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Theoretical aspects of metal cluster chemistry

D. Michael P. Mingos

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR

Abstract - During the last twenty years the Polyhedral Skeletal Electron Pair Theory and the isolobal analogy have provided a theoretical basis for the rapid experimental developments, which have occurred in metal cluster chemistry. These theoretical principles have been underpinned by m.o. calculations on specific molecules and more generally by the Tensor Surface Harmonic Theory. This paper will review the important theoretical developments and relate them to the experimental and structural data which have been obtained for cluster compounds in our own and other laboratories. In particular the application of theoretical principles for rationalising and predicting the structures of cluster compounds of the platinum metals and gold are discussed. The bonding requirements of interstitial atoms and fragments are discussed, particularly in the context of interstitial C, B, N and transition metal atoms and diatomic fragments, e.g. C_2 and C-H.

POLYHEDRAL SKELETAL ELECTRON PAIR THEORY

The historical development of the theoretical ideas which have contributed to the Polyhedral Skeletal Electron Pair Theory can be traced back to the pioneering work of Longuet-Higgins forty years ago. In the 1950's the contributions of Longuet-Higgins proved decisive since he not only provided a molecular orbital description of the bonding in diborane (ref. 1), but also pioneered the application of molecular orbital theory ideas to deltahedral borides and boranes (ref. 2). The three-centre two-electron description of B-H-B and B-B-B bonds was elegantly generalised into the **styx** formalism and applied to all known boron hydrides by Lipscomb (ref. 3). The molecular orbital analysis of polyhedral boranes resulted in the successful prediction of the octahedral and icosahedral borane anions some years before they were structurally characterised (ref. 4). Hoffmann and Lipscomb (ref. 5) also developed the molecular orbital methodology of Longuet-Higgins in a general molecular orbital analysis of polyhedral borane anions, $B_nH_n^{2-}$, in 1962.

In the 1960's Cotton and Haas (ref. 6) pioneered the development of molecular orbital ideas to metal cluster compounds of the early transition metals stabilised by halide ligands. Their analysis emphasised the important interactions which can result in such clusters from the overlap of the transition metal d orbitals. An alternative localised description of the bonding in such clusters, which resembled the **styx** methodology, was proposed by Kettle (ref. 7). These theoretical models tended to emphasise the inherent differences between metal and main group clusters and in common with ligand field theory tended to stress the role of the metal d orbitals.

By the mid-nineteen sixties the major classes of transition metal π-donor and acceptor clusters, and main group polyhedral borane and Zintl 'naked' clusters had been established but were viewed as distinct areas of inorganic chemistry. Experimental studies had, however, begun to indicate the artificiality of these subdivisions. The synthesis of polyhedral organometallic compounds from the reactions of acetylenes with metal carbonyls by Hübel and Braye and transition metallocarboranes by Hawthorne's group (ref. 8) clearly demonstrated that it was possible to synthesise polyhedral molecules with transition metal and main group atoms at the vertices. In addition the structural characterisation of $Rh_6(CO)_{16}$ by Dahl (ref. 9) provided a real difficulty for the theoretical models which were most widely used. The bonding in $Rh_6(CO)_{16}$ could not be explained by the effective atomic number rule and was not amenable to a molecular orbital analysis based on an extension of the molecular orbital schemes proposed for $[Mo_6Cl_8]^{4+}$ and $[Ta_6Cl_{12}]^{2+}$ by Cotton and Haas (ref. 6).

The structural and electronic relationships connecting main group and transition metal polyhedral molecules and the resolution of the bonding dilemma posed by molecules such as $Rh_6(CO)_{16}$ occured in the early nineteen seventies. The contributions of Williams, Wade, Rudolph and myself were particularly influential in breaking down the conceptual barriers separating the major areas of cluster chemistry. Until 1971 it was the accepted wisdom that the structures of the boranes B_nH_{n+4} and B_nH_{n+6} could best be described as fragments of icosahedra. Williams (ref. 10) recognised that these molecules were better described as fragments of the deltahedral borane anions $B_nH_n^{2-}$. Indeed the boranes B_nH_{n+4} and isoelectronic carboranes had structures which could be derived from $B_nH_n^{2-}$ by the loss of the most highly connected vertex. Similarly the boranes B_nH_{n+6} were related to those of B_nH_{n+4} by the loss of an additional adjacent vertex. Williams was responsible for the closo- ($B_nH_n^{2-}$), nido- (B_nH_{n+4}) and arachno- (B_nH_{n+6}) structural paradigm which is at the heart of the commonly accepted theory for polyhedral molecules.

