--), *Structure and Bonding* (1998--), and *Cryst. Eng. Comm.* (RSC) (1999). He was Chairman of the Inorganic Division of the Royal Australian Chemical Institute for the period 1985-89.

### **Honours and Awards (pre 2014)**

- 1993-4      Royal Society of Chemistry Lecturer for Australia and New Zealand
- 1994          Liversidge Research Lecture, Royal Society of New South Wales,
- 1995          FRACI (Fellow of the Royal Australian Chemical Institute)
- 1996          Burrows Lecture, Royal Australian Chemical Institute
- 1997          Stranks Memorial Lecture, University of Melbourne
- 1997          FAA (Fellow of the Australian Academy of Science)
- 1999          Albright and Wilson Lecturer, Warwick University, England
- 2000          3M Lecturer, University of Western Ontario, Canada
- 2002          Dwyer Lecturer, University of NSW
- 2011          David Craig Medal, Australian Academy of science

### **Biographical Source**

Personal communication

### **Scientific Publications of I.G. Dance**

Up to the year 2014 I.G. Dance had some 269 refereed publications, including 14 reviews and invited chapters of books.

## INORGANIC CHEMISTRY: FRONTIERS AND FUTURE\*

I. G. DANCE

*School of Chemistry, University of New South Wales, Kensington, N.S.W.*

**ABSTRACT.** Inorganic chemistry - the chemistry of all elements - has turned up some real surprises in the last few years. Even elemental carbon is undergoing a revolution, literally. Molecules which are simply binary combinations of the elements, such as  $M_xS_y$  and  $M_xC_y$ , have been discovered. These are molecular fragments of compounds otherwise known only as non-molecular solids, and are totally unexpected and unpredictable: their structures are being explored by computational methods. The multiple "non-bonded" interactions between inorganic molecules in crystals are being recognised and understood, and can be deployed in crystal engineering. Highly evolved molecular biology reveals tantalising chemical possibilities beyond current laboratory capabilities, such as the mild reduction of the most recalcitrant molecule in chemistry,  $N_2$ , by the enzyme nitrogenase. Insight into the mechanism of this enzyme comes from investigations of the clusters  $M_xC_y$ .

### Introduction

Professor Liversidge's instructions required that "the lectures shall be such as will primarily encourage research and stimulate the lecturer and the public to think and acquire new knowledge by research." I trust that by examining some of the current frontiers of inorganic chemistry, and by looking forward, this account will meet his expectations.

Of the many frontiers in inorganic chemistry, I will focus here on several that I see as contemporary and expanding. My approach is mainly inductive, and, consistent with the terms of the Liversidge endowment, seeks more to point to significant directions of research and less to review current knowledge.

What is inorganic chemistry, and where are its frontiers? The name "inorganic chemistry" reveals only what this science isn't, and is unsuitable, and anachronistic. However, I don't expect an imminent and positive renaming of this field of science, particularly since it took so long even to effect a logical renumbering of the periodic table. The old name of the Inorganic Division of the Royal Australian Chemical Institute, namely "Coordination and Metal-organic Chemistry", is more positively descriptive.

Inorganic chemistry is the chemistry of compounds of all of the elements, involving the fundamental chemical activities and attributes of (1) **synthesis**, (2) **structure** (geometric and electronic) and architecture for molecules and assemblies, and (3) **reactions and reactivity**. There are close and important connections with the fields of catalysis, and with materials and the materials sciences, and with the biological sciences. Like non-inorganic chemistry, it is supported by theory, by the innumerable spectroscopies, and by analysis.

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\*Liversidge Research Lecture delivered before the Royal Society of New south Wales, 9th August, 1994. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1995, **128**, 131-140.

## Structural Molecularity

One essential characteristic of compounds over the periodic table is the molecularity of their architectures and geometrical structures. Structural molecularity refers to the existence, or not, of the discrete groups of atoms which are termed molecules because they are surrounded by non-bonded boundaries. Actually, the boundaries which surround and define molecules are weakly bonding rather than non-bonding, but the significant fact is that the intermolecular attractive energies are an order of magnitude less than intramolecular bond energies. The significance of structural molecularity in inorganic chemistry can be illustrated with one of the frontiers, namely the chemistry of the element carbon. For a very long time our knowledge has been restricted to two allotropes of carbon, diamond and graphite. Both of these are nonmolecular: diamond is three dimensionally non-molecular because there are infinite extensions of strong bonds in three dimensions, while graphite is two-dimensionally nonmolecular. But then came C<sub>60</sub>, which is totally molecular and remarkably symmetrical, as shown in Figure 1. The bonds around the 12 pentagons and 20 hexagons in C<sub>60</sub> are arranged exactly as the seams in a

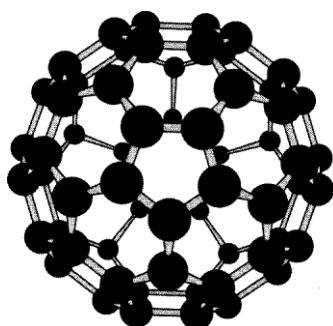


FIGURE 1. A molecular allotope of carbon, C<sub>60</sub>.

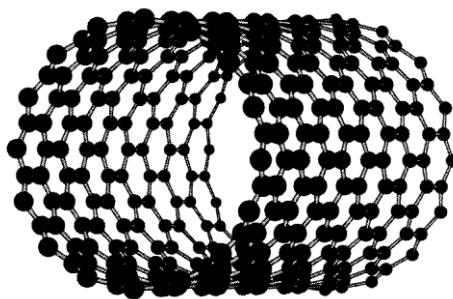


FIGURE 2. A short length of carbon nanotube.

soccer ball. The molecular allotropes of carbon are named "fullerenes", from the analogous architecture of the geodesic domes of Buckminster-Fuller. And not only is there one molecular allotope of carbon, but there are many fullerenes C<sub>n</sub>, some with n < 60 but most with n > 60. And there are geometrical isomers of individual fullerenes C<sub>n</sub>. Further, elemental carbon which is one-dimensionally non-molecular is known in the carbon nanotubes, which are like concentric rolls of graphite. Part of a single nanotube is illustrated in Figure 2. In a little over a decade the inorganic chemistry of a common and long-known element, carbon, has undergone a surprising revolution which is spawning a plethora of compounds with intriguing properties.

