The Structures and Fluxional Behaviour of the Binary Carbonyls; A New Approach. Part 2.† Cluster Carbonyls $M_m(CO)_n$ (n = 12, 13, 14, 15, or 16)

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A systematic quantitative survey of available n-vertex polyhedra for n = 12, 13, 14, 15, and 16 has been carried out and an examination of the extent to which carbonyl positions approximate to regular or semi-regular polyhedra made. It has been shown that the structures of many carbonyl clusters, including the distribution of terminal, edge-bridging, and face-bridging carbonyl groups, may be rationalised in terms of a simple model. This model is based on the observation that carbonyl ligands pack in space so as to minimise non-bonded interactions and that the structure of $M_m(CO)_n$ clusters is merely a reflection of the insertion of the M_m polyhedron within this $(CO)_n$ polyhedron.

DURING the last 20 years, X-ray crystallographic structure determinations of many transition-metal cluster carbonyls have been carried out, and it has been found that the carbonyl ligand can have several modes of coordination. As well as a terminal group, bonded to a single metal atom,[1] CO can act as a bridging ligand. The doubly- (or edge-) bridging carbonyl group may span a metal–metal bond symmetrically, as in $[Fe_3(CO)_9(PMe_2Ph)_3]$,[2] or with varying degrees of asymmetry, as in $[Fe_4(CO)_{13}]^{2-}$.[3] A metal–metal bond may be associated with a single carbonyl bridge, as in $[Co_4(CO)_{12}]$,[4] or with two, as in $[Fe_3(CO)_{12}]$.[5] Triply- (or face-) bridging carbonyl groups, spanning a triangular face of a metal cluster, are also known, for example in $[Rh_6(CO)_{16}]$.[6]

An intriguing problem has been the occurrence of different structural types in closely related compounds. for example, $[Co_4(CO)_{12}]$ [4] and $[Rh_4(CO)_{12}]$ [7] have molecular structures of C_{3v} symmetry, with both edge-bridging and terminal carbonyl groups, but the corresponding compound of the third member of this transition-metal triad, $[Ir_4(CO)_{12}]$, has T_d symmetry, with all carbonyls terminal.[8]

In addition, the metal clusters themselves show a wide variety of geometries. In $[Rh_6(CO)_{16}]$ the Rh_6 unit is octahedral,[6] but in $[Os_6(CO)_{18}]$ the Os_6 cluster is a bicapped tetrahedron.[9] Several attempts have been made to rationalise the observed metal cluster shapes,[10,11] and although no single theory can yet account for all observed structures, significant progress has been made.

However, no systematic attempt has yet been made to investigate and rationalise the distribution of carbonyl ligands in such clusters. Several proposals have been advanced to explain the occurrence of bridging carbonyls,[12] in particular that they serve to delocalise surplus negative charge around the cluster,[13] but none may be regarded as satisfactory.

It has been noticed by several researchers reporting individual crystal structures that the carbonyl ligands in these cluster molecules occupy positions which define (to a fair approximation) the vertices of regular and semi-regular polyhedra. In the crystal structure of the anion $[Fe_3H(CO)_{11}]^{-14}$ the position of the hydride ligand (undetectable by X-rays in the presence of a large number of heavy atoms) was deduced to be the 'missing' vertex of the *nido*-icosahedron defined by the 11 carbonyls. The structure of $[Fe_3(CO)_{12}]$ was correctly surmised from this observation (the twelfth carbonyl completing the icosahedron) at a time when crystal disorder in $[Fe_3(CO)_{12}]$ itself had prevented its detailed structure determination.

The dodecacarbonyls, $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$, which might be expected to have the same structure as $[Fe_3(CO)_{12}]$, possess the all-terminal structure in which the carbonyls define an anticuboctahedron.[15,16]

In 1975 it was proposed [17] that an important factor governing the structures of cluster carbonyl molecules and anions $[M_m(CO)_n]$ is the interaction between the carbonyl groups. The n carbonyls form a polyhedron which represents the most favourable way of packing them in space, and the M_m unit then orients itself inside this polyhedron so as to maintain close contact between the metal atoms and the surrounding carbonyl ligands. This orientation may be deduced from consideration of the sites available within the (CO)-polyhedron. It was assumed that the idealised geometry of the M_m unit is known; this may usually be derived by Wade's method.[11]

Thus, in $[Fe_3(CO)_{12}]$ the carbonyls define an icosahedron, and the bridged structure of C_{2v} symmetry arises as a simple consequence of placing a triangle of iron atoms within this icosahedron. However, although the icosahedron is the most favourable way of 'close packing' 12 carbonyls, there is insufficient space inside it to accommodate the larger Ru_3 and Os_3 triangles. Hence the molecules $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ possess the slightly less favourable anticuboctahedral packing of ligands, within which there is a larger interstice. It follows that these two molecules have the all-terminal D_{3h} structure.

The carbonyl ligand was assigned an effective radius of 3.02 Å and calculations were made on the basis of the close packing of spheres, to give the maximum size of metal-atom cluster that could be accommodated within a variety of 12-vertex polyhedra. A number of molecular structures could be explained by this method.

This proposal has been criticised on several grounds.[18] Firstly, the empirically derived 'hard-sphere radius' of

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† Part 1 is ref. 19.

3.02 Å for the CO ligand was criticised as being less than the van der Waals radius of carbon monoxide itself. However, in the real structures that had been considered, observation of the sizes of metal-atom clusters that could indeed occupy the central interstices of icosahedra and cuboctahedra (the sizes of which could be easily calculated from classical geometry) led to the conclusion that the carbonyl ligands behave as though they approximate to this radius. Moreover, the non-bonded contacts between carbonyl carbon atoms are considerably shorter than the van der Waals distances.

The second objection was that in molecules with many strong M–M and M–C bonds, non-bonded interactions could not govern the structure as their energy differences for different possible structures would be much smaller in magnitude than those arising from the bonding interactions.

The answer to this objection lies in the fluxional behaviour of cluster carbonyls in solution. At relatively low temperatures the carbonyl groups are shown by ^{13}C n.m.r. spectroscopy to be mobile over part or all of the metal cluster.[19] Transition states for the carbonyl scrambling processes involve the movement of terminal carbonyls into bridging positions, and *vice versa*, so that the molecules attain structures different from the ground state. Activation energies for such processes are sometimes very low {less than 5 kcal mol^{-1} * in the case of $[Fe_3(CO)_{12}]$[20]}, so it can be concluded that the adoption of a particular solid-state structure depends upon a fine balance of factors. Consideration of the sets of ligand orbitals available for bonding shows that there is essentially no difference between an icosahedron and a cuboctahedron as regards bonding capability to a metal cluster within the polyhedron.[21] If the large sum of the M–C bonding energies is nearly constant for the various available structures, the relatively small non-bonded repulsions between carbonyl groups will be important, and their optimisation *may* govern which overall structure is adopted. This may be a surprising conclusion but it is one based on the observation of real structures. The anion $[Ru_4H_3(CO)_{12}]^-$ has recently been shown to have two alternative solid-state structures even for very similar crystallisation conditions,[22] illustrating the delicate balance of forces involved.

Thirdly, it was pointed out [18] that in real molecular structures, the polyhedra defined by the carbonyl groups are ' not close approximations ' to the idealised polyhedra. It should be noted that the nature of the distortions from ideality may often be predicted; for example in $[Fe_3(CO)_{12}]$ the flattening of the icosahedron of carbonyls arises as a simple consequence of the need to bond to a flat metal-atom triangle within the ligand envelope. This does not alter the significance of the observation that, to a first approximation, the carbonyls do define an icosahedron. Some results on the quantitative effect of such distortions on the non-bonded repulsion energies are presented in this work. We show that the rationalisation of structures on the basis of optimisation of non-bonded interactions is valid for most metal cluster carbonyls, provided that the metal cluster has a shape which is reasonably spherical. Where its geometry is extremely anisotropic the need to maintain reasonable metal–carbonyl bonding distances becomes the most important structural factor. It is assumed that the metal-cluster geometry is predetermined by the number of electrons available for cluster bonding.[11]

Additionally, if the cluster is heterometallic, the different transition-metal atoms must not have greatly differing electronic requirements, which might impose restrictions on the co-ordination pattern of carbonyl groups.

Although the species possessing 12 carbonyl groups had been thoroughly examined and compared with the available 12-vertex polyhedra (some of which have been known for over 2 000 years), no study had been made of clusters with other numbers of carbonyl ligands. It had been observed that in some structures the carbonyls appear to define semi-regular polyhedra, but little information was available on the relative favourability of the possible n-vertex polytopes ($n \neq 12$).

The object of the present work has been to carry out a systematic quantitative survey of available n-vertex polyhedra, and to see to what extent carbonyl positions in clusters approximate to idealised close-packed structures. New results are presented for the cases $n = 13$, 14, 15, and 16.

METHOD OF CALCULATION

The strategy employed was to calculate the most favourable arrangements of points on the surface of a sphere, for numbers of points between 12 and 16. This acted as a model for predicting the polyhedral arrangement of carbonyl ligands in transition-metal cluster compounds $[M_m(CO)_n]$ ($12 \leqslant n \leqslant 16$).†

In addition, the relative favourability of different polyhedral forms was calculated; this gives a measure of how important a factor the non-bonded ligand interactions might be in governing overall molecular structure. Were the various available polyhedra to have almost identical repulsion energies, then non-bonded interactions would be insignificant in comparison with the other energy terms involved.

Procedure.—The ligands are constrained to lie on the surface of a sphere. The non-bonded repulsion between two ligands i and j is assumed to be proportional to the inverse q-th power of the distance R_{ij} between them, so that the total repulsion energy is as in (1) where the sum

$$E \propto \sum_{i \neq j} R_{ij}^{-q} \qquad (1)$$

is over all pairs of ligands. As the distance between a pair of points on a sphere is proportional to the angular distance Ω between them, we can write (2) for ease of calculation in

$$E \propto \sum_{i \neq j} \Omega_{ij}^{-q} \qquad (2)$$

spherical polar co-ordinates; this is the energy function to be minimised.

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* Throughout this paper: 1 cal = 4.184 J.

† Calculations have also been made for $n = 8$, 9, 10, and 11, but as the structures of carbonyls with these numbers of ligands {such as $[Fe_2(CO)_9]$} have been dealt with in a qualitative account elsewhere,[23] these results are not included here.

We would mention that if an attractive term were also included in the potential-energy expression (to give a Lennard-Jones type of expression), not only would the optimisation of the total energy be a much more difficult computational problem, but precise values of constants of proportionality would also be required. We are currently attempting further calculations along these lines. The exponent q may have any value, but throughout this work has been taken to have the reasonable value of six.

A detailed description of this methodology has been given by Claxton and Benson,[24] who investigated the optimum arrangement of seven ligands about a central atom, a controversial problem in Valence Shell Electron Pair Repulsion (Nyholm and Gillespie) Theory. An alternative approach, mentioned by them, would be to maximise the smallest distance between two adjacent points on the sphere; this method has been used only occasionally,[25] and its results do not correspond well to polyhedra observed in real molecules.

Polyhedra with up to ten vertices have previously been investigated as models for co-ordination spheres about large transition-metal, lanthanide, and actinide atoms.[24, 26-30] In general, there is no qualitative difference in the results obtained for different chemically reasonable values of q in $\sum_{i \neq j} R_{ij}^{-q}$. Calculations have also been carried out by Knop and co-workers [31] on polyhedra with up to 16 vertices, with the aim of finding the optimum form at various values of the exponent as it tends towards infinity (the 'hard-sphere approximation'). King [32] made quantitative calculations for the cases of ten and 12 vertices and listed possible polyhedral forms for up to 16 vertices, subject to restrictions on overall symmetry. These researchers stated explicitly that species of such high co-ordination number remain unknown; in no case has the arrangement of ligands around metal *clusters* been investigated in this way.

A systematic investigation of co-ordination polyhedra with nine and ten atoms led to the conclusion that the energetically most favourable polyhedra were those with triangular faces throughout.[28] This agrees with the conclusion of Frank and Kasper,[33] who described structures observed in metal alloy systems, and has relevance to the current work, as will be discussed below. The various nine-vertex polyhedra have been examined to find readily available distortions that could interconvert them; [27] energy barriers to fluxionality of nine-co-ordinate molecules could thus be estimated. This approach too is of importance in cluster carbonyls.[19]

The calculations presented here were performed using the program POLYTOPE, written by Dr. A. J. Stone. Polyhedra are described in terms of Föppl notation,[34] which specifies the number of vertices in successive latitudinal planes. For example, the icosahedron may be described as 1 : 5 : (5) : 1, possessing one vertex at each pole, separated by two layers of five vertices, each of which is a planar regular pentagon. The parentheses are used to indicate that the second plane of five is in a staggered orientation relative to the first.