Wade (ref. 11) recognised that this structural relationship could be related to the total number of valence electrons associated with skeletal bonding in boranes. Specifically if the structurally related series of boranes $B_nH_n^{2-}$, $B_{n-1}H_{(n-1)+4}$ and $B_{n-2}H_{(n-2)+6}$ were expressed in their deprotonated forms and thereby removing the complications associated with bridging hydrogens they shared a common number of skeletal electron pairs, i.e. $B_nH_n^{2-}$, $B_{n-1}H_{n-1}^{4-}$ and $B_{n-2}H_{n-2}^{6-}$ each have the same number, n+1, skeletal electron pairs. Consequently, Wade provided an electronic rationale for the Williams structural generalisation; the closo-, nido- and arachno- structures were related because they shared a common number of bonding molecular orbitals associated with the boron skeleton. A similar structural - electronic relationship had previously been recognised in simple main group inorganic molecules by Sidgwick and Powell and Nyholm and Gillespie (ref. 12), since molecules such as SF_6, BrF_5 and XeF_4 shared a common octahedral geometry, although in the latter two examples lone pairs replace fluorine atoms.

Wade (ref. 11) also demonstrated that these principles could be translated to polyhedral metal carbonyl clusters. In particular he suggested that the bonding problem associated with octahedral molecules such as $Rh_6(CO)_{16}$ could be resolved if it was assumed that each rhodium fragment donated three orbitals for skeletal bonding and formed a spectrum of skeletal molecular orbitals similar to those in $B_6H_6^{2-}$. He also defined some nido- and arachno- metal carbonyl clusters which conformed to the same principles.

Rudolph (ref. 13) provided the first attempt to account for the structural and electronic relationships proposed by Williams and Wade using semi-empirical molecular orbital calculations and also recognised that the same principles could be applied to boranes and carboranes with hetero- atoms if it was assumed that these atoms had a lone pair orbital directed away from the centre of the polyhedron. This idea was to prove important for extending the ideas to the Zintl ions, which had been synthesised by Corbett (ref.14).

It was apparent that main group and transition metal molecules were sharing common structural principles based on the formation of molecular orbital patterns which were sufficiently transferable to lead to similar closed shell requirements. I proposed (ref. 15) there were three major classes of polyhedral molecules - electron deficient, which included the closo-, nido- and arachno- structures highlighted in Williams' and Wade's work, electron precise clusters, based on three-connected polyhedral molecules and electron rich molecules. The latter had structures which could be derived from the three-connected structures by breaking a bond for each electron pair in excess of that required for forming element-element bonds along all edges of the polyhedron. In addition molecular orbital calculations (ref. 16) on isostructural deltahedral boranes and metal clusters, e.g. octahedral $B_6H_6^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ demonstrated that these molecules had similar closed shell requirements because the d-d overlaps in the metal cluster were

rather small and the boranes and metal clusters shared a common set of unavailable skeletal molecular orbitals. The number of unavailable molecular orbitals was controlled for both transition metal carbonyl and main group clusters by the topology of the cluster. Specifically the following characteristic number of molecular orbitals (Table 1) were identified which had a high proportion of s and p orbital character and were unsuitable for either skeletal bonding or ligand bond formation, because they were strongly antibonding between skeletal atoms and were hybridised towards the centre of the cluster.

Since main group and transition metal atoms contribute 4n and 9n valence orbitals respectively this leads to the following characteristic closed shell requirements for polyhedral molecules (Table 2).

TABLE 1 Unavailable molecular orbitals in specific classes of polyhedral molecules

Polyhedral class	Number of unvailable m.o.'s
closo-	2n-1
nido-	2n-2
arachno-	2n-3
three-connected	3n/2
rings	n

TABLE 2 Summary of closed shell requirements for main group and transition metal polyhedral carbonyl clusters

Polyhedral class	Number of available m.o.'s Main group	Transition metal	Number of skeletal m.o.'s
closo-	2n+1	7n+1	n+1
nido-	2n+2	7n+2	n+2
arachno-	2n+3	7n+3	n+3
three-connected	5n/2	15n/2	3n/2
rings	3n	8n	n

This relationship between the number of unavailable molecular orbitals and the skeletal geometry was confirmed by molecular orbital calculations on a wide range of metal clusters by Lauher (ref. 17) and Ciani and Sironi (ref. 18).