## The Domains of Inorganic Molecules

This frontier of inorganic chemistry, namely the occurrence of molecules and of molecular structure for compounds previously known only in non-molecular form, is occurring with many other fundamental inorganic compounds, as I will explain below. In order to develop this frontier and others, I will define a conceptual framework for the components of molecular metallocompounds. Figure 3 shows the molecular structures of the cluster compound [S<sub>4</sub>Cd<sub>10</sub>(SPh)<sub>16</sub>]<sup>4-</sup> which we have investigated. In this Figure the atoms are shaded according to location in the molecule.

These molecules can be viewed as having three domains, the domain **M** of the metal atom or atoms usually near the centre, surrounded by the domain of the ligand donor atoms

**D** bonded directly to the metals, which is then surrounded by the ligand framework **L** often composed of carbon and hydrogen. These domains are shown diagrammatically in Figure 4, with the same shading as Figure 3. Tens of thousands of other metallocompounds can be viewed the same way: they vary in size and shape but this analysis of molecular architecture is widely sustainable, and is implicit in most of the literature.

Two of the frontiers of inorganic chemistry involve modifications of this view: I am going to subtract and add domains. One of the frontiers involves molecules in which the ligand framework **L** no longer exists. The molecules contain only the **M** and **D** domains, and they are commonly encountered as binary compounds in **gas phase inorganic chemistry**. The metal and donor atoms, often quite intimately involved, are effectively in vacuum.

The expanded view of metallomolecules focuses on their periphery, domain **P**, and on its interaction with the environment of the molecule, domain **E** (see Figure 5). In the condensed phases, where most chemistry occurs, every molecule has an environment, and interacts with that environment through weak interactions. This is the frontier of **supramolecular inorganic chemistry** [Dance, 1995].

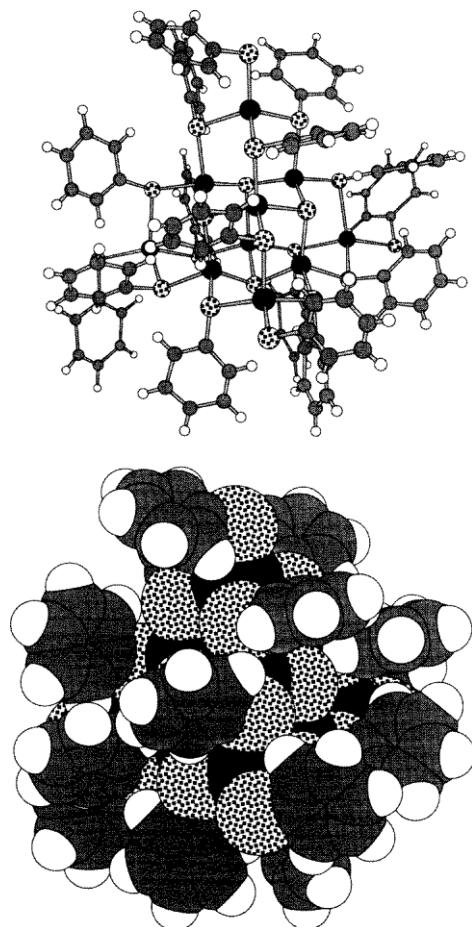


FIGURE 3. Skeletal and space-filling pictures of  $[S_4Cd_{10}(SPh)_{16}]^{4-}$ , representing the domains. The metal atoms are dark, the donor atoms bonded to the metal are speckled, and the outer atoms are grey (carbon) or white (hydrogen).

Supramolecular chemistry is the chemistry of non-bonds, or "chemistry beyond the molecule", or interactions across the boundaries of molecules [Lehn, 1990]. Supramolecular chemistry is precisely the interaction between the periphery of a molecule and its environment. Supramolecular chemistry is distinct from supermolecular chemistry, which deals with big molecules. The importance and significance of interactions across molecular boundaries has of course been known for a long time in molecular biology, and its significance is well recognised in that context. But only in recent years has that knowledge been developed for non-biological molecules, and for metallomolecules and inorganic compounds this is a frontier yet to be explored.



FIGURE 4. The domains of a metallocompound, **M**, **D**, and **L**.

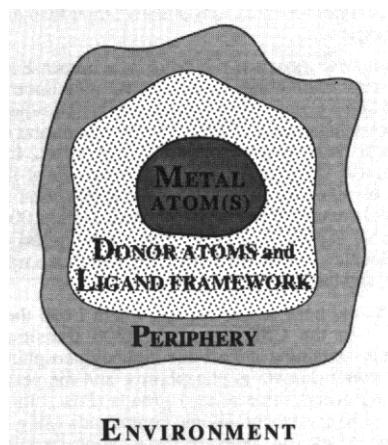


FIGURE 5. The domains of a metallocompound in a condensed phase environment.

There are two other important themes that I will describe. One is the relationship between molecular biology and metallochemistry, and the other is the contribution of computational methods to the development of metallochemistry. Thus the four principal frontiers of inorganic chemistry to be championed here are:

- Supramolecular metallochemistry - the total view
- Gas-phase metallochemistry - the fundamental and pristine state, indicating possibilities and opportunities
- The contributions of computational methods - which are now powerful
- The knowledge-base of molecular biology - and its recognition and use in inorganic chemistry

I will first develop and illustrate some of the concepts of supramolecularity for metal containing compounds, concentrating on the interface of the molecular periphery and the environment. Then I will describe some of our gas-phase inorganic chemistry, the cut-down and pristine view of inorganic chemistry, which reveals the fundamentals and the possibilities and opportunities. This will involve a brief description of the power of contemporary computational methods for these compounds, and finally I will look at naturally occurring systems, in particular the amazing enzyme nitrogenase.