Input data for the program consist of a polyhedron described in spherical polar co-ordinates in terms of this notation; we can define the number of vertices that are to be in each successive layer. The program then minimises $\sum_{i \neq j} \Omega_{ij}^{-q}$ whilst preserving these initially defined layers of vertices as regular polygons, all points being maintained on the surface of a sphere. We can also choose the value of the exponent q. The value obtained for the optimum repulsion energy is in unscaled units, but we can list various polyhedra in order of favourability.

To find the optimum arrangement of n points, we merely set n independent points free on the surface of the sphere. One may be fixed at a pole ($\theta = 0, \phi = 0$) to give two fewer independent variables; this simply defines the co-ordinate axes in advance.

To find less favourable forms, we specify individual polyhedra in terms of Föppl notation. For a thorough study we must calculate the energies of all possible polyhedra for each value of n; this becomes a very lengthy procedure as the number of vertices n increases, because of the large number of polyhedra involved. If for example we are listing all 13-vertex polyhedra with four latitudinal layers of vertices, the problem is essentially to find all combinations of four integers which add up to 13. Then polyhedra with five layers of vertices must be considered, and so on.

For a cluster molecule $[M_m(CO)_n]$ with a roughly spherical metal cluster surrounded by an envelope of n identical neutral ligands, the predicted ligand polyhedron is that with the minimum non-bonded repulsion energy $\sum_{i \neq j} \Omega_{ij}^{-q}$. This is subject to the central interstice of the polyhedron being sufficiently large to accommodate the M_m cluster. The metal cluster will orient itself within the (CO)-polyhedron to optimise the metal-carbonyl bond strengths, and from this will follow the configuration of terminal, edge-, and face-bridging carbonyls in the molecule. Alternative forms of the ligand polyhedron will be those closest in energy to the optimum form, although the difference in repulsion energy between various (CO)-polyhedra is expressible only as a percentage change.

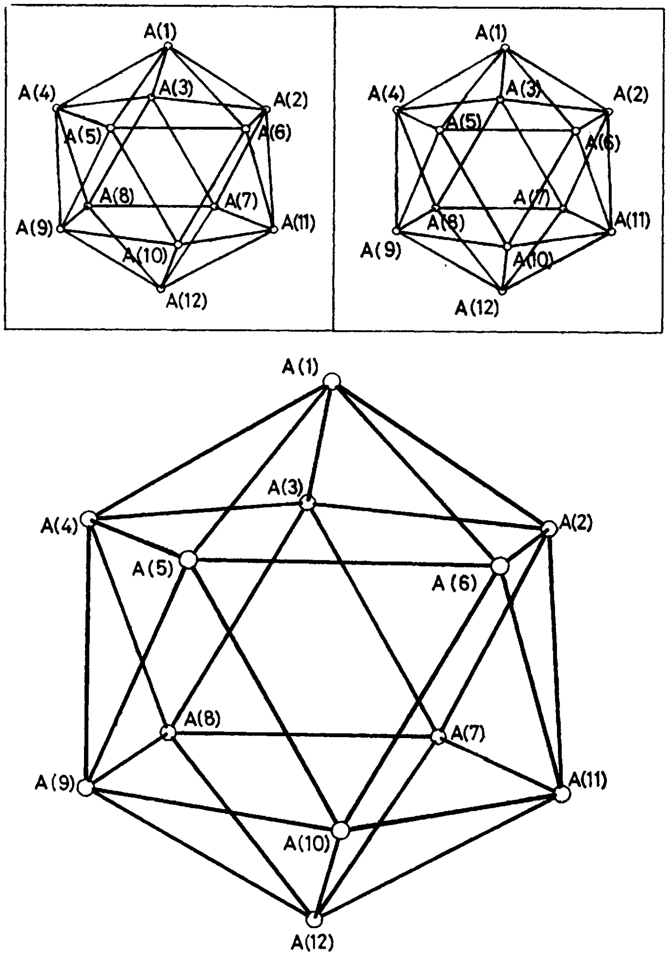
The above scheme may possibly be extended to cluster carbonyls in which some ligands have been substituted by tertiary phosphines. In this case there is an additional variable: the steric bulk of different phosphines.[35]

We have compared the structures of cluster carbonyls which have been determined by *X*-ray crystallography with the predictions of the above method. In most publications of structures, attention is focused on the metal-cluster geometry and upon whether or not there are bridging carbonyls. However, provided that crystallographic co-ordinates are available, the polyhedron defined by the carbonyl groups may be investigated.

A primary assumption [17] has been that the CO ligand has a fixed effective radius. In real metal-carbonyl structures, as the M-C distance varies, there is a more or less equal and opposite change in the C-O distance. This is merely a statement of the synergic effect. Thus the M $\cdots$ O distance is not especially sensitive to either the atomic number of the metal or the charge on the complex. Hence it may be seen that the polyhedron described by the carbonyl groups is best represented by the arrangement of oxygen atoms, and throughout this work all references to $(CO)_n$ polyhedra are concerned with those designated by the oxygen atoms.

For each crystal structure, the polyhedron defined by the carbonyl oxygen atoms is drawn using the computer program PLUTO, written by Dr. W. D. S. Motherwell. By inspection of the arrangement of vertices it may be seen whether the ligand polyhedron corresponds to that predicted on the basis of optimisation of non-bonded interactions.

A more quantitative examination of the real oxygen-atom polyhedra may be carried out by analysis of the crystallographic co-ordinates. Using a modification of a program written by Dr. P. R. Raithby, the co-ordinates are converted to spherical polars, taking as the origin the mean of all the oxygen-atom co-ordinates. Each oxygen atom has its own values of (r, θ, ϕ); the standard deviation in the lengths of the radius vectors r_i is calculated, to give a measure of the accuracy of fit onto the surface of a sphere. Input of these co-ordinates (θ, ϕ) to the program POLYTOPE, holding them fixed instead of optimising (an option available in the program), enables the 'real' value of $\sum_{i\neq j} \Omega_{ij}^{-6}$ to be calculated as a single number whose excess over the ideal value indicates the degree of deviation from the ideal form. This involves varying the lengths of the radius vectors r_i so that all the oxygen atoms lie on the surface of the sphere, a procedure previously introduced in the analysis of dihedral angles between faces of ligand polyhedra.[28, 36]



	θ	ϕ
1	0·0	0·0
2	63·435	0·0
3	63·435	72·000
4	63·435	144·000
5	63·435	216·000
6	63·435	288·000
7	116·565	36·000
8	116·565	108·000
9	116·565	180·000
10	116·565	252·000
11	116·565	324·000
12	180·000	0·0

FIGURE 1 The icosahedron. Mono and stereo views, and co-ordinates

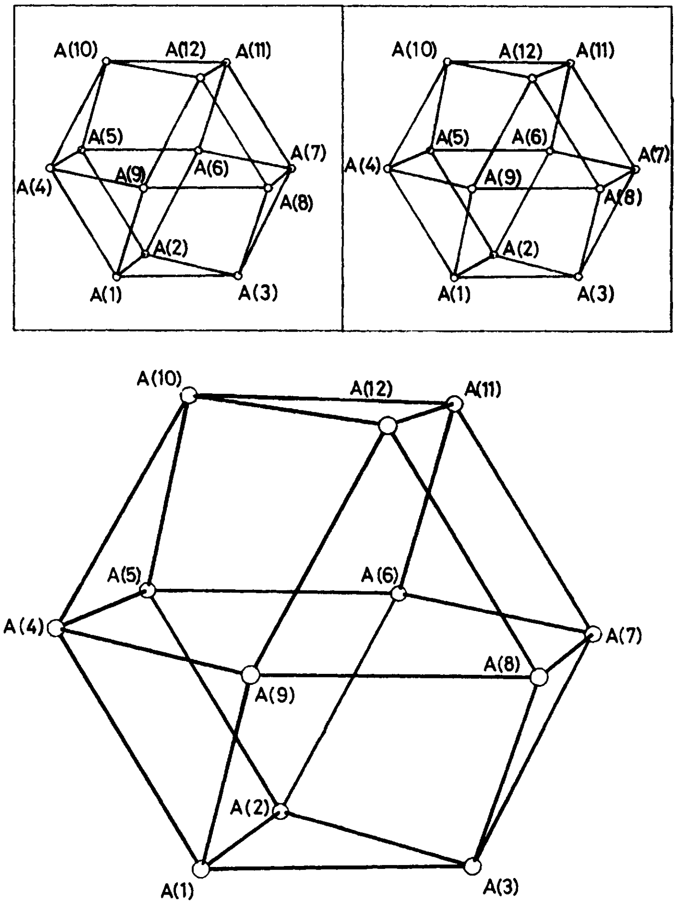
TABLE 1

The three most favourable 12-vertex polyhedra

Order of favourability	Description	Energy $\sum_{i\neq j}\Omega^{-6}$	Percent above minimum
1	1 : 5 : (5) : 1 icosahedron	16.718	
2	4 : (4) : 4 or 3 : 6 : (3) cuboctahedron	19.288	15.37
3	3 : 6 : 3 anticuboctahedron	19.297	15.42

RESULTS

For n = 12.—Molecules with 12 carbonyl groups have already been dealt with [17] and will be surveyed only briefly

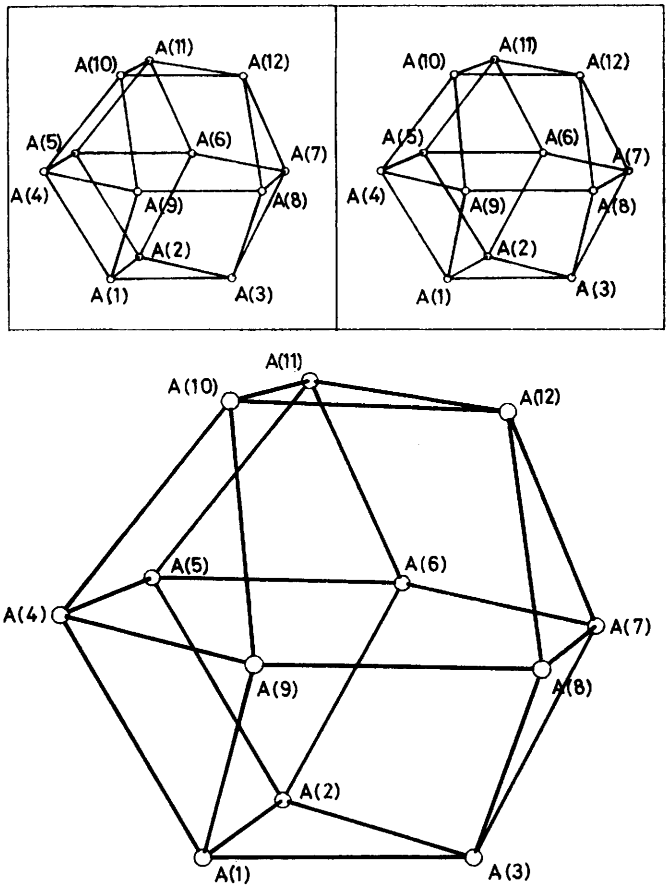


	θ	ϕ
1	35·264	0·0
2	35·264	120·000
3	35·264	240·000
4	90·000	30·000
5	90·000	90·000
6	90·000	150·000
7	90·000	210·000
8	90·000	270·000
9	90·000	330·000
10	144·736	60·000
11	144·736	180·000
12	144·736	300·000

FIGURE 2 The cuboctahedron

here. Several different types of structure are known for clusters with 12 carbonyl ligands. They were rationalised purely on the basis of radius ratio considerations; a given (CO)-polyhedron was calculated to possess a particular interstice radius and a metal cluster of larger size than this would be unable to fit inside the polyhedron.

Calculations of the most favourable 12-vertex polyhedra based on optimisation of ligand–ligand repulsion energies confirm these findings (Table 1). Diagrams of these polyhedra, together with their spherical polar co-ordinates, are given in Figures 1—3.



	θ	ϕ
1	35·256	0·0
2	35·256	120·000
3	35·256	240·000
4	90·000	30·000
5	90·000	90·000
6	90·000	150·000
7	90·000	210·000
8	90·000	270·000
9	90·000	330·000
10	144·744	0·0
11	144·744	120·000
12	144·744	240·000

FIGURE 3 The anticuboctahedron

However, for values of n greater than 12, it is found that interstice radii do not increase uniformly with $\sum_{i\neq j}\Omega_{ij}^{-6}$ for the various available polyhedra. Hence radius ratio considerations are not so useful. Another problem is that the value of 3.02 Å for the effective radius of the carbonyl ligand, derived empirically for n = 8—12, does not work well for higher polyhedra as it leads to interstice sizes which are unreasonably large to accommodate the metal clusters. This difficulty may be overcome by dividing the size parameter for the CO ligand into two parts: (i) a ' non-bonded radius ' corresponding to distances between oxygen atoms of adjacent CO groups and (ii) a ' bonded radius ' derived from the distance between the oxygen atom and the metal atom to which the carbonyl is bonded. This in turn requires a consistent set of values for metal atom radii; hitherto the values obtained from bulk metals have been employed, but it may be necessary to adapt this by taking metal atom radii appropriate to ' single bonds ' in typical cluster carbonyls. The precise definition of a metallic ' single bond length ' is currently a matter of some dispute; [37] further work is in progress with the aim of obtaining a self-consistent set of carbonyl group radii.

