The Optimum Geometries of Transition Metal Clusters

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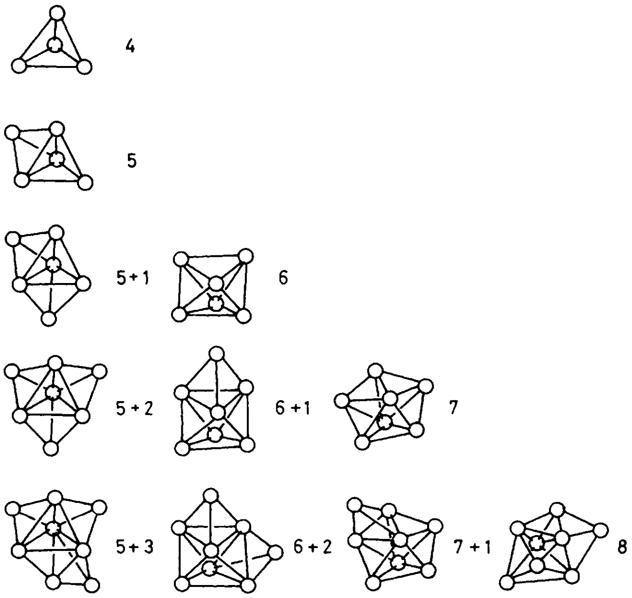
In comparison with the boranes, the polyhedral structures of transition metal cluster species are relatively compact; this difference is attributable to the important bonding effects of the valence d-electrons in transition metal clusters which favour cluster bonding based on close packing, and also show up in photoelectron spectroscopy.

The combination of semi-empirical molecular orbital calculations and symmetry arguments has led to some important generalisations which relate the observed structures of cluster compounds to their polyhedral skeletal geometries and their valence electron counts.[1] This note is intended to complement the usual electron counting rules; we have chosen to focus on the forces responsible for transition metal cluster bonding and comment on the kinds of cluster structures they may lead to.

Aggregates of inert gas atoms containing up to a few dozen atoms preferentially form polytetrahedral or polyicosahedral clusters.[2] Such a preference is not seen in the cluster species formed by main group elements such as boranes and their derivatives which form open or cage-like polyhedra. By contrast, transition metal cluster compounds, especially high nuclearity carbonyls, show a marked tendency to form more *compact* cluster structures, which are based on fused polyhedra (tetrahedra, octahedra *etc.*) or capped polyhedra, and represent 'low volume' structures (*see below*) for a given nuclearity. However, despite these significant variations in cluster structures, deltahedra *albeit* of different types (for example, octahedron or bi-capped tetrahedron) predominate cluster chemistry. These variations presumably reflect differences in the forces between cluster atoms, although, of course, it must also be recognised that most cluster species are ligated.

The openness of the boranes and carbaboranes can be readily understood in terms of the relative lack of bonding electrons in these species; their bonding through electron delocalisation over several centres is not comparable with the weak Lennard-Jones pair-potential interatomic interactions operative in inert-gas atom clusters.[2] While there is an extensive theoretical chemistry of first-row element cluster species much less quantitative information is available for transition metal species. For this reason we have chosen to base this comment on results from metal physics and relevant experiment information on metal cluster compounds.



Scheme 1. Possible deltahedra containing 4—8 vertices.

It can be shown that the *cohesive energy* per atom, U, at or near the equilibrium geometry in the bulk metals throughout the d-block of the Periodic Table is determined by the width, W_d, of the d band and the extent of its occupancy, measured by the number of d electrons per atom, N_d. In the close-packed periodic structures of the metals each atom has the same environment and W_d can be expressed in terms of the atomic radius S, the atomic connectivity Z, and the interatomic separation R.[3] The results of *quantitative* calculations of the electronic structure of the bulk metals can be given a simple but reasonably accurate representation by the formula (1),[3,4] where C is a constant related to the identity of the metal which need not be specified here. The significance of this formula is that it tells us that, provided the antibonding levels in the d band are incompletely filled ($N_d < 10$), the *d electrons alone* are effectively responsible for bonding between transition metal atoms; even in the Group 8 metals for which $7 < N_d < 9$, the bonds are reasonably strong by chemical standards.[4]

$$U \simeq N_d\,(10 - N_d)\,(W_d/20) = CN_d\,(10 - N_d)\sqrt{Z}\,(S/R)^5 \tag{1}$$