### **Supramolecular Metallochemistry**

Why is supramolecular chemistry so important? Most of the processes of life depend on molecular recognition, and on the concerted and synergistic actions of molecular assemblies. Processes such as the pumping of nutrient chemicals and waste chemicals through cell walls, the conversion of solar energy into chemical energy, the catalysis of reactions under remarkably mild conditions, and the operation of the amazing molecular computer called the brain, all depend on supramolecular chemistry. Nature is the expert supramolecular chemist, and nature, that is evolved molecular biology, uses metals and inorganic materials. Evolved molecular biology has developed supramolecular chemistry to a sophistication far greater than that of any laboratory chemist. Evolved molecular biology reveals amazing possibilities for chemistry, and thereby presents the challenge to understand and possibly deploy these possibilities.

But there is no need to be a molecular biologist to be involved with supramolecular chemistry. As chemists we practice supramolecular chemistry every time we crystallise a molecular compound. The formation of crystals is one of the supreme supramolecular events, and every structure of a crystal is the consequence of innumerable non-bonded interactions.

What are the characteristics and magnitudes of the "non-bonding" interactions? There are the van der Waals repulsive interactions at short distances, and the van der Waals attractions at longer distances, according to the curve in Figure 6. Note that the conventional van der Waals separations and the radii derived from them refer to the closest possible approach, which is slightly repulsive. The attractive interactions, responsible for the condensed phases, are at longer distances, and there is another set of van der Waals radii characterising these attractive interactions for the elements, just as there is a set of values for the magnitudes of the attractive energies at the shallow minima. Van der Waals interactions following curves of this type are described analytically in computer programs for supramolecular chemistry.

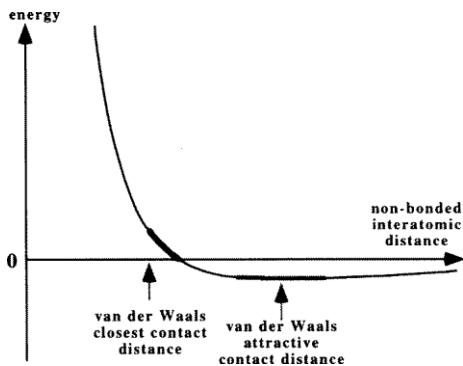


FIGURE 6. The repulsive and attractive interaction regimes between "non-bonded" atoms.

There is another interaction, the coulombic forces between regions of excess or deficient electron density in molecules. This is expressed in terms of partial charges on atoms. There are two important attributes of the coulombic interaction, namely its magnitude, and its extent. For metallocompounds the partial charges on atoms can be appreciable, up to about  $\pm 1$  electrons, and as a consequence the coulombic contributions to the total energies are often substantially larger than the van der Waals energies.

It is important to recognise that there is an immense amount of data on supramolecular chemistry of metallocompounds available in the Cambridge Crystallographic Database (CSD). Just as crystallisation is common, so determination of crystal structure is very largely a routine operation, frequently practised, and the journals are full of pictures of molecular structure obtained by diffraction analysis of crystal structure. In the 1993 version of the Database there are 115,000 entries, of which 45,000 contain transition metals. The supramolecular information here for metallocompounds is immense, and has been largely ignored.

I will expound here on one aspect, which I call the **phenyl factor**. In the CSD there are 4300 transition metal compounds containing at least one triphenylphosphine ligand. Here the donor domain is phosphorus, and the periphery of each ligand brings three phenyl groups (Ph). In the CSD there are 1150 crystals of anionic compounds using  $\text{Ph}_4\text{P}^+$  or  $\text{Ph}_4\text{As}^+$  as the cation. Each of these cations is fully coated with phenyl groups.

Phenyl and related aryl groups in domain **P** have specific supramolecular interactions. These are responsible for the characteristic herringbone crystal structure of benzene and its abnormally high melting point. The two interaction motifs for benzene molecules and phenyl groups are the **edge to face** and **offset face to face** conformations. These geometries are determined by coulombic attractions between the partial positive charges on H atoms and the negative  $\square$ -electron density of the aromatic. The net attractive energy for a pair of phenyl groups is calculated to be almost 10 kJ per mole.

This is known (albeit subconsciously) to many synthetic chemists, who know that phenylated molecules often have lower solubility and form better crystals. It is also the reason why there are so many compounds with  $\text{Ph}_3\text{P}$  ligands, and so many salts with  $\text{Ph}_4\text{P}^+$  in the Cambridge database: these are the compounds that are easier to isolate and easier to obtain as good crystals, for reason of the phenyl factor. It is also the reason why many metal complexes with extensive heterocyclic ligands have low solubility, and why the trick to increase solubility is to introduce alkyl substituents which are impediments to both of the favourable non-bonded conformations. There are many other ligand systems

with these effects: the benzenethiolate ligand gives compounds more easily crystallised than other thiols, and the same applied to phenoxides. Supramolecular chemistry is behind much of the folklore of laboratories engaged in synthetic coordination chemistry.

There is a caveat. The interpretation of crystal structure data to provide information on molecular structure can be invalid if the molecule is conformationally fluxional, because the total energy of the interactions between the molecule and its environment, particularly where phenyl groups are involved, can be larger than the intramolecular conformational energies. Details of molecular stereochemistry could be influenced by the environment in the crystal. Much of the discussion of fine details of molecular structure deriving from crystal structure data is probably unwarranted: the high precision of the crystal structure results can be deluding, because it is tempered by the low accuracy with respect to the structure of the molecule in solution.