The structures of cluster compounds such as $Os_6(CO)_{18}$ and $[Rh_7(CO)_{16}]^{3-}$ revealed capped geometries not previously observed in main group chemistry. The former has a capped trigonal bipyramidal structure and the latter a capped octahedral structure. A capping principle (ref. 19) was developed from Hoffmann and Lipscomb's molecular orbital calculations (ref. 5) to account for these structures. This molecular orbital analysis recognised that the capping process, which places an additional atom over the face of the parent cluster does not, in general, alter the number of bonding skeletal molecular orbitals Therefore, series of capped cluster compounds exist with the closed shell requirements summarised in Table 3.

TABLE 3 Summary of closed shell requirements for capped transition metal cluster compounds

Polyhedral geometry		Number of skeletal m.o.'s	Number of available m.o.'s
$Ru_6(CO)_{18}^{2-}$	octahedral	7 (n+1)	7n+1
$Rh_7(CO)_{16}^{3-}$	capped octahedral	7	7n
$Os_8(CO)_{22}^{2-}$	bicapped octahedral	7	7n-1
$Os_{10}(CO)_{24}^{2-}$	tetracapped octahedral	7	7n-3

Each capping atom causes an increment in the total electron count by 12, because it creates an additional three skeletal antibonding and unavailable molecular orbitals and only six available molecular orbitals. A more detailed molecular orbital analysis of the capping principle revealed situations where the generalisation would break down because of the absence of a suitable symmetry match between the orbitals of the capping atom and those of the parent polyhedron (ref. 20).

It is apparent from the discussion above that the structural principles which were developed in the 1970's had complicated origins and many chemists contributed independently to the final complex of ideas. The structural and electronic relationships are collectively described as either the Polyhedral Skeletal Electron Pair Theory (ref. 19) or Wade's Rules. The ideas have proved to be surprisingly useful for analysing the structures of a wide range of polyhedral molecules, however by their very simplicity there are a number of notable exceptions to the theory. These exceptions can be classified into various categories, which generally reflect the limitations of the basic assumptions.

Firstly, the assumption concerning the distribution of available and unavailable molecular orbitals depends critically on the presence of metal-ligand combinations which generally conform to the effective atomic number rule (ref. 21). In particular, metals in the middle of the transition series with π-acid ligands are most likely to conform to the generalisations. Platinum and gold clusters which form many complexes which have fewer valence electrons than that predicted from the effective atomic number rule also form clusters which deviate from the Polyhedral Skeletal Electron Pair Theory (ref. 22). Similarly, metals of the earlier transition metals with π-donor ligands do not conform to the generalisations. In these compounds it is not unusual for the metal-ligand fragments to donate four orbitals for skeletal bonding and thereby create additional unavailable molecular orbitals from the d_{xy} (delta symmetry) atomic orbitals (ref. 23).

Secondly, it was initially assumed that a particular skeletal geometry gives rise to a particular spectrum of molecular orbitals with a large h.o.m.o - l.u.m.o. gap and therefore is characterised by only one closed shell electron configuration. This is not always the case because certain skeletal geometries generate molecular orbitals in the frontier orbital regions which can remain unoccupied or utilised in bonding. This happens particularly in the lower symmetry clusters where the atoms no longer lie on a single spherical surface. The group theoretical aspects of this problem are now well understood and deltahedra which have multiple electron counts can be clasified as follows (ref. 24):

Polar deltahedra have a single atom on the three fold axis and have 3p + 1 (p is an integer) atoms can be associated with either n or n + 2 skeletal electron pairs (c.f. Table 2) where closo deltahedra are generally associated with n+1 skeletal electron pairs.

Bipolar deltahedra have two atoms on the principal rotation axis and can be characterised by either n+1 or n+3 skeletal electron pairs.