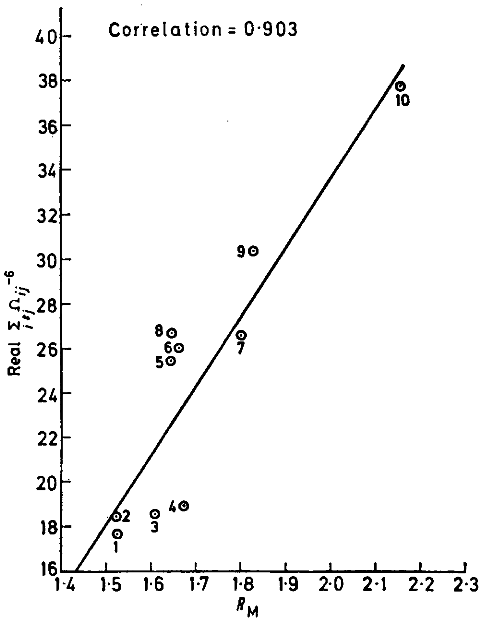


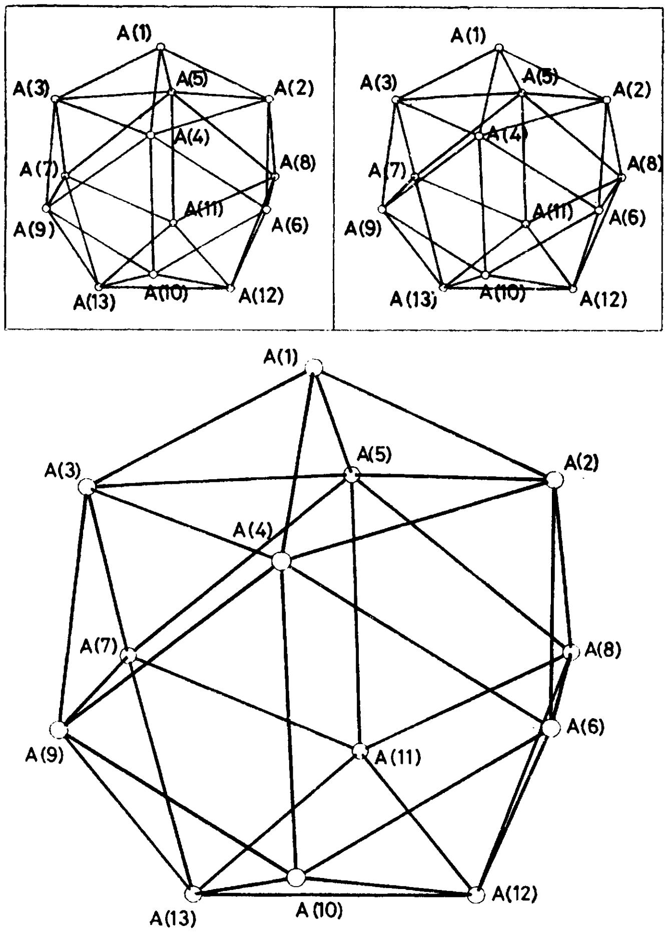
FIGURE 4 Plot of real value of $\sum_{i\neq j}\Omega_{ij}^{-6}$ against R_m for dodecarbonyl species (R_m is the mean distance of the metal atoms from their centre of gravity). Points: 1 $[Co_4(CO)_{12}]$, 2 $[Fe_3(CO)_{12}]$, 3 $[Co_2Ir_2(CO)_{12}]$, 4 $[Rh_4(CO)_{12}]$, 5 $[Ru_3(CO)_{12}]$, 6 $[Os_3(CO)_{12}]$, 7 $[Ni_5(CO)_{12}]^{2-}$, 8 $[Ir_4(CO)_{12}]$, 9 $[Ni_6(CO)_{12}]^{2-}$, and 10 $[Pt_6(CO)_{12}]^{2-}$

In the results presented below for other values of n, the primary consideration has been the optimisation of $\sum_{i\neq j}\Omega_{ij}^{-6}$.

pplying this criterion to 12-carbonyl structures, we can see that a wider range of polyhedra has been observed than in species with other numbers of carbonyls.

As well as the forms most favourable in terms of minimisation of $\sum_{i\neq j}\Omega_{ij}^{-6}$, a number of higher-energy forms are known, while others of intermediate energy remain unobserved. In these structures, there is clear correlation between the real value of $\sum_{i\neq j}\Omega_{ij}^{-6}$ and the size of the enclosed metal-cluster unit (Figure 4). This implies that the minimisation of steric repulsions between carbonyls is of greatest importance in small metal clusters, where there is less room on the cluster surface. When the metal cluster is larger, the carbonyl polyhedron may adopt a sterically less favourable form, presumably for electronic reasons.

For n = 13.—The eight most favourable polyhedra for $n = 13$ vertices are listed in Table 2. The best 13-vertex polyhedron corresponds to an edge-bridged icosahedron (note that the icosahedron may be viewed as six layers of two vertices). It is depicted in Figure 5, together with its co-ordinates. The second best 13-vertex polyhedron corresponds to a face-capped icosahedron. It is depicted in Figure 6 together with its co-ordinates. The next best 13-vertex polyhedron may be viewed as an icosahedron in which one of the pentagonal layers of five vertices has been replaced by a hexagonal layer of six. Note the occurrence of seven polyhedral forms with closely similar values of $\sum_{i\neq j} \Omega_{ij}^{-6}$ (within 6% of the optimum), followed after a large interval by a form with much higher energy.



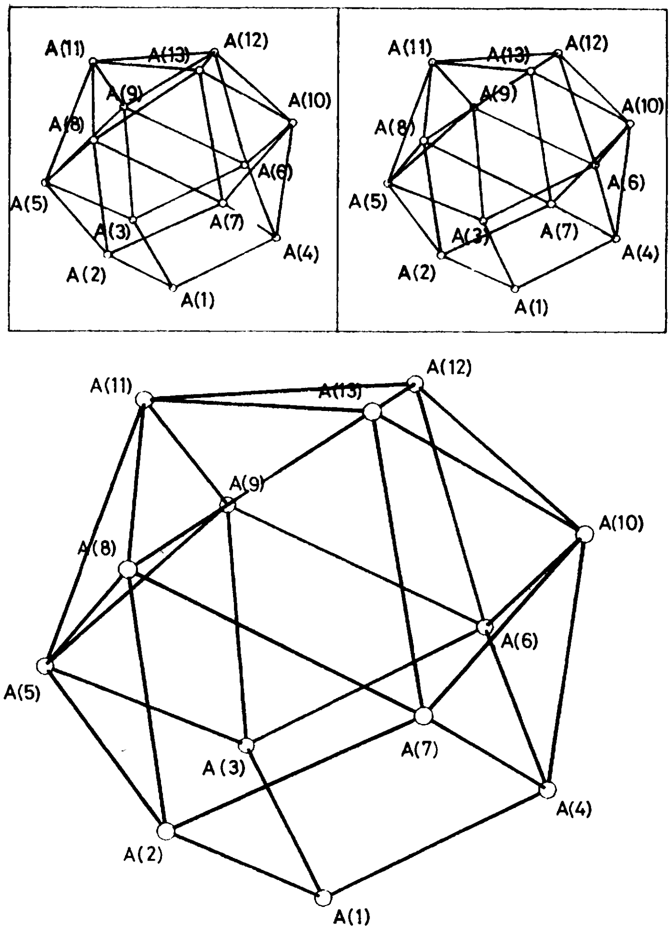
	θ	φ
1	0·0	0·0
2	53·016	90·000
3	53·016	270·000
4	60·344	0·0
5	60·344	180·000
6	97·066	54·499
7	97·066	234·499
8	97·066	125·501
9	97·066	305·501
10	123·776	0·000
11	123·776	180·000
12	150·194	90·000
13	150·194	270·000

FIGURE 5 The best 13-vertex polyhedron (edge-bridged icosahedron). The unique vertex is labelled A(1)

TABLE 2

Favourable polyhedra for $n = 13$

Order of favourability	Description	Energy $\sum_{i\neq j} \Omega_{ij}^{-6}$	Percent above minimum
1	1 : 2 : (2) : 2 : (2) : 2 : (2)	26.044	
2	1 : 3 : (3) : 3 : (3)	26.065	0.081
3	1 : 5 : 6 : 1	26.231	0.718
4	3 : (3) : 3 : 4	26.826	3.003
5	1 : 4 : (4) : 4	26.845	3.076
6	3 : 6 : 4	27.120	4.131
7	1 : 5 : (5) : 2	27.597	5.963
8	3 : 5 : (5)	29.883	14.740



	θ	φ
1	0·0	0·0
2	53·855	0·0
3	53·855	120·000
4	53·855	240·000
5	81·151	60·000
6	81·151	180·000
7	81·151	300·000
8	108·874	0·000
9	108·874	120·000
10	108·874	240·000
11	143·825	60·000
12	143·825	180·000
13	143·825	300·000

FIGURE 6 The second best 13-vertex polyhedron (face-bridged icosahedron), viewed 'upside down' to correspond with Figure 7

The only binary carbonyl with 13 ligands whose crystal structure has been determined is $[Fe_4(CO)_{13}]^{2-}$.[3] A tetrahedron of iron atoms is enveloped by 13 carbonyls to give this structure. Figure 7 shows the molecular geometry, and the polyhedron defined by the oxygen atoms viewed from the same direction. It may be seen that this polyhedron is a 1 : 3 : (3) : 3 : (3) arrangement, with the unique vertex corresponding to the triply bridging carbonyl group beneath the base of the Fe_4 tetrahedron. The oxygen atoms lie on the surface of a sphere of radius $R_O = 3.848$ Å, within a standard deviation of 8.9%. This standard deviation is misleadingly high because the triply bridging carbonyl is naturally held closer in to the centre of the cluster than the terminal ones, to maintain sensible M–C bond lengths. The real value of $\sum_{i\neq j}\Omega_{ij}^{-6}$ is 28.697, which approximates well to the ideal value of 26.065. Even so, this is above the values for some other polyhedra (see Table 3); some factors giving rise to high real values of $\sum_{i\neq j}\Omega_{ij}^{-6}$ are discussed below.

Note that the (CO)-polyhedron found in $[Fe_4(CO)_{13}]^{2-}$ matches the symmetry of the Fe_4 unit very well (in fact both have C_{3v} symmetry). Attempts to marry two polyhedra of grossly different symmetries will in most cases lead to a number of M–CO contacts of unreasonable distance, and to some carbonyls occupying bonding positions that are not well defined (*i.e.* not clearly terminal, edge-bridging *etc.*). We believe that this is why the 1 : 2 : (2) : 2 : (2) : 2 : (2) configuration of carbonyls, which has a slightly lower $\sum_{i\neq j}\Omega_{ij}{}^{6}$, is not adopted in $[Fe_4(CO)_{13}]^{2-}$. In passing, it may be emphasised that the symmetry of the icosahedron (n = 12) is extremely high (point group I_h), so that it may accommodate metal clusters with geometries as disparate as the triangle and the tetrahedron to give viable molecular structures.

For n = 14.—The six best polyhedra for $n = 14$ are presented in Table 3. The most favourable polyhedron for $n = 14$ vertices is the bicapped hexagonal antiprism, a 1 : 6 : (6) : 1 arrangement with D_{6d} symmetry. It is depicted with co-ordinates in Figure 8. The second best 14-vertex polyhedron is 1 : 4 : (4) : 4 : 1, which corresponds to the omnicapped cube. It is shown in Figure 9. Both these polyhedra were described in 1967 by Muetterties and Wright;[38] the only real example of 14-co-ordination mentioned by them occurs in the silicide $SiMo_3$.

