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# The Challenge of Polynuclear Inorganic Compounds

## Why this Conference?

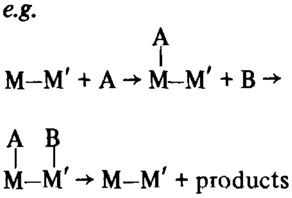
There has developed, in recent years, increased awareness of the potential importance of molecules containing polymetallic centres. Of primary concern has been the involvement of compounds containing such centres in catalytic processes, and this concern has been reflected in the growth and development of metal-cluster chemistry. Further stimulus has come from the discovery that many proteins and enzymes require two or more metal ions for their activity, and from a need to understand the nature of the active site and intermetallic interplay in these metallo-species.

Approaches have been developed for the design and synthesis of oligo-metallic compounds in order to exploit the above-mentioned potential.

One strategy has been to design and prepare multidentate ligands capable, through the siting of their donor atoms, of bringing metals into juxtaposition (*e.g.* compartmental, face to face, constrained ligands, extendable macropolycycles, *etc.*). The development of these so-called binucleating ligands has led to the successful synthesis of homo- and heterobinuclear metal complexes which have found application in the area of biomimicry.

A second approach has been the synthesis of oligo-metallic complexes predominately organometallic in nature – in which two metals, or more, are held in close proximity by suitable bridging units. This then allows the movement of a substrate (on one metal) and a reagent (on the second metal) into close proximity for specific interaction (*e.g.* activation of a fixed substrate in close proximity) prior to eventual release of the product.

*e.g.*



$$M{-}M' + A \rightarrow \overset{A}{\overset{\uparrow}{M}}{-}M' + B \rightarrow$$

$$\overset{A}{\overset{\uparrow}{M}}{-}\overset{B}{\overset{\uparrow}{M'}} \rightarrow M{-}M' + \text{products}$$

Attempts to understand the nature and reactivity of metal–metal interactions have led also to important physico-chemical applications. As well as providing the observation of new coordination geometries and environment for metal ions, the polymetallic species have given fresh insight into the nature of magnetic interactions between metal ions, and interesting electro-chemical studies.

Lately, coordination compounds have been numerically predominant among all novel chemical compounds that have been prepared. This stems from the availability of novel ligands and a deeper knowledge of the coordinating properties of such species. Given the time, we can foresee that every metal ion will be used as a substrate with all possible, presently known ligands. Things being as they are, the term 'novel' coordination compounds can be misleading since many of them are more or less predictable as far as geometry and bonding properties are concerned.

Getting new compounds, in contrast, involves the synthesis of a species with unprecedented coordinative environment and/or redox properties which could not be directly predicted. In principle this aim can be reached when two ions of the same metal or of different metals are bound *via* particular ligands which are able to link them electronically in such a way as to allow transfer of electron density from one metal center to the other through the polydentate ligand, upon demand. The nature of the ligand can (*i*) constrain the moiety into unusual geometries and (*ii*) induce an unexpected and versatile electron density thanks to its ability to transmit electronic effects among the two metal centers. This will entail diverse reactivities and will open up novel catalytic possibilities through a tailored design. Therefore the importance of polynuclear compounds is related to the preparation of chemical species having an outstanding reactivity which can be exploited also in the catalytic field. Moreover, they can act as models for biological systems, particularly when such metal ions as copper, iron, molybdenum, cobalt, zinc, *etc.* are involved.

The formation of polynuclear compounds, with the concomitant modification of the reactivity of metal centers, may sometimes impart stability to *per se* unstable species (labile intermediates).

Last, but not least, of great interest is the circumstance that the presence of several metal ions linked by the same ligand molecule may affect significantly the chemical properties of the ligand itself. In other words, a mutual electronic and/or steric interaction takes place along the metal ion–binucleating ligand–metal ion chain resulting in a modified reactivity of both the metal centers and the connecting moiety. Also these molecular structures bearing metal ions in close proximity may undergo multi-electron processes of foremost importance in the activation of small molecules.

We therefore felt that the time was appropriate to review, by means of a Conference, the present state of the subject area emphasising oligo-metallic interaction rather than large metal clusters. This brought

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together research workers concerned with many different aspects of the subject in order to stimulate discussion.

## The Conference

The conference consisted of 9 plenary lectures supported by 19 contributed papers and 13 poster presentations. These contributions centred on the general themes of ligand design and the synthesis of bimetallic species; the use and role of bimetallic compounds in chemical reactions: physico-chemical applications of bimetallic systems and the role of bimetallic centres in bioinorganic chemistry.

The development and classification of binucleating ligands was discussed by D. E. Fenton, together with the potential application of binuclear complexes as models for bimetalloenzymes such as haemocyanin.

This theme was expanded on by S. M. Nelson in an elegant contribution which detailed the synthesis and structural characterization of bimetallic complexes derived from macrocyclic Schiff bases and introduced the role of such complexes as hosts for small substrates such as dioxygen and acetylenes.

J. A. McCleverty introduced the concept of functionalised metal complexes capable, through the nature of the functional centre, of forming homo- or hetero-bimetallic complexes. These species were based on tris(3,5-dimethyl pyrazoyl)borate derivatives of molybdenum and tungsten and raised the question of the influence of the electrochemical behaviour of the above group on the reactivity of the partner metal system.

The theme of chemical reactivity was introduced by J. Halpern with a typical tour de force on the mechanistic aspects of binuclear oxidative-addition and reductive-elimination reactions. It appears that although binuclear centres may be directly involved with these processes, the systems so far studied do not reveal any distinctive reactivity patterns, or roles, for the binuclear centre.

Indeed in some cases the reactive species are mononuclear complexes. The problem of involvement of metal–metal bonds in the activation of organic molecules via the cooperative action of two different metal centres was discussed by R. Poilblanc. Several proposals for reaction pathways and future ligand design to produce bifunctional ligands having present hard and soft bonding capacity to facilitate heterobimetallation were presented. The influence of electronic and steric factors, particularly in α-diimine ligands, on the formation of ruthenium clusters was clearly shown in the lecture of K. Vrieze. This work also raised the interesting aspect of ligand stabilization of reactive cluster intermediates prior to their future reaction to give novel compounds.

The contribution made by bimetallic species in the understanding of physico-chemical phenomena was made clear in the presentation of O. Kahn. A strategy was presented to allow the synthesis of polynuclear complexes with expected magnetic properties. After dealing with the origins of ferro- and antiferro-magnetic coupling in binuclear arrays it was clearly shown that it is possible to engineer specific complexes having precise magnetic properties.

N.M.R. now provides a plethora of techniques that the chemist may use in attempting to understand molecular behaviour. The lecture of S. Aime demonstrated the role of multinuclear n.m.r. studies in the area of transition metal carbonyl clusters and indicated that there could be a link between intermolecular ligand mobilization and skeletal rearrangements within the molecular framework.

Polynuclear metalloproteins are well established and A. Scozzafava drew attention to the nature and activity of the bimetallic sites in bovine superoxide dismutase and the blue copper oxidases. An understanding of such sites and their activity will enable the chemist to synthesise corroborative models which in turn can be exploited in other areas of chemistry to obtain and harness the catalytic efficiency of the nature systems.

Throughout the meeting it was clear that the future of this area provides much scope for the creative imagination and experimental skill of the chemist. The choice of the title 'The Challenge of Polynuclear Inorganic Compounds' was therefore in retrospect, fully justified and this challenge remains for all chemists for the future.

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