Ligand–Ligand Interactions and the Structures of Simple Binary Carbonyls

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Summary Non-valence interactions are calculated for a number of ligand polyhedra and shown not to be a singly important factor in determining the structures of simple binary transition metal carbonyls.

Johnson has proposed recently[1] that the structures of simple binary carbonyls can be rationalised, for a given arrangement of metal atoms, by the carbonyl polyhedra being determined by close-packing principles (hard sphere interactions). Thus for first row metal carbonyls such as $[Fe_3(CO)_{12}]$, the mixed bridging–terminal carbonyl arrangement was held to approximate an icosahedral geometry whereas in the isoelectronic ruthenium and osmium complexes, with their larger metal–metal bond lengths, the carbonyl ligands are distributed over the metal polyhedra so as to approximate a semiregular cuboctahedron.

There are two points of concern. Johnson[1] proposed an effective 'radius' for co-ordinated carbon monoxide of 3·02Å, a value which is much less than the van der Waals diameter of carbon monoxide itself; the theoretical justification for the assumed value needed to be determined. Secondly, the actual ligand arrangements are not close approximations (*vide infra*) to the regular and semiregular polyhedra and it seemed useful to study, rather more quantitatively, the ligand–ligand interactions in the observed structures.

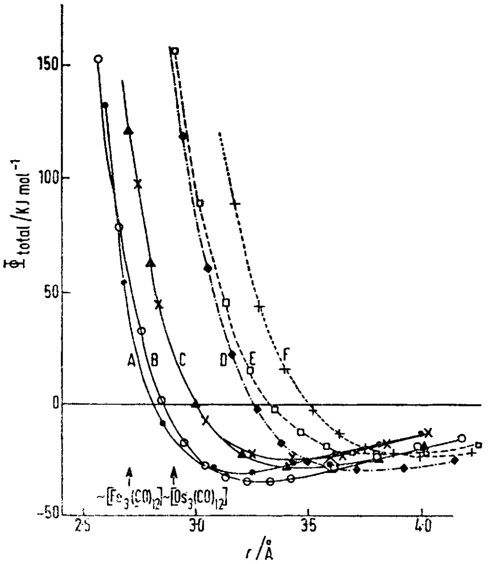

Figure. The interligand non-bonded interactions in carbonyl polyhedra. (A) icosahedron with Lennard–Jones molecule–molecule potential functions (ref. 3); (B) icosahedron with atom–atom potential functions (ref. 5); (C) cuboctahedron based on summation of atom–atom (ref. 5) and molecule–molecule (X) (ref. 3) interactions; (D) hexagonal antiprism; (E) hexagonal prism; and (F) truncated tetrahedron, all based on atom–atom potential functions (ref. 5). r is the distance (Å) from the centre of the polyhedron to the carbon atoms.

The non-valence interactions in metal carbonyls have been calculated through two models to ensure that our conclusions are not closely dependent upon the adopted intermolecular potential energy function. Firstly (spherically symmetric) molecular interactions were summed *via* Lennard–Jones (6-12)[2] or (6-exp)[3] expressions.† The Figure shows the total ligand–ligand potential energy summed *via* the 6-exp potential; the 6-12 function gave very similar results. Potential energies based on the Hill equation[4] are different only in that they have a less steep repulsive interaction. Equally the Figure demonstrates that the potential energies, summed *via* the pairwise atom potentials of Dashevsky,[5] are very similar to the molecule–molecule results. The atom–atom calculations have been extended to the cases of other semiregular polyhedra (Figure).

The potential energies, shown as a function of the distance r from the centre of the polyhedron to the carbon atoms, have been summed only for nearest neighbour interactions and assume a linear centre–C–O bond angle and a C–O bond distance of 1·2 Å. We can conservatively conclude the following.