Non-polar deltahedra which have no atoms on the principal symmetry axis are characterised by either n, n + 1 or n + 2 skeletal electron pairs.

Examples, of these multiple closed shell requirements are particularly prevalent in metal clusters and metallocarboranes where the overlap integrals are smaller and therefore the h.o.m.o - l.o.m.o. gaps are sufficiently small to permit these alternative electron counts.

Thirdly, large differences in the electronegativities of the atoms or their mutual overlap integrals can lead to deviations from the closed shell requirements summarised in Table 2. Small atomic perturbations do not lead to major changes in the spectrum of molecular orbitals associated with the cluster polyhedron and therefore the closed shell requirements remain valid. However, large differences either in electronegativities or overlap integrals can lead to a spectrum of molecular orbitals which no longer bears a strong resemblance to that of the parent molecule and deviations from the generalisations result (ref. 25).

Finally, if the metal-ligand fragment does not have axial symmetry then the overlap integrals associated with the p_x and p_y (or d_{xz} and d_{yz}) may be very different and result in a large perturbation in the spectrum of molecular orbitals. The angular C_{2v} $Pt(PPh_3)_2$ fragment provides many examples of this type of behaviour and has been the subject of numerous detailed molecular orbital calculations (ref. 26).

ISOLOBAL ANALOGIES

In the 1960's Ligand Field Theory had taught the inorganic chemist much concerning the relative splittings of d orbitals in high symmetry transition metal complexes and the importance of the d electron count in influencing the sterochemistries, reactivities and stabilities of mononuclear complexes. The focus of the theory was very much the d orbitals of the transition metal and little attention was paid to the metal s and p orbitals. This methodology therefore was of little value for building up the molecular orbitals of a cluster compound from those of simpler metal containing fragments. In an important paper published in 1975 Hoffmann and Elian (ref. 27) demonstrated that the bonding capabilities of low symmetry metal carbonyl fragments depended on symmetry allowed orbital mixings between the metal d, s and p orbitals. In particular conical and angular $M(CO)_m$ fragments had hybrid orbitals pointing away from the ligands which had the appropriate directional qualities to overlap with the orbitals of other metal atoms, ligands or fragments. Moreover, the number and symmetry of these out-pointing hybrid orbitals could be predicted from a semi-localised description of the bonding. The fragments generally retained a memory of the localised orbitals of the parent 18

electron compound and created an out-pointing hybrid orbital for each ligand lost. For example, a d^6 conical $M(CO)_3$ fragment has three hybrid out-pointing orbitals which point towards the vertices of the parent $M(CO)_6$ octahedron. A knowledge of the frontier orbital characteristics of these fragments has proved to be invaluable for building up the molecular orbitals of more complex molecules. The numerous elegant papers by Hoffmann and his coworkers during the last 25 years bear testament to the importance of this methodology (ref. 28).

The recognition of the occurrence of these characteristic frontier orbitals also provided a direct connection with the Polyhedral Skeletal Electron Pair Theory ideas described above. The presence of three out-pointing hybrid orbitals in an $M(CO)_3$ fragment provided an analogy with a B-H fragment which also has three out-pointing hybrid orbitals. The similarity explained why metal carbonyl and borane clusters had a similar spectrum of molecular orbitals and their electron structures could be unified within a common set of electron counting rules. Hoffmann and Mingos (ref. 29) proposed the term <u>isolobal</u> to describe the similar bonding capablities of main group and transition metal fragments. This <u>isolobal</u> analogy has proved to be useful not only to account for the electronic structures of metal cluster compounds, but also as a useful method for selecting reagents for the designed syntheses of heterometallic cluster compounds. Gordon Stone and his group have been particularly effective in utilising these concepts (ref. 30).