TABLE 3

Favourable polyhedra for $n = 14$

Order of favourability	Description	Energy $\sum_{i\neq j}\Omega_{ij}^{-6}$	Percent above minimum
1	1 : 6 : (6) : 1	35.051	
2	1 : 4 : (4) : 4 : 1	36.296	3.552
3	1 : 5 : (5) : 3	37.364	6.599
4	4 : 6 : 4	37.614	7.312
5	1 : 5 : 6 : 2	37.844	7.968
6	3 : (3) : 3 : 5	38.712	10.445

Two cluster carbonyls with 14 carbonyl ligands have been crystallographically characterised, and their atomic co-ordinates published. They are $[Co_6(CO)_{14}]^{4-}$ [39] and $[Co_4Ni_2(CO)_{14}]^{2-}$.[40] Both have the same structure in which an octahedron of metal atoms possesses six terminal CO

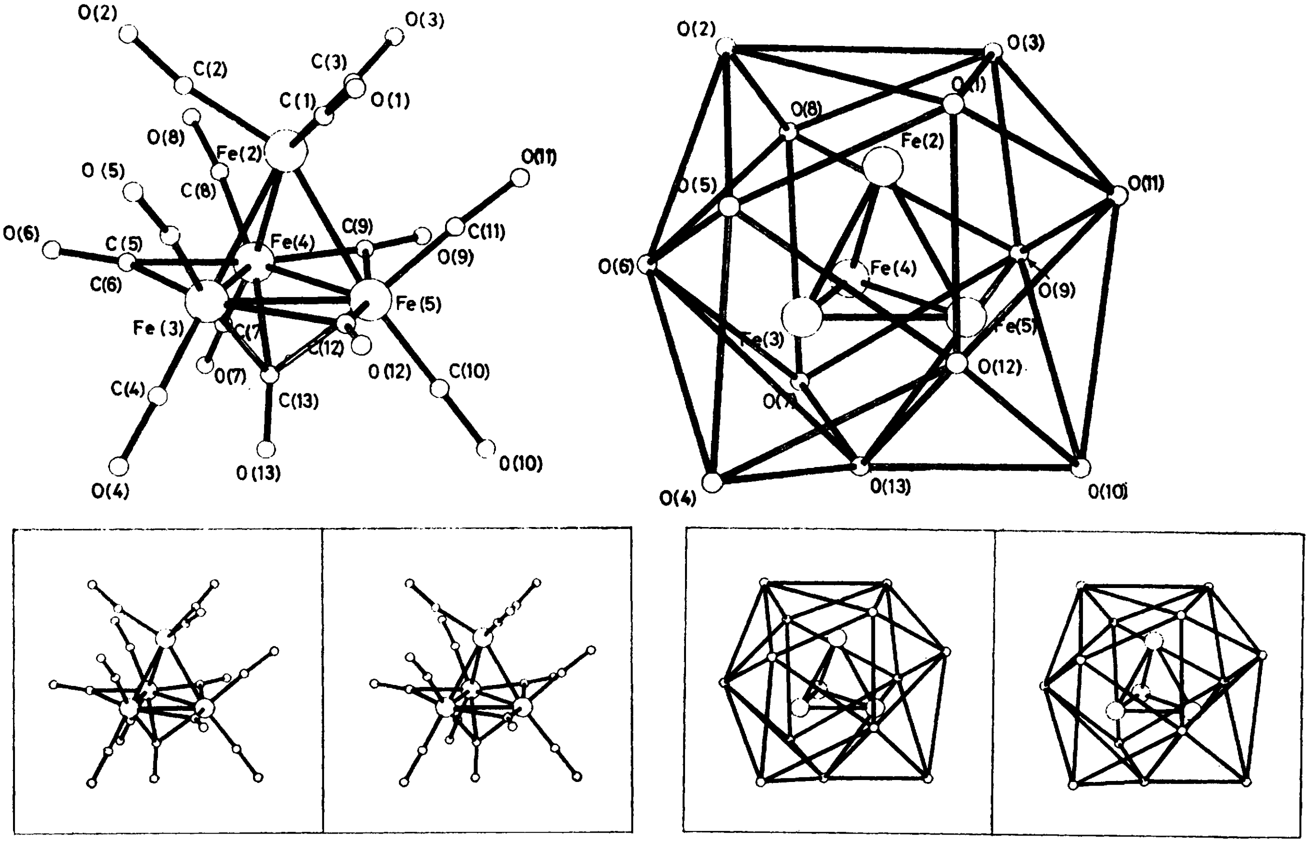
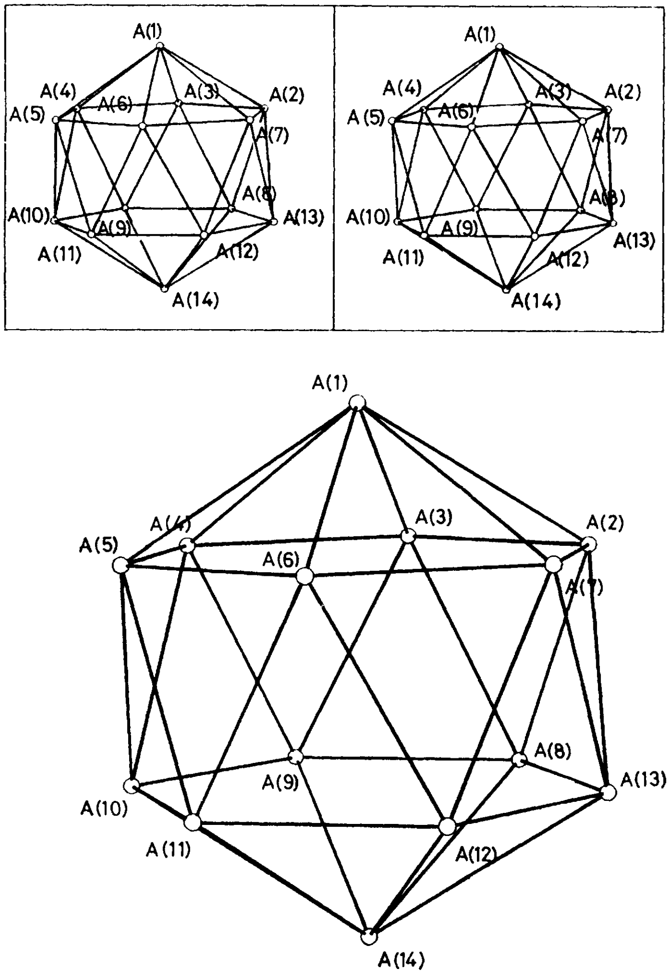


FIGURE 7 The structure of $[Fe_4(CO)_{13}]^{2-}$ The molecular diagram is shown, together with a diagram of the polyhedra, formed by the iron and oxygen atoms. The unique (triply bridging) carbonyl oxygen is labelled O(13)

groups (one per metal atom) and eight triply bridging carbonyls (one per face of the octahedron). It may be seen from Figure 10 that *this structure follows as a natural consequence of placing an octahedron inside an omnicapped* *cube*. The structure of $[Co_4Ni_2(CO)_{14}]^{2-}$ is in fact disordered, so that all the metal atoms are equivalent; the Co_4Ni_2 octahedron adopts a disordered orientation within an invariant ligand polyhedron. This disorder masks any effects that may arise from the cluster being heterometallic (see below). The possession of O_h symmetry by both the metal-atom cluster and the carbonyl polyhedron is significant. However, if we align the six-fold axis of a D_{6d} 1 : 6 : (6) : 1 ligand polyhedron with the three-fold axis of a metal-atom octahedron, we arrive at a reasonable alternative structure with six terminal, six edge-bridging, and two face-bridging carbonyls. The adoption of the O_h structure may well arise from radius ratio considerations. The 1 : 6 : (6) : 1 arrangement is known in metal alloy structures.[33]



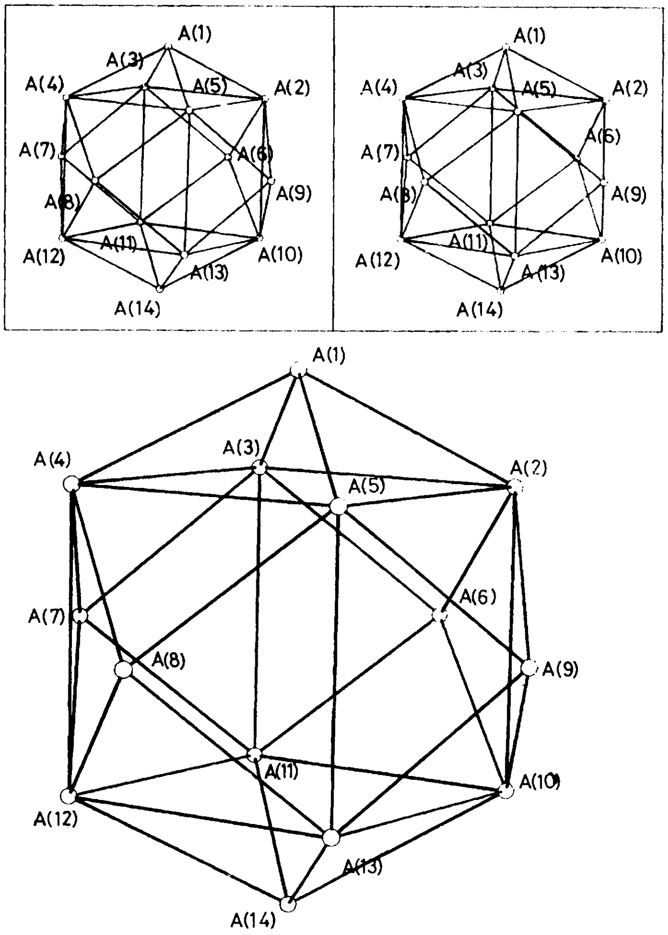
	θ	φ
1	0·0	0·0
2	63·885	0·0
3	63·885	60·000
4	63·885	120·000
5	63·885	180·000
6	63·885	240·000
7	63·885	300·000
8	116·115	30·000
9	116·115	90·000
10	116·115	150·000
11	116·115	210·000
12	116·115	270·000
13	116·115	330·000
14	180·000	0·0

FIGURE 8 The most favourable 14-vertex polyhedron

Fitting the oxygen atoms onto the surface of a sphere leads to the following results.

$[Co_6(CO)_{14}]^{4-}$: Radius of sphere, R_O = 4.068 Å ± 11.67%
Real value of $\sum_{i \neq j} \Omega_{ij}^{-6} = 38.785$

$[Co_4Ni_2(CO)_{14}]^{2-}$:
Radius of sphere, R_O = 4.087 Å ± 11.94%
Real value of $\sum_{i \neq j} \Omega_{ij}^{-6} = 36.695$



	θ	φ
1	0·0	0·0
2	54·736	0·0
3	54·736	90·000
4	54·736	180·000
5	54·736	270·000
6	90·000	45·000
7	90·000	135·000
8	90·000	225·000
9	90·000	315·000
10	125·264	0·000
11	125·264	90·000
12	125·264	180·000
13	125·264	270·000
14	180·000	0·0

FIGURE 9 The second most favourable 14-vertex polyhedron (omnicapped cube)

It may be seen from the real values of $\sum_{i\neq j} \Omega_{ij}^{-6}$ that the 14-vertex polyhedra described by the carbonyls in these two species are almost exact approximations to the ideal form. The variation in r_O between the two types of O atom in the polyhedron (eight of which form the cube, the faces of which are capped by the other six) gives rise to a large standard deviation in R_O, but inspection of the diagrams shows that the oxygen atoms do define an almost ideal semi-regular polyhedron.

The anion $[Co_6C(CO)_{14}]^-$ has also been investigated crystallographically;[41] its structure involves a different pattern of bridging carbonyls but atomic co-ordinates are not available and so it has not yet proved possible to analyse this ligand polyhedron.

For n = 15.—The six most favourable polyhedra for $n = 15$ vertices are given in Table 4. The most favourable polyhedron is a 3 : (3) : 3 : (3) : 3 arrangement. It is known to occur in metal alloy structures.[33] Fifteen-co-ordinate molecular species have never been considered, and little appears to be known about 15-vertex polyhedra from a mathematical point of view. Figures 11 and 12 show the two best polyhedra together with their spherical polar co-ordinates.

TABLE 4

Favourable polyhedra for $n = 15$

Order of favourability	Description	Energy $\sum_{i\neq j} \Omega_{ij}^{-6}$	Percent above minimum
1	3 : (3) : 3 : (3) : 3	46.755	
2	1 : 6 : (6) : 2	48.702	4.164
3	1 : 5 : 3 : (3) : 3	48.926	4.643
4	1 : 5 : 6 : 3	49.197	5.223
5	2 : (2) : 7 : 2 : (2)	49.482	5.833
6	1 : 5 : (5) : 2 : (2)	50.877	8.816

X-Ray crystallographic investigation of several cluster carbonyl molecules and anions with 15 ligands has been carried out. (*i*) $[Co_6(CO)_{15}]^{2-}$.[42] An octahedron of metal atoms is enveloped by a ligand polyhedron which may be seen to be a 3 : (3) : 3 : (3) : 3 arrangement (Figure 13). This gives rise to the structure of three edge bridges, three face bridges, and nine terminal carbonyls. Analysis of the oxygen-atom co-ordinates gives the following results.