The phenyl factor appears in a variety of structures. Some years ago we synthesised and determined the crystal structures of some compounds  $\text{Cd}(\text{S-Aryl})_2$ , which have complex polycyclic and non-molecular structures [Dance, Garbutt, Craig and Scudder, 1987; Dance, Garbutt and Bailey, 1990; Dance, Garbutt and Scudder, 1990]. For example, the cadmium compound with 2-methylbenzenethiolate when crystallised from *N,N*-dimethylformamide (DMF) has the formula  $\text{Cd}_7(\text{SC}_6\text{H}_4\text{-2-Me})_{14}(\text{DMF})_2$  [Dance, Garbutt and Scudder, 1990]. In order to simplify and interpret this structure, we published diagrams which had the phenyl groups removed, to reveal the chains and cycles of Cd and S atoms. However, this is a crystal structure dominated by the phenyl factor. In fact the crystal is composed mainly of aryl groups which arrange themselves in face-to-face and edge-to-face conformations: the Cd-S sequences threading through relatively small spaces, and the DMF molecules are included to fill space, with their coordination to Cd being secondary.

Examples of the phenyl factor occur throughout the crystal chemistry of anionic metal polysulfide compounds, frequently crystallised with  $\text{Ph}_4\text{P}^+$  cations. An example is  $(\text{Ph}_4\text{P}^+)_4[\text{In}_2(\text{S}_4)_2(\text{S}_6)_2\text{S}_7]^{4-}$ , [Dhingra and Kanatzidis, 1993] in which the cations construct elaborate networks with multiple attractive phenyl-phenyl interactions. Figure 7 shows this layer of attractively interacting cations in this crystalline compound.

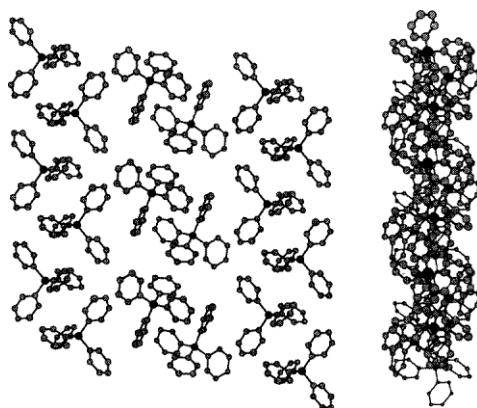


FIGURE 7. The layer of attractively interacting  $\text{Ph}_4\text{P}^+$  cations in crystalline  $(\text{Ph}_4\text{P}^+)_4[\text{In}_2\text{S}_{27}]^{4-}$ : (a) front view; (b) side view.

We have recognised a supramolecular motif which occurs frequently in crystals of this type [Dance and Scudder, 1995]. The motif involves two  $\text{Ph}_4\text{P}^+$  cations embracing through three phenyl groups each, such that hydrogen atoms on each Ph group are attracted to C atoms of the next ring on the other cation, with the interactions arranged fairly symmetrically around the array of six Ph groups involved in the embrace.

In short, the cations are calling the supramolecular tune in these compounds. These features provide opportunities for crystal design and engineering. There is a gold mine for research here. With understanding of crystal structures (as distinct from molecular structures) it will be possible to design and fabricate materials using these supramolecular principles. There is a large volume of design data available in the Cambridge crystallographic database.

### Inorganic Gas Phase Chemistry

In the following I strip away all of the environment, and all of domains **L** and **P**, and look at molecular systems which contain only metals atoms and donor atoms. In many cases these will be binary compounds,  $\text{M}_x\text{E}_y$  ( $\text{E}$  = any element), previously known only with non-molecular structure as metal oxides, sulfides, nitrides, phosphides, and carbides.

Our research here involves synthesis in the gas phase, through ablation of a solid using a high energy laser pulse, creating atoms, ions and molecular fragments in the plasma plume above the hot surface of the solid (see Figure 8). As these cool they

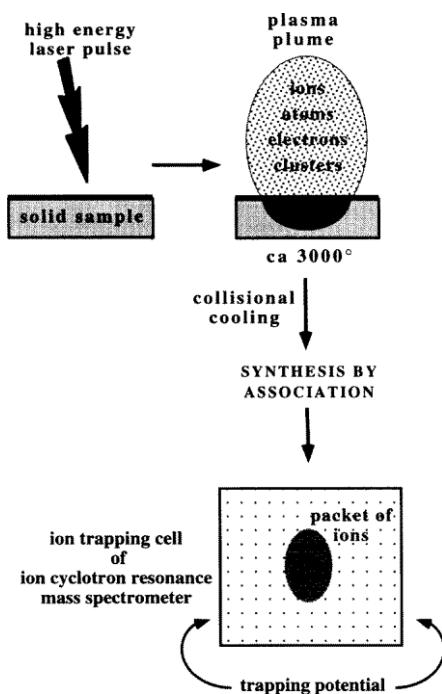


FIGURE 8. Simplified representation of the gas phase synthesis experiments using laser ablation for generation of precursors, and product containment and monitoring in an ion trap mass spectrometer.

reassemble to form molecules and clusters. These are contained in the ion trap of a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, where they can be separated, held, monitored, and reacted with other gaseous reagents. It is important to

recognise that this is unlike conventional mass spectrometry, because it does not reveal molecules present in the precursor solid but rather allows synthesis by assembly of atoms, ions, and small fragments liberated from the precursor. Further, the time scale for experiments in the ion trap ranges up to 100 seconds, which is very many orders of magnitude larger than in ion beam experiments.

I will present a representative selection of our results. When CoS is subject to laser ablation the mass spectrum of negative ions contains 83 peaks, each of which is a new molecule containing only Co and S [El Nakat, Fisher, Dance and Willett, 1993]. Prior to this cobalt sulfide was known only as a non-molecular solid, and our result reveals an unexpected vista of cobalt sulfide molecular chemistry. Figure 9 contains a map of the compositions of these new ions  $[Co_xS_y]^-$  obtained by laser ablation of a sample of CoS, and also a map of  $[Cu_xS_y]^-$  from a similar experiment involving copper.