A complete description of <u>isolobal</u> analogies has been given by Hoffmann (ref. 28) and will not be recounted here. It has proved to be an enduring and useful concept, although in common with many other central concepts in inorganic chemistry it is not without its ambiguities. Specifically, a particular $M(CO)_m$ fragment can be related not only to a parent octahedral 18 electron compound, but also trigonal bipyramidal d^8 and tetrahedral d^{10} 18 electron parents. Therefore, the number of hybrids utilised in bonding is variable and to a large extent depends on the bonding capablities of the fragment to which $M(CO)_m$ is attached. Similarly, it is generally assumed that in a $M(CO)_m$ fragment derived from an octahedron there is a set of t_{2g} non-bonding orbitals. However, these orbitals do not always remain non-bonding and can enter into strong π-bonding interactions. For example, $Cr(NH_3)(CO)_5$, $Cr(CO)_5(CR_2)$ and $[Cr(CO)_5(CR)]^+$ all contain the C_{4v} $Cr(CO)_5$ fragment but in the latter two examples the t_{2g} orbitals are involved in significant multiple bonding and can no longer be classified as non-bonding. Lower symmetry angular fragments can also provide difficulties for the <u>isolobal</u> analogy because of their ambiguous bonding capabilities. For example, the angular $Pt(PPh_3)_2$ fragment may be classified as <u>isolobal</u> with CH_2, BH or CH^- depending on the relative involvement of the metal p_y and d_{yz} metal orbitals.

MORE RECENT DEVELOPMENTS

In 1980 Anthony Stone (ref. 31) proposed a general theoretical model which accounted for the electron counting rules which had been defined by the Polyhedral Skeletal Electron Pair Theory. A particle on a sphere type free electron approach had been attempted previously to account for the bonding in such clusters, but had foundered because the wave functions which are tangential to the sphere defined by the cluster have p orbital contributions which have nodes at the atomic centre as well as those nodes between the atoms which define the relative bonding and antibonding character of the molecular orbital. Stone elegantly circumvented this problem by using vector harmonic functions to describe the tangential wave functions. This approach confirmed that deltahedral clusters are generally characterised by n + 1 skeletal electron pairs (approximately 1 radial and n tangential) and that metal clusters and boranes shared a common set of unavailable skeletal molecular orbitals (see Table 1). In a subsequent paper (ref. 32) Stone and Alderton demonstrated that the occurrence of n+2 and n+3 skeletal molecular orbitals in <u>nido</u>- and <u>arachno</u>- clusters was a direct consequence of the symmetry properties of the tangential molecular orbitals in clusters.

The group theoretical consequences of the Stone Tensor Surface Harmonic Model have been recognised by Ceulemans (ref. 33), Fowler (ref. 34) and Johnston and Mingos (refs. 24 and 35). These group theoretical analyses have provided an economical and general method for accounting for the apparent exceptions to the Polyhedral Skeletal Electron Pair Theory. They have also provided a basis for understanding the symmetry rules which govern the activation energies for intramolecular rearrangement processes in polyhedral boranes and clusters (ref. 36). These results are consistent with the diamond-square-diamond mechanism for polyhedral rearrangements first proposed by Lipscomb.

The Polyhedral Skeletal Electron Pair Theory was extended to condensed clusters in 1983 (ref. 37) and the theoretical basis of these ideas was analysed using Stone's Tensor Surface Harmonic Theory. The occurrence of condensed clusters originating from vertex, edge and face sharing in clusters is particularly prevalent in transition metal cluster chemistry and therefore these generalisations represented a useful extension to the capping principle proposed earlier.

The characterisation of very high nuclearity cluster compounds with up to fifty metal atoms during the last ten years has been a tremendous achievement by the chemists and crystallographers involved. These compounds generally have close packed structures of metal atoms, based either on cubic, hexagonal or icosahedral packing schemes. In these high nuclearity cluster compounds the connection between skeletal geometry and the total number of valence electrons is lost, but nonetheless their closed shell requirements can be estimated reasonably accurately from a polyhedral inclusion principle (ref. 38).

The role of interstitial atoms in metal cluster compounds continues to be an intriguing problem in cluster chemistry. In recent papers (refs. 39 and 40) we have discussed the manner in which diatomic C_2 fragments are stabilised in intersitial cluster sites and also speculated on the consequences of putting single carbon atoms into large interstitial cavities. The molecular orbital calculations have suggested that the carbon atoms in such an environment should be much more reactive towards electrophiles such as H^+.

SUMMARY

During the last twenty years the creative tension between experimentalists and theoretical chemists has provided a theoretical model which can account for the geometries and closed shell requirements of a very wide range of cluster compounds. There are of course exceptions to the generalisations, but many of them can be understood in terms of the deviations of the cluster geometry from spherical and can be analysed using a combination of group theory and perturbation theory ideas.

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