Radius of sphere fitted to O atoms, $R_O = 4.127$ Å ± 8.8%

Real value of $\sum_{i\neq j} \Omega_{ij}^{-6} = 56.865$

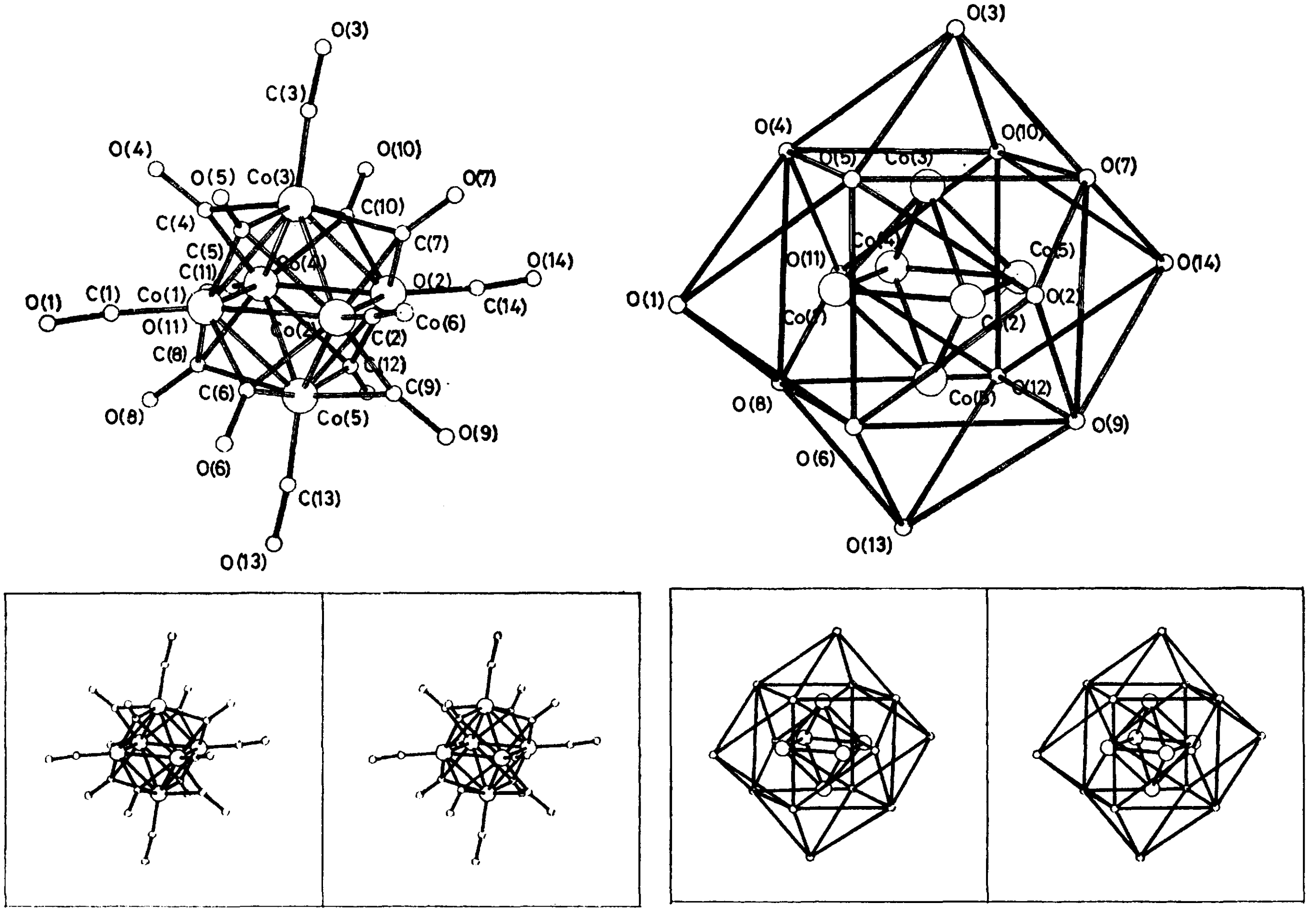
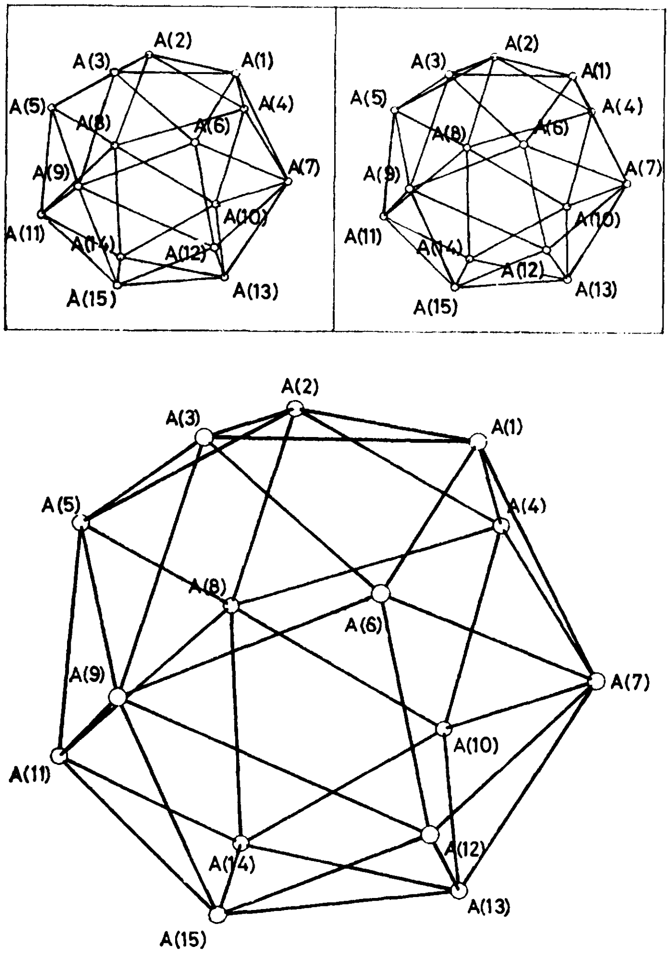


FIGURE 10 The structure of $[Co_6(CO)_{14}]^{4-}$. The anion $[Co_4Ni_2(CO)_{14}]^{2-}$ is isostructural

This latter figure for the ligand repulsion energy is disconcertingly high; possible reasons for this are discussed below.

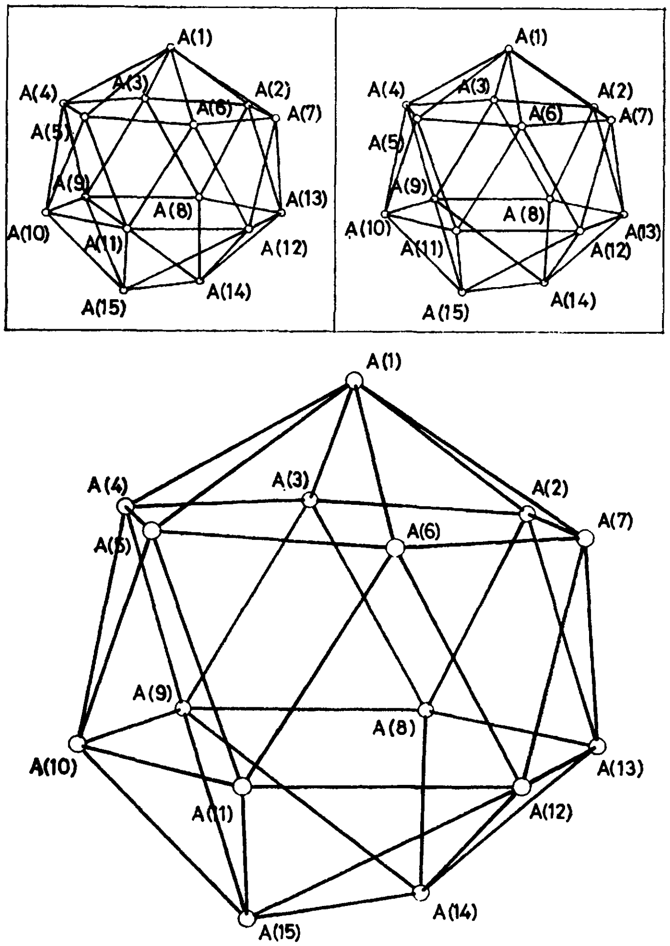
(*ii*) $[Rh_6C(CO)_{15}]^{2-}$.[43] For this molecule, electron counting according to Wade's scheme[11] shows that 18 electrons are available for cluster bonding; this means that the geometry of the cluster should be based on a polyhedron with eight vertices, two of which will be 'missing' (*arachno*-structure). The observed structure, a trigonal prism, is consistent with this, but is by no means a unique possibility.

Given this anisotropic metal-cluster geometry, which does not approximate to a spherical metal fragment, it would not be expected that the carbonyl groups will be distributed in a configuration based on optimisation of interactions on the surface of a sphere. In fact the (CO)-polyhedron in $[Rh_6C(CO)_{15}]^{2-}$ does approximate to the 3 : (3) : 3 : (3) : 3 form, an arrangement well suited to match the symmetry of the metal cluster (Figure 14). Thus the molecule possesses nine edge-bridging carbonyls, one on each edge of the Rh_6C unit, and six terminal carbonyls, one per rhodium atom. Analysis of the oxygen-atom co-ordinates shows that they fit onto the surface of a sphere with a 12.2% standard deviation in their radial distances from the origin. The real value of $\sum_{i \neq j} \Omega_{ij}^{-6}$ is extremely high (60.293), showing that the carbonyl polyhedron is distorted, as expected for this anisotropic cluster.



	θ	ϕ
1	33·498	0·0
2	33·498	120·000
3	33·498	240·000
4	65·529	59·344
5	65·529	179·344
6	65·529	299·344
7	90·000	-7·448
8	90·000	112·552
9	90·000	232·552
10	114·471	45·760
11	114·471	165·760
12	114·471	285·760
13	146·502	-14·895
14	146·502	105·105
15	146·502	225·105

FIGURE 11 The most favourable 15-vertex polyhedron



	θ	ϕ
1	0·0	0·0
2	60·355	0·0
3	60·355	60·000
4	60·355	120·000
5	60·355	180·000
6	60·355	240·000
7	60·355	300·000
8	108·676	30·000
9	108·676	90·000
10	108·676	150·000
11	108·676	210·000
12	108·676	270·000
13	108·676	330·000
14	155·967	0·0
15	155·967	180·000

FIGURE 12 The second most favourable 15-vertex polyhedron

(*iii*) $[Rh_5Pt(CO)_{15}]^-$.[44] The metal cluster is octahedral, in accordance with Wade's scheme.[11] There are 11 terminal and four face-bridging carbonyls; each rhodium atom has two terminal carbonyls and the platinum atom one. Even though the differing electronic requirements of