Similar results are obtained with other metal sulfides [Dance and Fisher, 1994]. Figure 10 maps the compositions of the molecular sulfides formed by iron and nickel. These charts give the composition rules for molecules of compounds previously seen only as non-molecular solids, and as minerals. We have no predictive methodology for such compounds, and now seek to determine the new chemical principles that are contained in their compositions and structures. This chemistry is unexpected and unprecedented, and yet reveals the fundamentals of inorganic binary compounds. This frontier is a binary analog of the fullerene frontier for elemental carbon.

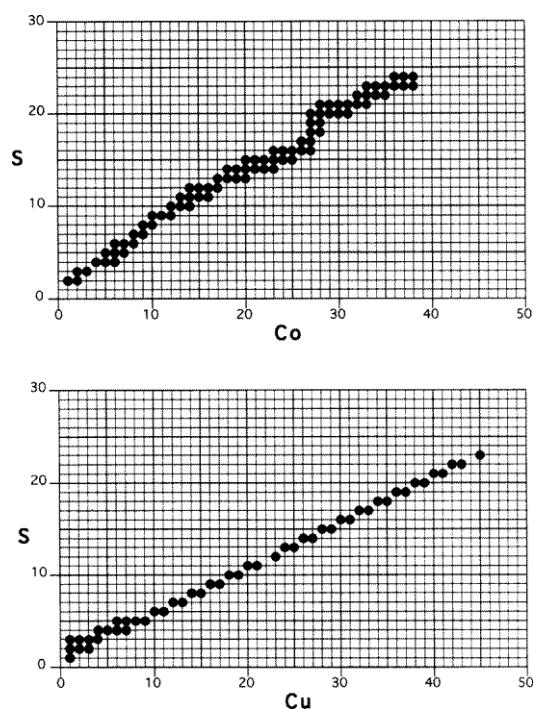


FIGURE 9. Maps of the compositions of the ions  $[Co_xS_y]^-$  generated by laser ablation of CoS, and of the  $[Cu_xS_y]^-$  ions formed by laser ablation of various copper solid solids.

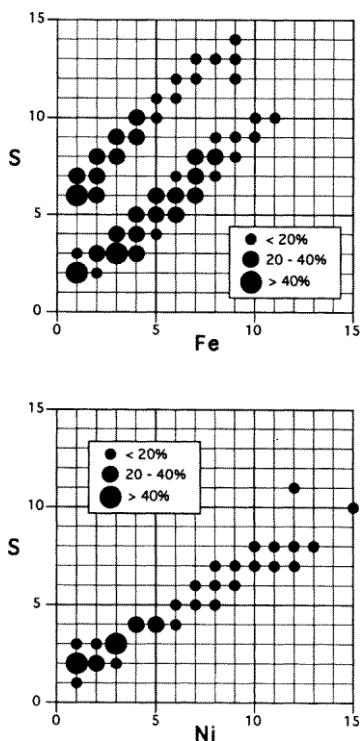


FIGURE 10. Maps of the observed compositions of the ions  $[M_xS_y]^-$  formed by laser ablation of the sulfides of iron and nickel.

It is possible to separate these ions in the gas phase, and thereby to keep just one composition in the ion trap, and then to study its reactions and reactivity. There are as yet no direct data about structure, and experimental access to structural information is rather difficult with the very low concentrations in the gas phase. Our experiments occur at pressures of less than  $10^{-8}$  mbar.

In this situation, where intriguing new molecules are glimpsed but cannot be easily subjected to spectroscopic characterisation, important insight can be provided by theory and computational methods. In these compounds where the bonds are likely to be unusual, force-field methods which require pre-definition of bonds are quite unsuitable. The appropriate technique is quantum theoretical calculation of the electronic structures of these compounds, coupled with geometry optimisation by minimisation of the electronic energy. There are various levels of quantum theory which have been applied to transition metal compounds, but the density functional methodology which I will describe and have used extensively is very promising for inorganic chemistry, and for big molecules with big atoms.

### Density Functional Theory

Density functional theory, which has been used in solid state physics for decades, is quantum theory in which the conventional Schrodinger equation is re-expressed (by the Hohenberg-Kohn theorem) in terms of the electron density. The difficulty in quantum theory is evaluation of the two-electron interaction energies for complex systems: these two-electron interactions are the exchange and the correlation energies. In density functional theory these energies are derived from their expressions for an electron gas. In

effect this is *ab initio* quantum theory, in which there are no empirical parameters, but there are variations in the "functionals" which describe the exchange and correlation energies. The two important advantages of density functional methods (relative to conventional Hartree-Fock methods) are the suitability for inorganic molecules where exchange and correlation energies are more significant, and computational expediency which allows investigation of larger molecules with accessible computing resources.

The methods I use are embodied in the computer program DMol, with geometry optimisation by energy minimisation. The accuracy and power of this computational chemistry are demonstrated by results for the large metal selenide cluster  $\text{Cu}_{29}\text{Se}_{15}(\text{PPri}_3)_12$ , optimised as  $\text{Cu}_{29}\text{Se}_{15}(\text{PH}_3)_12$ , pictured in Figure 11. The calculated bond distances are generally within 0.05 Å of those measured for  $\text{Cu}_{29}\text{Se}_{15}(\text{PPri}_3)_12$ . This provides confidence in the application of density functional methodologies to the newly observed inorganic clusters with unknown structures. I see a very valuable future for density functional theory in inorganic chemistry.