The fact that metal–metal bonds in cluster species have comparable lengths and strengths to those observed for bulk transition metals suggests that the electronic structure of a metal atom in a cluster cannot be very different from that of an atom in the bulk metal.[1,3] If so, equation (1) provides the basis for a working hypothesis for metal cluster energetics. From equation (1) the width of the d band, W_d, in a transition metal system, for fixed R, is proportional to $\sqrt{Z}$, so equation (2) applies, where K is a constant determined by equation (1). An approximate value for the 'd band width' in metal cluster species can be obtained by simple proportion [equation (3)], assuming that the bulk metal and the cluster have near enough the same metal–metal bond lengths. If there is a substantial difference a R^{-5} correction must be made in accordance with equation (1). This formula certainly works well when checked against SCF-MSW-X_α calculations on naked transition metal clusters;[5,6] given that some hybridization will occur between the cluster d band and the ligand-shell,[7] equation (3) is expected to give at least a *lower* bound to the d band widths of ligated metal clusters.

$$W_d = K\sqrt{Z} \tag{2}$$

$$W_d^{\mathrm{cluster}} = \left(\frac{Z^{\mathrm{cluster}}}{Z^{\mathrm{bulk}}}\right)^{1/2}.W_d^{\mathrm{bulk}} \tag{3}$$

Experimental evidence to support this approach is found in the results of photoelectron spectroscopy (p.e.s.) of metal

Table 1. A comparison of calculated and experimental d-band widths for some metal cluster carbonyls.

Cluster	Z/R^5 formula	Chemical pseudopotential	E.H./CNDO	Photoelectron spectroscopy
$Co_4(CO)_{12}$	2.2	—	—	$2.5 \pm 0.5^{a,b}$
$Co_6(CO)_{14}^{4-}$	2.5	3.2^{c} (2.4 for bare Co_6)	1.1^{d}	—
$Ru_3(CO)_{12}$	2.7	3.4^{c}	1.9^{e}, 3.0^{f}	$3.0 \pm 0.5^{b,f}$
$Ru_6(CO)_{18}$	3.8	—	2^{g}	—
$Ir_4(CO)_{12}$	3	—	—	3.5 ± 0.5^{b}
$Os_3(CO)_{12}$	2.9	3.7^{c}	—	3.0 ± 0.5^{b}
$Os_6(CO)_{18}$	4	4.3^{c}	—	4.0 ± 0.5^{a}
$Pt_3(CO)_6^{2-}$	4	4.5^{h}	1.5^{i}	—
$Fe_3(CO)_{12}$	2.1	2.0^{j}	—	2.0 ± 0.5^{b}

[a] Ref. 8. [b] Ref. 9. [c] D. W. Bullett, CRAY1 calculations at MPI, Stuttgart (1984/1985), and *Chem. Phys. Lett.*, 1987, in the press. [d] D. M. P. Mingos, *J. Chem. Soc. A*, 1974, 133. [e] D. R. Tyler, R. A. Levenson, and H. B. Gray, *J. Am. Chem. Soc.*, 1978, **100**, 7888. [f] D. Ajo, G. Granozzi, E. Tondello, and I. Fragala, *Inorg. Chim. Acta*, 1979, **37**, 191. [g] S. D. Wijeyesekera and R. Hoffmann, *Organometallics*, 1984, **3**, 949. [h] Ref. 10. [i] D. J. Underwood, R. Hoffmann, K. Tatsumi, A. Nakamura, and Y. Yamamoto, *J. Am. Chem. Soc.*, 1985, **107**, 5968. [j] D. W. Bullett and E. P. O'Reilly, *Surf. Sci.*, 1979, **89**, 274.

cluster compounds. Some p.e.s. data for metal cluster carbonyls[8,9] are reported in Table 1 together with values estimated from equation (3) and results from a variety of molecular orbital methods. In making comparisons between calculated d-band widths and p.e.s. results we quote the experimental values to within ±0.5 eV; this range is large enough to accommodate the band broadening effects of vibrational progressions (0.1 eV) and spin–orbit coupling (possibly ≈0.5 eV in 5d metals, otherwise unlikely to be important) which are not explicitly included in the calculations. In a tetrahedral cluster for example, $Z = 3$, so that $W_d^{\text{cluster}} = 1/2 W_d^{\text{bulk}}$ since the connectivity in both hexagonal and cubic close packing is 12; for $Co_4(CO)_{12}$ a value of $W_d = 2.2$ eV is calculated on this basis (R^{-5} corrections based on the crystallographic data for these clusters and the bulk metals have been included in the values reported in Table 1). Table 1 shows that the metal physics results are generally quantitatively superior to the semi-empirical quantum chemistry methods and this gives us some confidence in the use of the concept of d electron metal–metal bonding in transition metal cluster chemistry. It should be recognised however that the $\sqrt{Z}$ formula derived for the ideal bulk metals cannot be expected to be completely accurate for clusters containing non-equivalent metal atoms, and we do not use it to discriminate between closely related cluster structures. Mulliken population analyses of calculations for metal cluster carbonyls show N_d values close to those found in the corresponding bulk metals;[10] this fact, taken together with the satisfactory estimation of W_d^{cluster} using the $\sqrt{Z}$ formula, equation (3), leads us to expect that similar forces are important in clusters and bulk systems. In this respect we disagree with the view expressed in Section 2 of ref. 1 which discounts a bonding role for the d band in Group 8 metal cluster compounds.