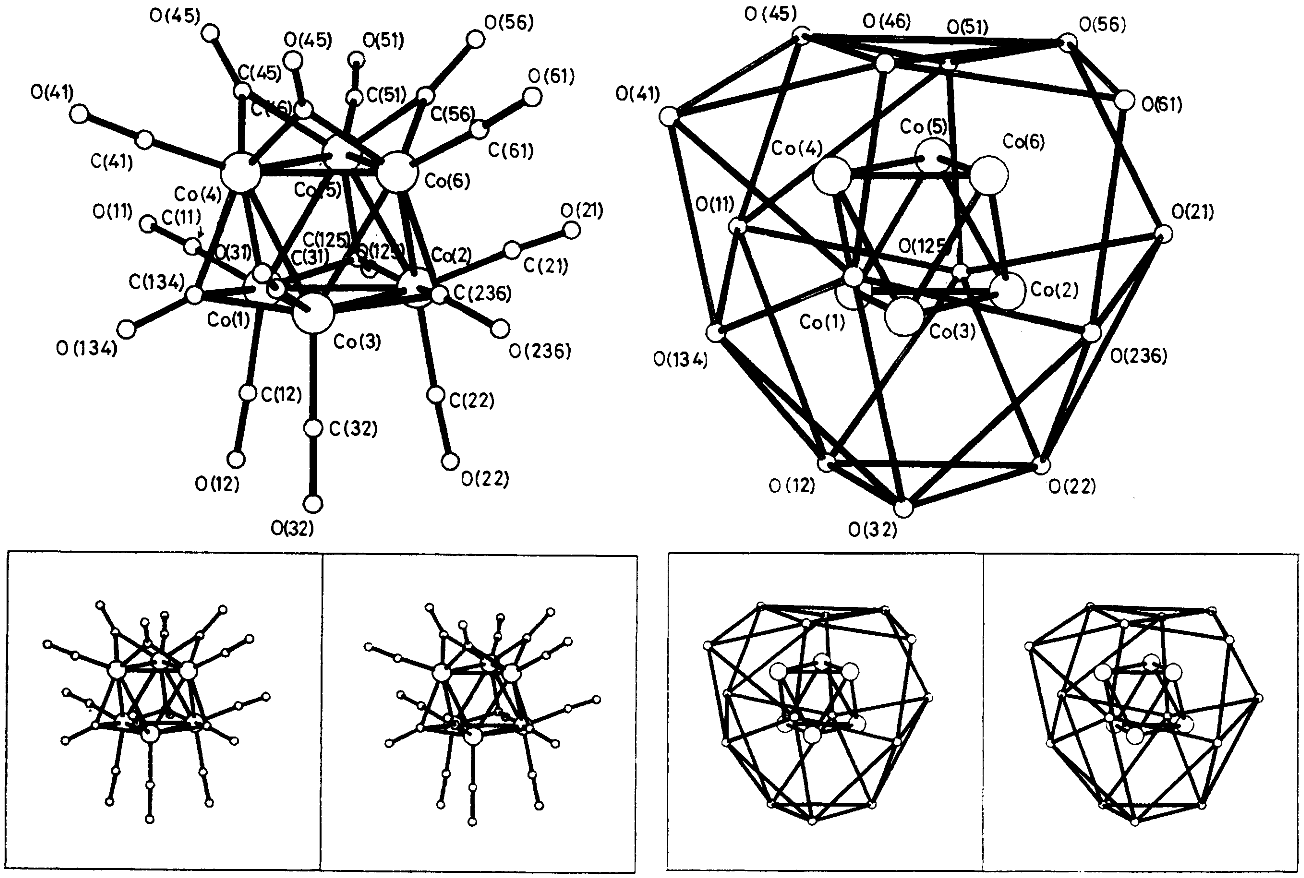


FIGURE 13 The structure of $[Co_6(CO)_{15}]^{2-}$

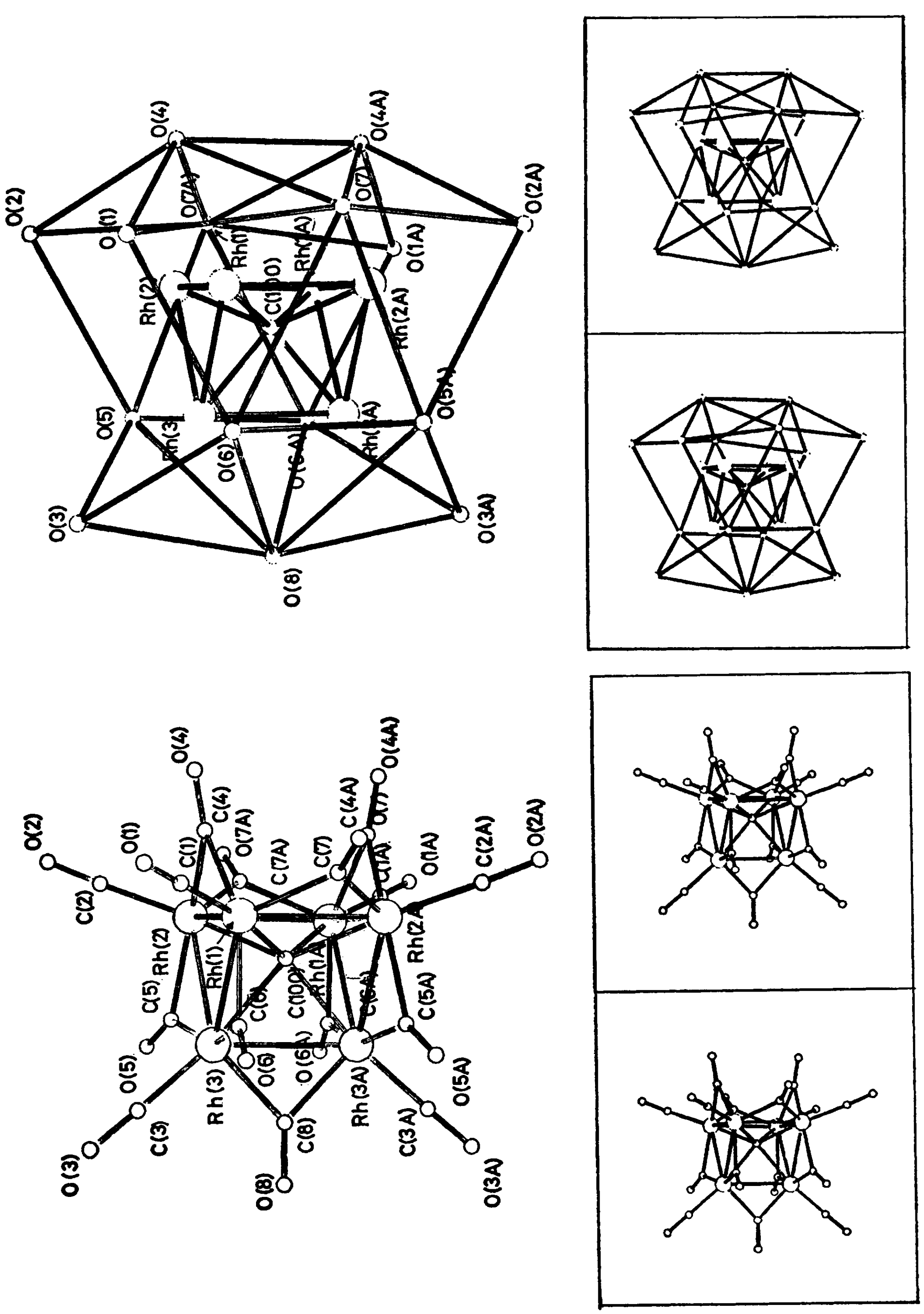


FIGURE 14 The structure of $[Rh_6C(CO)_{15}]^{2-}$

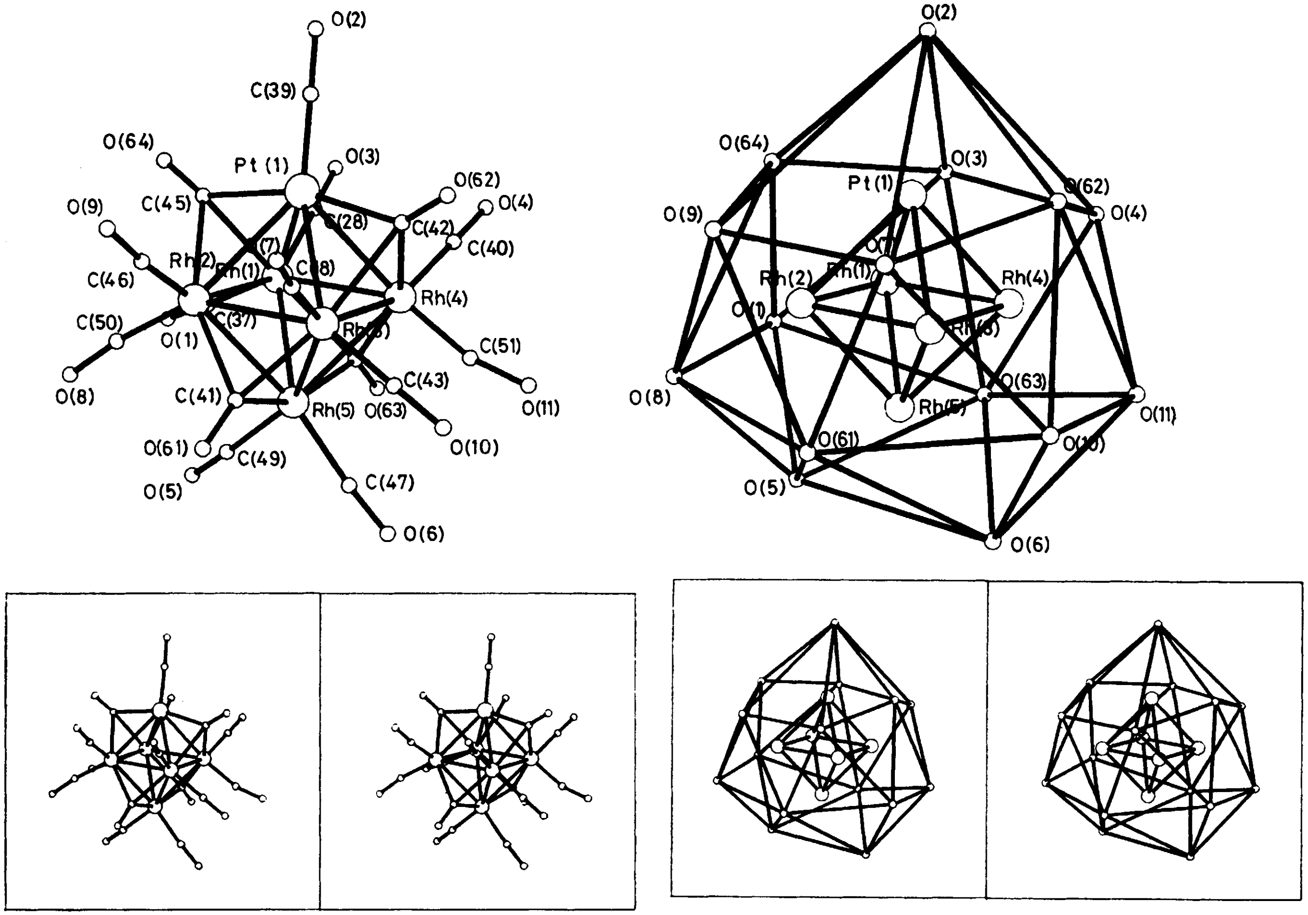


FIGURE 15 The structure of $[Rh_5Pt(CO)_{15}]^-$ The single terminal carbonyl on the platinum atom, labelled O(2), may be regarded as the unique vertex of a 1 : 6 : (6) : 2 polyhedron

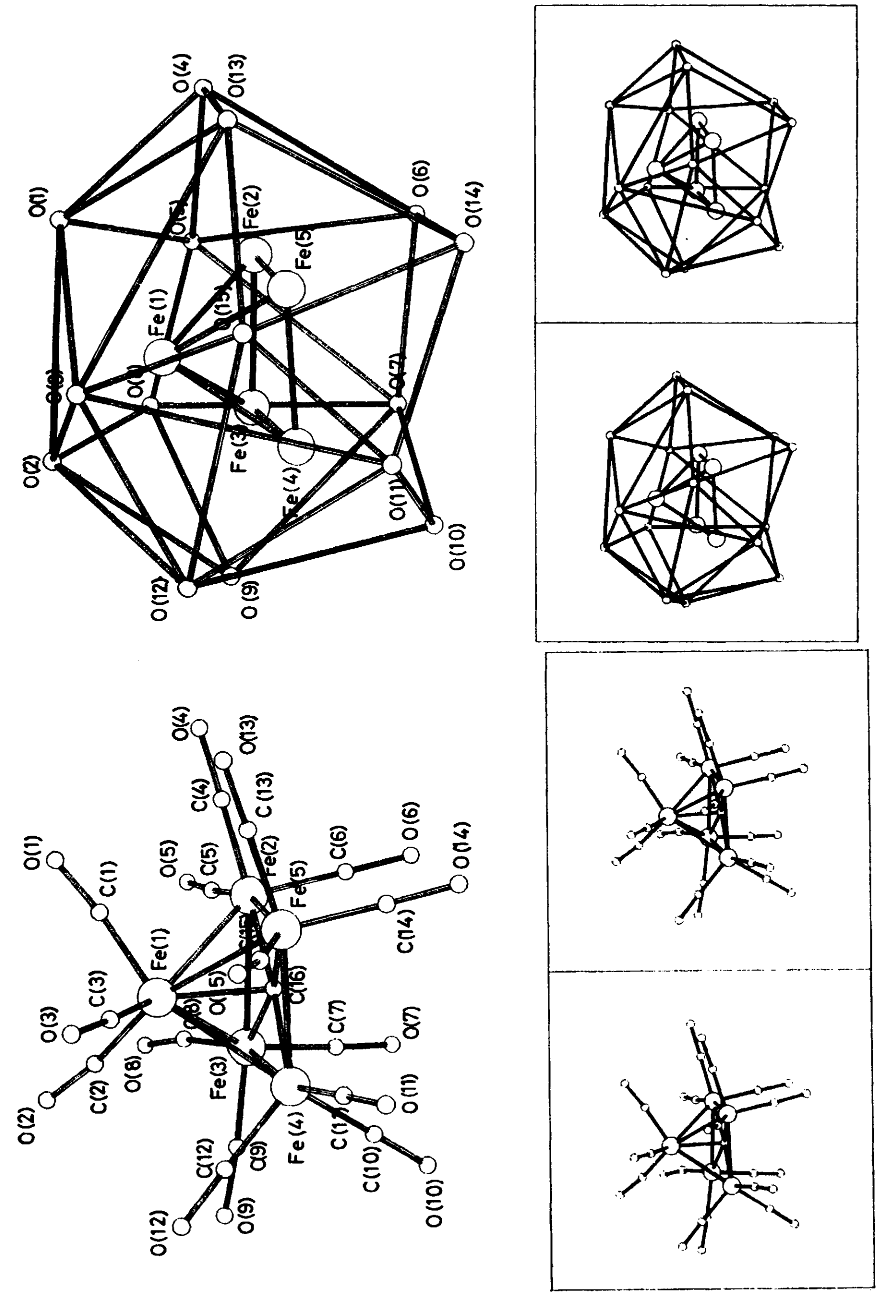
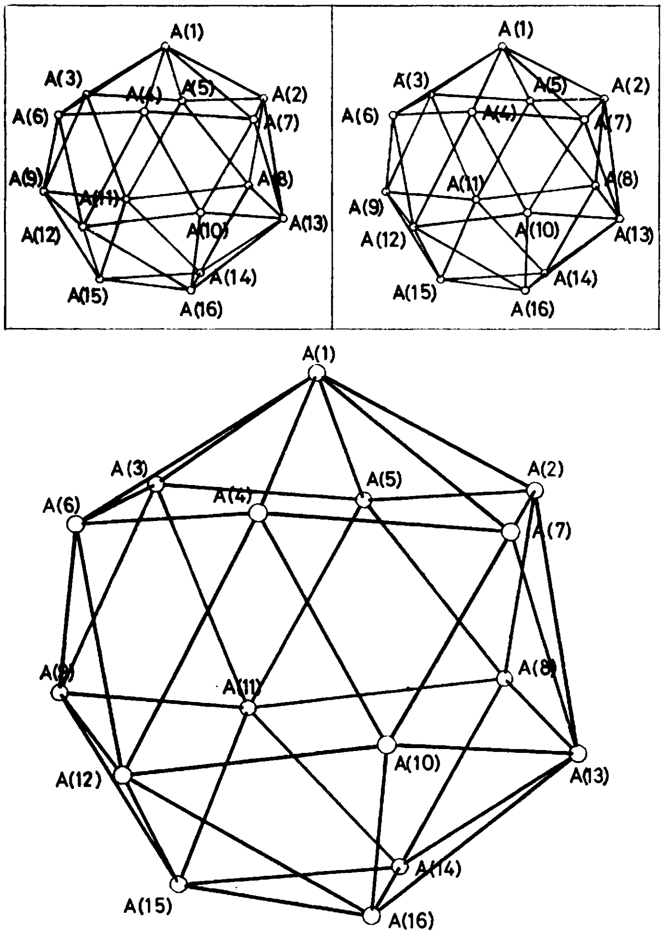