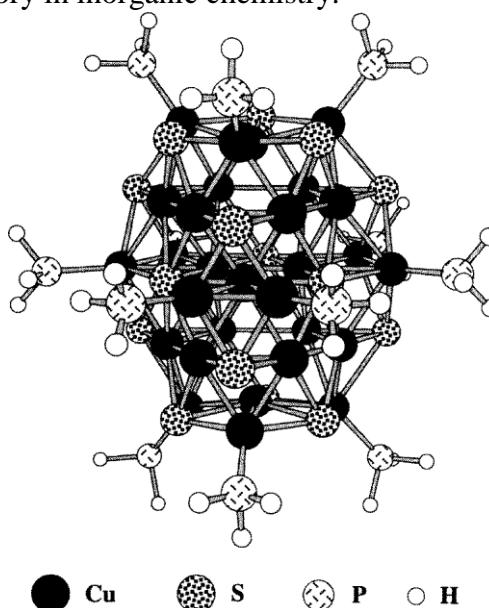


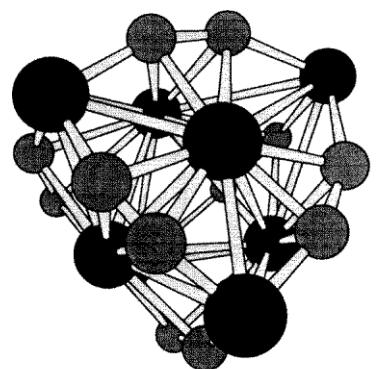
FIGURE 11. The calculated structure of  $\text{Cu}_{29}\text{Se}_{15}(\text{PH}_3)_12$ , which is virtually identical with the measured structure of  $\text{Cu}_{29}\text{Se}_{15}(\text{PPri}_3)_12$ .

The density functional calculations minimise the energy and thereby optimise the geometry for a postulated geometrical structure. They enable the mapping of the geometry-energy hypersurfaces of the newly discovered inorganic molecules, and elucidation of the new structural and bonding principles. Using this method I have been able to explore and optimise the structures of many of the metal sulfide clusters. These results, and the structural principles they reveal, are too voluminous to report here, but I will provide some results for a different new frontier in gas phase inorganic chemistry, that of metal carbon clusters.

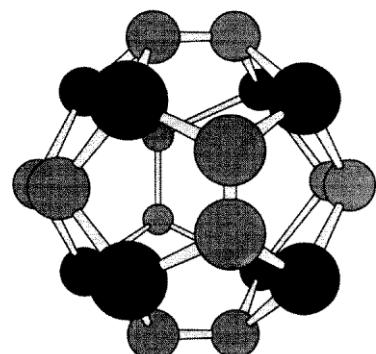
In addition to the fullerenes, there are metallofullerenes in which metal atoms reside inside or outside the carbon cages, and there are metal-filled carbon nanotubes. A related, but different class of unprecedented binary metal-carbon compounds, are the **metallocarbohedrenes**, which are clusters of approximately equal numbers of metal and

carbon atoms. Metallocarbohedrenes are generated in the gas phase by reaction of metal clusters with hydrocarbons.

The first metallocarbohedrene to be detected, in 1992, was  $\text{Ti}_8\text{C}_{12}$ . The original proposal for its structure was the cube of Ti with  $\text{C}_2$  groups parallel to the edges, as shown in Figure 12(a). However, I was able to show by density functional calculations that the alternative structure in Figure 12(b) is very much more stable, by more than  $1000 \text{ kJ mol}^{-1}$  [Dance, 1992]. This structure has four inner Ti atoms and four outer Ti atoms, which form slightly folded diamonds on the surface, and the  $\text{C}_2$  groups are cradled in the diamonds, along the long diagonals. All other theoretical investigations have now confirmed the much greater stability of this alternative structure, and the  $\text{C}_2$  group



b



a

FIGURE 12. (a) The original proposal for the structure of the metallocarbohedrene  $\text{Ti}_8\text{C}_{12}$ . (b) The most stable structure for  $\text{Ti}_8\text{C}_{12}$ , as revealed by density functional calculations.

diagonal to a diamond shaped array of metal atoms is a prominent geometrical feature of other stable metallocarbohedrenes.

An interesting sequence of copper carbohedrenes has been reported recently, with many belonging to the general series  $[\text{Cu}_{2n+1}\text{C}_{2n}]^+$ . Using density functional calculations I have defined the structural principles for them [Dance, 1993a]. In Figure 13 are shown the optimised structures for  $[\text{Cu}_{13}\text{C}_{12}]^+$  and for  $[\text{Cu}_{25}\text{C}_{24}]^+$  [Dance, 1993b]. Again a key structural feature is the occurrence of  $\text{C}_2$  groups diagonal to  $\text{Cu}_4$  quadrilaterals.

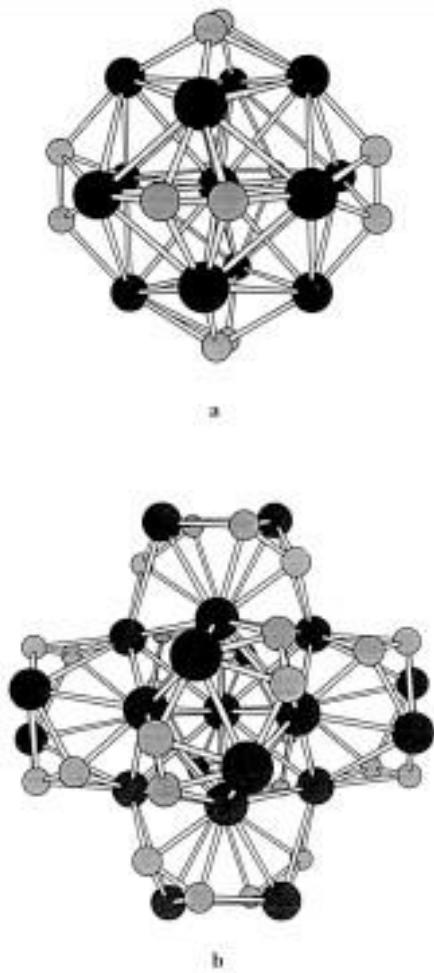


FIGURE 13. The optimised structures of the copper carbohedrenes (a)  $[\text{Cu}_{13}\text{C}_{12}]^+$ , (b)  $[\text{Cu}_{25}\text{C}_{24}]^+$ .