We now return to a discussion of cluster structures. It is not difficult to justify the idea that deltahedra, as opposed to polyhedra containing square, pentagonal, or hexagonal faces, are energetically the most stable, since equation (1) shows that the cohesive energy increases with increasing Z. Other things being equal, therefore, one should expect structures in which Z is maximized, *i.e.* deltahedra, since they possess the greatest connectivities for a fixed number of vertices; *e.g.* in the regular octahedron all connectivities = 4, whereas in the trigonal prism all connectivities = 3. A similar argument can be made for main-group element cluster species, at a qualitative level at least, since semi-empirical molecular orbital theories suggest that the one-electron energy in clusters bonded *via* s- and p-electron interactions should be directly proportional to the connectivity Z with a distance dependence of about R^{-3}. The differences in cluster volume need further consideration however.

The interaction energy in a bulk transition metal can be expressed quantitatively in the form of a pair-potential[4] [equation (4)], where R is the interatomic separation as before. It may be helpful to note here that equation (4) is completely analogous to the use of Lennard-Jones potentials for inert gas atom clusters[2] (and also to the Born–Mayer pair potential model conventionally used to describe closed shell ionic crystals); here the metal–metal bonding is due to covalency mediated by the d electrons. The d electron interactions are *strongly attractive*, whereas the 'sp' electrons give rise to *repulsive* interactions when R is near the equilibrium metal–metal distance which is fixed by the condition that the attractive and repulsive forces on each atom should just balance; equation (4) evaluated at $R = R_{eq}$ determines the cohesive energy in equation (1). Since the repulsive forces involve the metal atom cores and are quite short range,[4] *compact structures* are to be expected for aggregates of transition metal atoms.

$$\underset{\text{(d component)}}{E(R) = E(R)^{\text{att.}}} + \underset{\text{('sp' component)}}{E(R)^{\text{rep.}}} \qquad (4)$$

Calculations of the volumes occupied by m-vertex polyhedra (Table 2) confirm that, in general, the most compact structures, at least for moderately small values of m, are those produced by face-sharing tetrahedra; for example, the octahedron occupies more space than the triple tetrahedron, and the pentagonal bipyramid has a greater volume than the quadruple tetrahedron. In Scheme 1 we present a systematic arrangement of the series of possible deltahedra for given values of m; within any one series all deltahedra have the same number of vertices, edges, and faces in accordance with Euler's theorem. They are inter-related by the simple migration of *one* edge and so might be interconverted by facile low-energy processes. As one progresses across any one given line of structures, *e.g.* $m = 7$, tricapped tetrahedron, monocapped octahedron, to pentagonal bipyramid the

Table 2. Volumes occupied by some simple compact polyhedra. Three dimensional figures may be characterised by the geometrical invariant $I = S/V^{2/3}$, where S is the surface area and V the volume. In these calculations the length of the polyhedral edge is taken as 2.

Figure	I	S	V	Vertices
Tetrahedron	7.206[a]	3.464	0.3333	4
Trigonal bipyramid	6.810[a]	5.196	0.6666	5
Bicapped tetrahedron	6.928	6.928	0.9999	5 + 1
Octahedron	5.719[a]	6.928	1.3333	6

[a] Taken from P. Pearce, 'Structure in Nature is a Strategy for Design,' The MIT Press, Cambridge, Massachusetts, 1978, p. 155.

geometric unit occupies an increasing volume. In each case, the polytetrahedral structure is the most compact, possesses the greatest cohesive energy, and is *electron-precise* according to the conventional electron counting rules. The less compact structures, *e.g.* the monocapped octahedron, are electron deficient, but also possess a lower cohesive energy. The very open structures found to the extreme right of each series, *e.g.* the pentagonal bipyramid, are the *least* compact, have the lowest cohesive energies, and require, at least according to current bonding theories, the smallest number of cluster bonding electrons.

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