FIGURE 16 The structure of $[Fe_5C(CO)_{15}]$

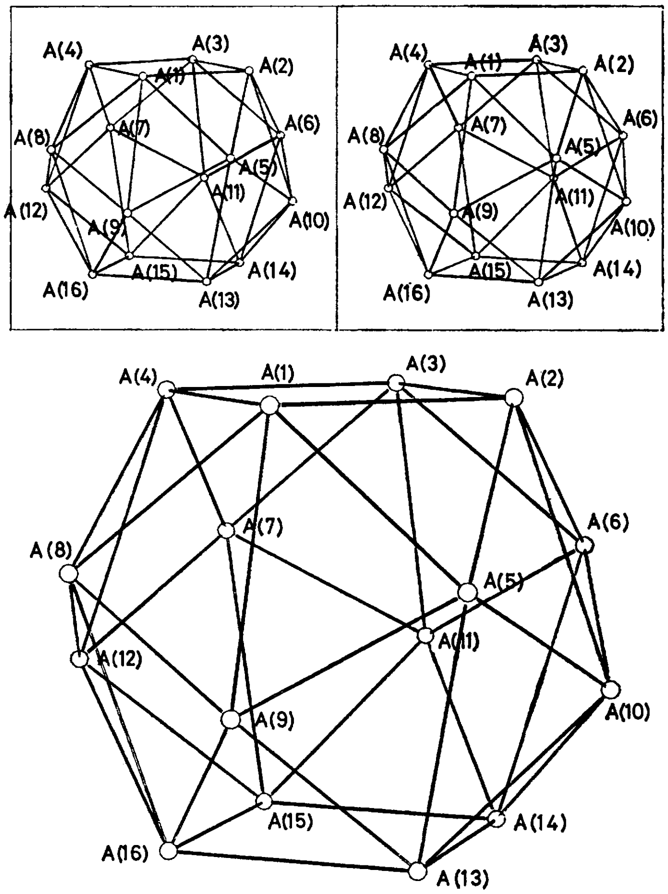
Rh and Pt undoubtedly impose restrictions on the ligand co-ordination, the ligand polyhedron resembles 1 : 6 : (6) : 2 (Figure 15), which is the second most favourable 15-vertex form. The oxygen atoms fit into a sphere with R_O = 4.360 Å ± 8.96%. The real value of $\sum_{i \neq j} \Omega_{ij}^{-6}$ is 61.237, a high value which probably reflects the electronic factors operating in this heterometallic cluster.



	θ	φ
1	0·0	0·0
2	55·586	0·0
3	55·586	120·000
4	55·586	240·000
5	61·064	61·490
6	61·064	181·490
7	61·064	301·490
8	100·699	26·892
9	100·699	146·892
10	100·699	266·892
11	109·471	89·798
12	109·471	209·798
13	109·471	329·798
14	149·695	35·463
15	149·695	155·463
16	149·695	275·463

FIGURE 17 The most favourable 16-vertex polyhedron

(*iv*) [Fe$_5$C(CO)$_{15}$]. In this molecule, one of the first cluster carbonyls to be characterised,[45] the metal cluster is a square pyramid, with the carbon atom occupying the square face. It would not be expected that the carbonyls enveloping such an anisotropic structure would conform to the model of mutual repulsion of points on a sphere, and it may be seen (Figure 16) that the carbonyls do not define an easily characterised polyhedron as they are constrained to bond to the iron atoms. This is particularly clear in the configuration of ligands about the open square face of the pyramid. In accordance with this, the real value of $\sum_{i \neq j} \Omega_{ij}^{-6}$ is 68.692, which is extremely high. Perhaps surprisingly, though, the oxygen atoms fit onto a sphere of radius R_O = 4.211 Å within a standard deviation of only 4.7%.



	θ	φ
1	39·218	0·0
2	39·218	90·000
3	39·218	180·000
4	39·218	270·000
5	78·311	45·000
6	78·311	135·000
7	78·311	225·000
8	78·311	315·000
9	101·689	0·000
10	101·689	90·000
11	101·689	180·000
12	101·689	270·000
13	140·782	45·000
14	140·782	135·000
15	140·782	225·000
16	140·782	315·000

FIGURE 18 The 4 : (4) : 4 : (4) polyhedron

For n = 16.—The six most favourable polyhedra for *n* = 16 vertices are listed in Table 5. The best polyhedron is the 1 : 3 : (3) : 3 : (3) : 3 form, a face-capped derivative of the best 15-vertex structure (Figure 17). Next is 4 : (4) : 4 : (4), four staggered layers of four vertices (Figure 18). At slightly higher energy comes the tetra-capped truncated tetrahedron, a 1 : 6 : 3 : (3) : 3 arrangement (Figure 19). It is one of several modifications of the 1 : 3 : (3) : 3 : (3) : 3 form which have almost identical values of $\sum_{i\neq j}\Omega_{ij}^{-6}$ and differ only in whether pairs of layers of three vertices are constrained to form regular coplanar hexagons. This polyhedron is well known in metallurgy and mineral chemistry.[33,38,46] Truncation of a tetrahedron by removal of its vertices results in a 12-vertex polyhedron with four hexagonal faces; capping of these faces with four additional vertices produces this 1 : 6 : 3 : (3) : 3 structure. The four capping vertices, indicated in Figure 19, are distinguished by their possession of six neighbours as opposed to the five of other vertices. Because of this readily identifiable feature, we have chosen to describe the real 16-ligand polyhedron in terms of this well known semi-regular polyhedron rather than the 1 : 3 : (3) : 3 : (3) : 3 form; this is consistent with the fact that in the real structures the relevant groups of six oxygen atoms deviate very little from coplanarity (a typical root-mean-square deviation from the least-squares plane is 0.1 Å).

TABLE 5

Favourable polyhedra for $n = 16$

Order of favourability	Description	Energy $\sum_{i\neq j}\Omega_{ij}^{-6}$	Percent above minimum
1	1 : 3 : (3) : 3 : (3) : 3	61.052	
2	4 : (4) : 4 : (4)	61.219	0.274
3	1 : 6 : 3 : (3) : 3	61.259	0.339
4	1 : 3 : (3) : 6 : 3	61.694	1.052
5	1 : 5 : 7 : 3	64.253	5.243
6	1 : 5 : (5) : 5	64.526	5.690

The 4 : (4) : 4 : (4) arrangement [which is quite distinct from 1 : 3 : (3) : 3 : (3) : 3, with four-fold rather than three-fold symmetry] has never been observed in metal–carbonyl clusters, nor in 16-co-ordination in metals. The reason for this is unclear, but may be connected with radius ratio considerations. The 4 : (4) polyhedron (square antiprism) and 4 : (4) : 4 arrangement (cuboctahedron) are well known for eight- and twelve-co-ordination. The 4 : (4) : 4 : (4) arrangement becomes the optimum form in the 'hard-sphere approximation' of infinite exponent.[31]

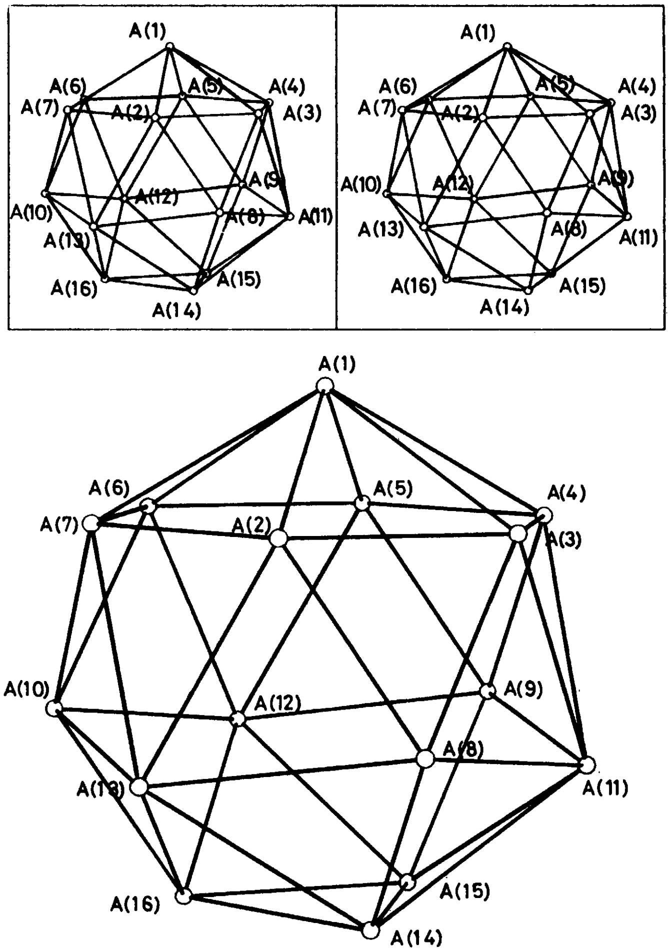
The crystal structures of several 16-carbonyl clusters have been determined. (*i*) $[Rh_6(CO)_{16}]$.[6] This molecule has 12 terminal and four triply bridging carbonyl groups. The six rhodium atoms form an octahedron, in accordance with Wade's scheme.[11] The carbonyl polyhedron is the 1 : 6 : 3 : (3) : 3 form (Figure 20), and the octahedron is oriented within it so that the four 'capping' (six-co-ordinate) vertices correspond to the four triply bridging carbonyls in the molecule. This structure is a consequence of placing an O_h octahedron within a *quasi*-tetrahedron The oxygen-atom co-ordinates yield the following results

Radius of sphere fitted to oxygen atoms = 4.385 Å ± 7.92%

Real value of $\sum_{i\neq j}\Omega_{ij}^{-6} = 78.235$

The real value of the ligand repulsion energy is very high; factors that may contribute to this are discussed below.

(*ii*) $[Fe_6C(CO)_{16}]^{2-}$.[47] Again the metal cluster adopts an octahedral geometry, this time with an interstitial carbon atom. The (CO) polyhedron is again the 1 : 6 : 3 : (3) : 3 form; however, the metal cluster adopts an alternative orientation within this polyhedron to give a structure with 13 terminal and three semi-bridging carbonyl groups (Figure 21). The reason for the adoption of this second relative alignment of the two polyhedra may well be connected with the smaller size of the Fe_6C unit compared to that of the Rh_6 octahedron. The need to maintain reasonable M–CO bonding distances may determine the orient-



	θ	ø
1	0·0	0·0
2	58·181	0·0
3	58·181	60·000
4	58·181	120·000
5	58·181	180·000
6	58·181	240·000
7	58·181	300·000
8	100·991	30·000
9	100·991	150·000
10	100·991	270·000
11	109·117	-30·000
12	109·117	90·000
13	109·117	210·000
14	149·902	30·000
15	149·902	150·000
16	149·902	270·000

FIGURE 19 The tetra-capped truncated tetrahedron. Six-co-ordinate vertices are labelled A(1), A(11), A(12), and A(13).