The C<sub>2</sub> group which appears to be a fundamental feature of the metallocarbohedrenes is formally C<sub>2</sub><sup>2-</sup>, or acetylide, which is isostructural with cyanide, CN<sup>-</sup>. Therefore we have commenced investigations of gas phase metal cyanide chemistry. While there is an immense literature on metal cyanides and their applications in solution and in solids, prior to our research only one paper mentioned metal cyanides in the gas phase.

The laser ablation of copper cyanide or silver cyanide generates series of positive ions with the composition  $[\text{M}_x(\text{CN})_{x-1}]^+$  and negative ions  $[\text{M}_x(\text{CN})_{x+1}]^-$  [Dance, Dean and Fisher, 1994]. These retain the formal M<sup>+1</sup> oxidation state. Again the question arises, what are there structures? The structural principles which evolve from the density functional investigations of various postulates are very different from those of the copper carbohedrenes. The most stable structures are those in which cyanide forms a linear bridge between metal atoms, which are themselves two-coordinate, forming long linear molecules, as shown in Figure 14. These are unique molecules in chemistry: the  $[\text{Cu}_5(\text{CN})_6]^-$  ion is more than 30 Å long, and yet only one atom thick. In addition to the image of an abacus invoked in Figure 14, these molecules suggest spear-like concepts. This research on the fundamentals of copper and silver cyanide molecules in the gas phase reveals possibilities for new structures and properties in metal cyanide chemistry. There

are no analogs of these linear structures amongst crystalline metal cyanides, and the challenge is now how to stabilise such molecules in crystals.

The gas phase chemistry of zinc and cadmium cyanides is equally intriguing [Dance, Dean and Fisher, 1995]. The anions observed after laser ablation belong to a general series  $[M_x(CN)_{2x+1}]^-$ . The structure type which is supported by computational investigations, using both density functional and force-field methods, is a helix of the type shown in Figure 15. Here each metal atom is three-coordinate, approximately planar, with one terminal cyanide ligand and connected by two linear cyanide bridges to adjacent metal atoms in the helix. The helix is maintained by coulombic attractions between bridging cyanide ligands and the contiguous metal atoms in the preceding and succeeding turns of the helix. The terminal cyanide ligands are not radial to the axis of the helix, but bent slightly in order to increase the coulombic energy with contiguous metal atoms. Stability is also maintained if the helix contains 6.7 metal atoms per turn rather than the 5.7 metal atoms per turn shown in Figure 15.

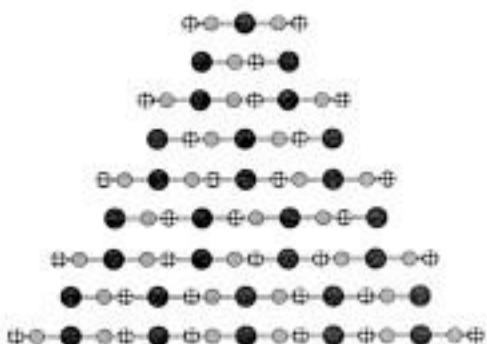


FIGURE 14. The structures of the gaseous metal cyanide Ions  $[Cu_x(CN)_{x-1}]^+$  and  $[Cu_x(CN)_{x+1}]^-$ . Cu atoms are dark, C atoms grey, N atoms hatched.

The metal cyanide helices in Figure 15, and the metal cyanide spears of Figure 14, have been assembled in the gas phase from M and CN fragments. These new architectures are not present in the precursor solids, and now the challenge is synthesis of the newly revealed structures in condensed phases.

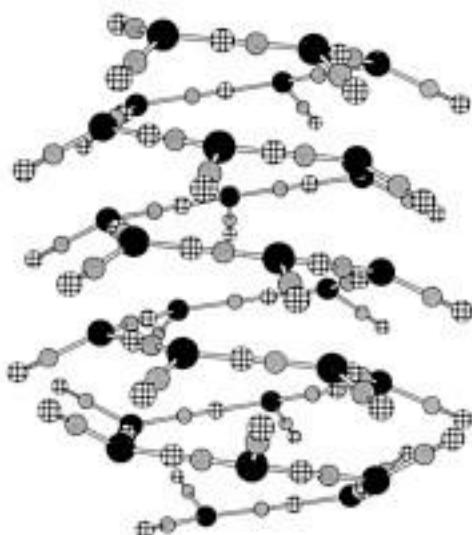


FIGURE 15. The proposed helical structure of  $[Zn_{27}(CN)_{55}]^-$ .

Finally, having described research on new polymetal compounds containing the  $C_2^{2-}$  and  $CN^-$  ligands, I will turn to another diatomic ligand which is isoelectronic with them, namely  $N_2$ . The special interest in  $N_2$  and metal clusters occurs for the enzyme **nitrogenase**, which effects the biological reduction of  $N_2$ . This is most intriguing chemistry. The  $N_2$  molecule is one of the most recalcitrant in chemistry, with a very strong triple bond. Industrial processes for the hydrogenation of  $N_2$  (developed by Haber during the first world war and now used principally for production of fertilisers), involve pressures of 100 - 1000 atm, temperatures of 400 - 500°C, iron catalysts, and cause only partial conversion. Meanwhile the enzyme nitrogenase, present in bacteria symbiotic with plants, catalyses the reduction of  $N_2$  to the amines of life at a  $N_2$  pressure of 0.8 atm and ambient temperature. It is established that the active site where  $N_2$  is bound and reduced is a metal sulfide cluster, containing iron and (normally) molybdenum. The question which tantalises inorganic (and other) chemists is simply: How does it work? What is the mechanism?

In 1993 the structure of the main proteins of the enzyme, and of the active site, were revealed by X-ray diffraction of crystals [Kim and Rees, 1992; Chan, Kim and Rees, 1993; Bolin, Campobasso, Muchmore, Mortenson and Morgan, 1993]. The essential features of the  $Fe_7MoS_9$  cluster at the active site are shown in Figure 16, together with the significant protein environment and the two connections between the cluster and the protein. While this structural revelation was a major breakthrough, the new information referred to the inactive enzyme, and the question of the site of binding of  $N_2$  and the question of mechanism remained unanswered.