(i) For a given total potential energy, and within the experimental range of bond distances in metal clusters, the size of the central hole, which Johnson argues[1] is of importance, follows the sequence icosahedron < cuboctahedron < hexagonal antiprism < hexagonal prism < truncated tetrahedron. Johnson's order for preferred carbonyl polyhedra is icosahedron < cuboctahedron < puckered bihexagon < eclipsed bihexagon, as the metal cluster changes from Fe_3 to Ni_6 and Pt_6; that sequence is consistent with the calculations. Perhaps, more importantly, we note that for $\Phi_{total} = 0$ (effectively the hard sphere approximation), we have 'limiting radii', r as follows: icosahedron 2·86, cuboctahedron 3·01, hexagonal antiprism 3·26, hexagonal prism 3·33, and truncated tetrahedron 3·50 Å. Johnson, apparently from observations of average non-bonded distances in actual structures, gives values of 2·86 and 3·02 Å respectively for the icosahedron and cuboctahedron.

(ii) More disconcertingly, our calculations show no reason, on the basis of ligand–ligand interactions alone, for abandoning the icosahedron for a cuboctahedral ligand array as the size of the metal skeleton is increased. The potential curves become coincident and cross at $r \geqslant 3·7$ Å and, for the *idealised* arrangements of carbonyl ligands in $[Os_3(CO)_{12}]$ ($r = 2·9$ Å), the icosahedral geometry (Φ_{total} -10 kJ mol^{-1}) is 30 kJ mol^{-1} more stable than that of the cuboctahedron (Φ_{total} 20 kJ mol^{-1}); for $[Fe_3(CO)_{12}]$ (r *ca.* 2·7 Å) the *idealised* icosahedral arrangement (Φ_{total} 60 kJ mol^{-1}) is 60 kJ mol^{-1} more stable than that which can be calculated for a cuboctahedral array (Φ_{total} 120 kJ mol^{-1}). There is nothing really surprising about this result since the total bonding energy of the cluster will include substantial metal–ligand and metal–metal overlap terms. It is implicitly presumed,[1] however, that these do not depend

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† Multipolar interactions make only a small contribution to the lattice' energy and to the determination of the equilibrium geometries of three-dimensional and two-dimensional molecular arrays (R. Mason in 'Perspectives in Structural Chemistry,' Vol. III, eds. J. D. Dunitz and J. A. Ibers, Wiley, New York, 1970: T. A. Clarke, I. D. Gay, and R. Mason, *Surface Sci.*, 1975, **50**, 137).

markedly on whether the ligand geometry is icosahedral or cuboctahedral. In short, the polyhedral hole radii do not have an upper limit determined by ligand–ligand interactions; rather these depend more on the geometry of the ligand polyhedron and not on the average radius found in typical cluster molecules.

(iii) The binary carbonyls have structures in the solid state whose ligand arrangements deviate considerably from icosahedra or cuboctahedra. Thus pairwise ($r < 4{\cdot}5$ Å) summations of the ligand–ligand interactions for the *observed* structures of $[Fe_3(CO)_{12}]$[6] and $[Os_3(CO)_{12}]$[7] show that they are respectively 30 and 32 kJ mol^{-1} more repulsive than those in an idealised icosahedron and cuboctahedron. Placing three or four carbonyl ligands on a single metal atom, obviously to maximise metal–ligand bond energies, inevitably leads to strong interligand repulsions.

It seems that any calculations based on the observed structural arrangements have less predictive value than those relating to ideal polyhedra which, as Johnson suggests, reflect some of the general trends in the structural chemistries of cluster species. We note finally a rather obvious result: the larger the cluster, the more regular the carbonyl arrangement and ligand–ligand interactions may indeed be the predominant structure determining factor. Thus the ligand–ligand interactions in the observed (bicapped tetrahedron) structure[8] of $[Os_6(CO)_{18}]$ are more stable by *ca.* 23 kJ mol^{-1} than those which can be calculated for an octahedral arrangement {such as is found in $[H_2Ru_6(CO)_{18}]$[9] and, in fragment form, in $[Os_7(CO)_{21}]$[10]}. However, the general separation of ligand interactions as the major factor discriminating one structure from another does not seem justified. Factorisation of the structure-determining parameters may come from a self consistent force field study of the binary carbonyl which we have in hand.

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