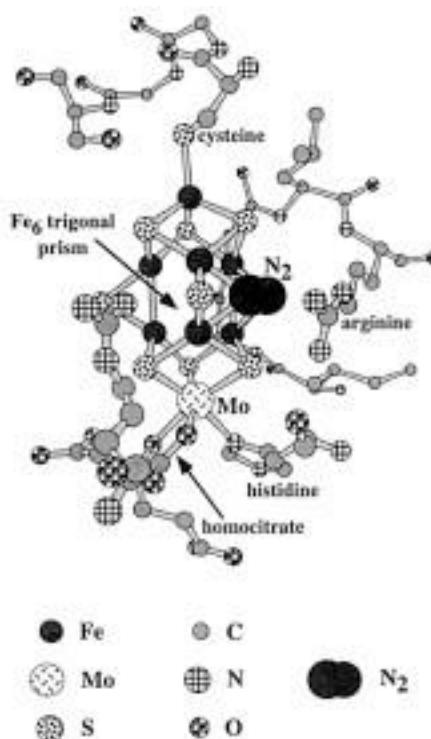


FIGURE 16. The  $Fe_7MoS_9$  cluster which is the active site of nitrogenase. The cluster is connected to the protein only at the cysteine bonded to the top Fe atom and the histidine bonded to Mo at the bottom. The homocitrate which chelates to the Mo atom is an essential component. Nearby protein residues which are significant for the mechanism are marked.

In this context my investigations of the binding of  $C_2^{2-}$  to the faces of metal clusters allowed me insight into the possibilities for nitrogenase [Dance, 1994]. The six iron atoms at the centre of the  $Fe_7MoS_9$  cluster constitute an approximate trigonal prism, with three quadrilateral faces similar to those which bind  $C_2$  in the metallocarbohedrenes. There are iron carbohedrenes with structures similar to the other metallocarbohedrenes mentioned above. Examination of the protein surrounds revealed that one of these faces was very suitable for binding of  $N_2$ . Further, it was known from the metallocarbohedrene investigations that the most bonding configuration for  $C_2$  was along the long diagonal of an  $M_4$  rhombus, while location of  $C_2$  parallel to an edge of rectangular  $M_4$  was antibonding. This factor connected with the fact that the  $Fe_7MoS_9$  cluster was connected to the protein only at its ends, with the Mo end anchored while rotation about the Fe-cysteine bond would be unrestricted. If the top section of the cluster and the  $Fe_6$  trigonal prism rotated slightly relative to the bottom section, the  $Fe_4$  face at which  $N_2$  is postulated to bind could change between a rectangle and rhombus, and provide the bonding and antibonding configurations for  $N_2$ .

These hypotheses were evaluated by density functional calculations of the ligated  $Fe_7MoS_9$  core, with bound  $N_2$ , and small twists about the long axis. These calculations support the hypothesis that twisting of the cluster core will be a factor in the binding of  $N_2$  and then in the weakening of the triple bond of bound  $N_2$ .

This model was developed further, in terms of the supply of  $H^+$  to the  $N_2$  during the course of reduction. There are two sulfide ions which flank the binding site and doubly bridge pairs of Fe atoms on the vertical edges of the  $Fe_6$  trigonal prism. Calculations show that addition of electrons to the cluster causes greatest variation of partial atom charge at these flanking S atoms, which become more basic on reduction. Further, these sulfide ions are able to participate in hydrogen bonds to residues behind the binding face. Thus there is a straightforward hypothesis which involves these two S atoms becoming more basic during reduction, and transferring to the coordinated  $N_2$  a pair of  $H^+$  introduced via hydrogen bonds. This feature of the mechanism is also supported by density functional calculations.

After reduction, product ammonia leaves the active site. The binding site and mechanism which I advance explains this stage, because the homocitrate is located to just below the site, and provides a hydrophilic environment for the egress of the hydrophilic ammonia.

Full details of this research and the proposed mechanism are published [Dance, 1994]. The model is holistic, accounting for the essential nature of iron but not molybdenum, the limited axial connection of the cluster to protein, the exposed face of under-coordinated iron atoms as binding site, doubly-bridging sulfide ions flanking the binding face which provide proton transfer pathways, the sixfold coordination of molybdenum providing an anchor point for torsional twist of the binding site, the  $Fe_7MoS_9$  core allowing electron reservoir action, the homocitrate as provider of local hydrophilic environment for product egress.

The investigations of the mechanism of nitrogenase provide a connection between the frontier of gas phase cluster chemistry to the frontier of evolved molecular biology.

To summarise and conclude: I have shown that gas phase inorganic chemistry coupled with ion trap mass spectrometry and density functional theory enables investigations similar to those of the more conventional condensed phases, with syntheses, separations, measurements of reactivities and reactions, and approaches to structures. This research involving the pristine state, reveals the fundamentals of inorganic chemistry, and indicates possibilities that might not otherwise have been contemplated. Certainly gas phase inorganic chemistry is provocative.

Then I have included all of the domains of the condensed phases, including the environment of a molecule which is often ignored. I have shown something of the nature and effects of the supramolecular interactions for metallo-compounds, different from those of non-metal compounds, and different from lattices containing monatomic ions. What we know as the outcomes of evolved molecular biology (that is supreme supramolecular chemistry) such as the chemistry effected by the enzyme nitrogenase, indicates that there are many further enticing processes and materials still to be developed.

I conclude that the frontiers of inorganic chemistry are indeed rich and certainly not "inorganic". The future is exciting.

Finally, I acknowledge with pleasure the contributions to this research made by Dr Marcia Scudder, Dr Keith Fisher, Professor Phil Dean, previous and current students Robert Garbutt, Garry Lee, John Cusick, John El -Nakat, Dawit Gizachew, and Ma Nu Li. Resources provided through the Australian Research Council, the University of New South Wales, and Australian Numerical Simulations and Modelling Services (at ANSTO) are very gratefully acknowledged.

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