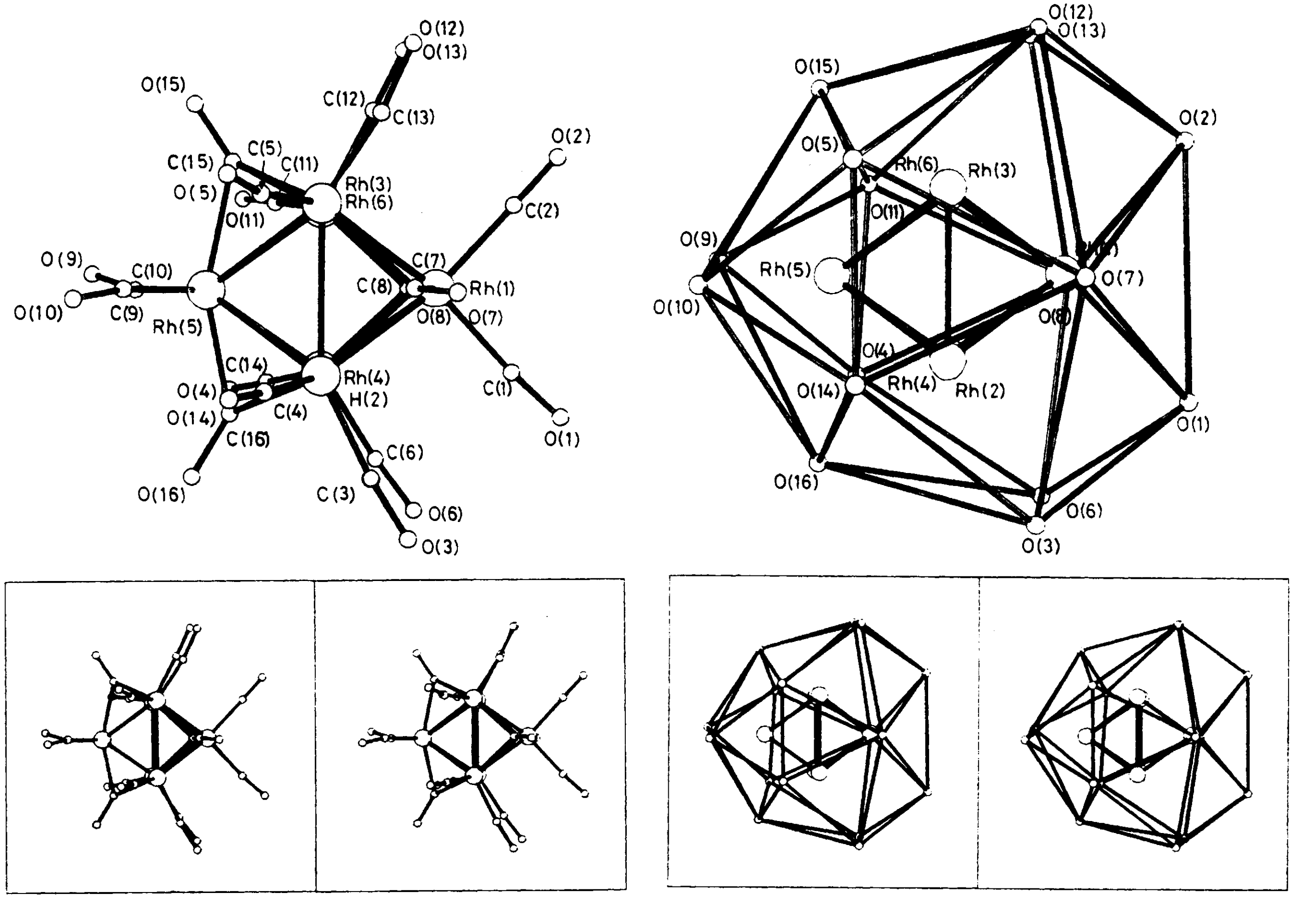


Figure 20 The structure of $[Rh_6(CO)_{16}]$. Six-co-ordinate vertices of the oxygen-atom polyhedron are labelled O(7), O(8), O(15), and O(16)

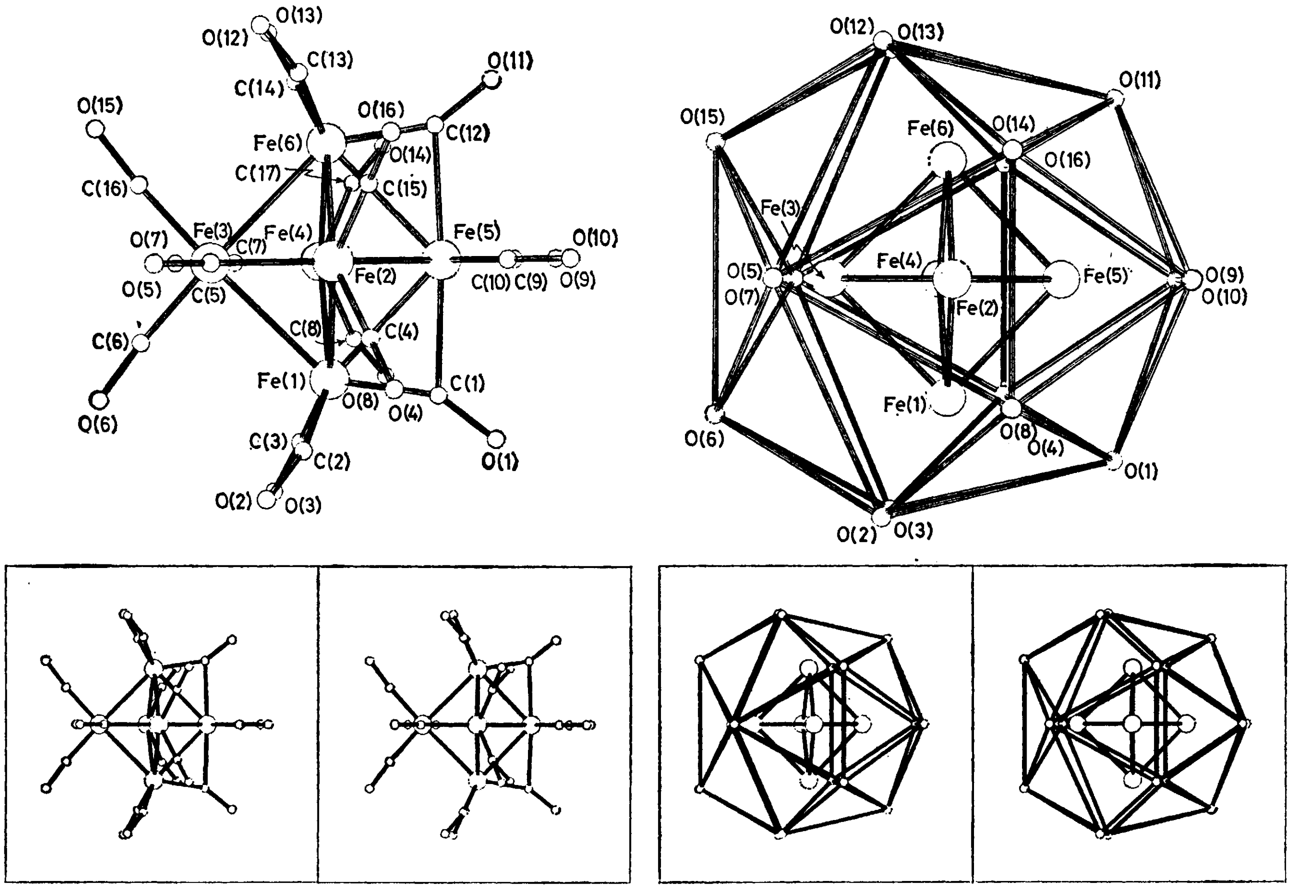


FIGURE 21 The structure of $[Fe_6C(CO)_{16}]^{2-}$. Note the identity of the ligand polyhedron with that of Figure 20, and the different orientation of the metal octahedron

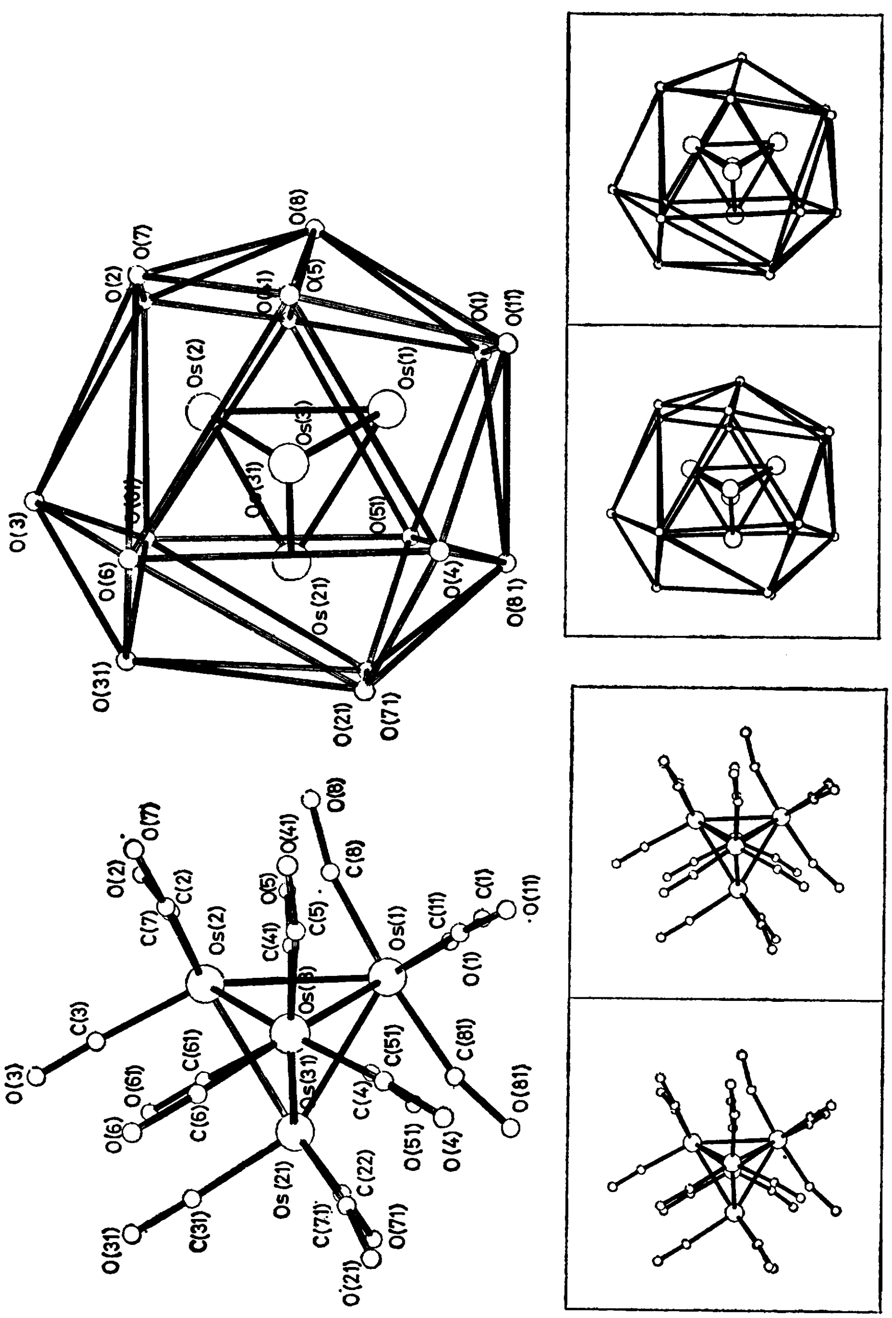


FIGURE 22 The structure of $[Os_5(CO)_{16}]$, viewed along the axis of the trigonal bipyramid. Six-co-ordinate vertices of the ligand polyhedron are O(6), O(8), O(61), and O(81)

ation within the 16-vertex polyhedron. For this anion we get the following results.

Radius of sphere fitted to oxygen atoms, R_O = 4.241 Å ± 4.75%

Real value of $\sum_{i \neq j} \Omega_{ij}^{-6} = 69.698$

(*iii*) $[Os_5(CO)_{16}]$.[48] This molecule has a trigonal bipyramidal Os_5 unit, in accordance with Wade's scheme.[11] Its structure is difficult to understand in terms of orthodox electron counting, because one unique osmium atom is bonded to *four* terminal carbonyls whereas the other four osmium atoms are each bonded to three carbonyls. Because the metal-cluster unit is rather aspherical, it might be expected that our simple points-on-a-sphere calculations would not be applicable to this molecule. However, Figure 22 reveals that the structure is simply a consequence of accommodating a trigonal bipyramid within a **1** : **6** : **3** : (3) : 3 ligand polyhedron. The value for the ligand repulsion energy is extremely high. It may arise as a consequence of the anisotropy of the metal-cluster unit to which the carbonyl groups must bond.

Radius of sphere fitted to O atoms, R_O = 4.323 Å ± 7.27%

Real value of $\sum_{i \neq j} \Omega_{ij}^{-6} = 86.670$

In addition to these carbonyls, the crystal structures of

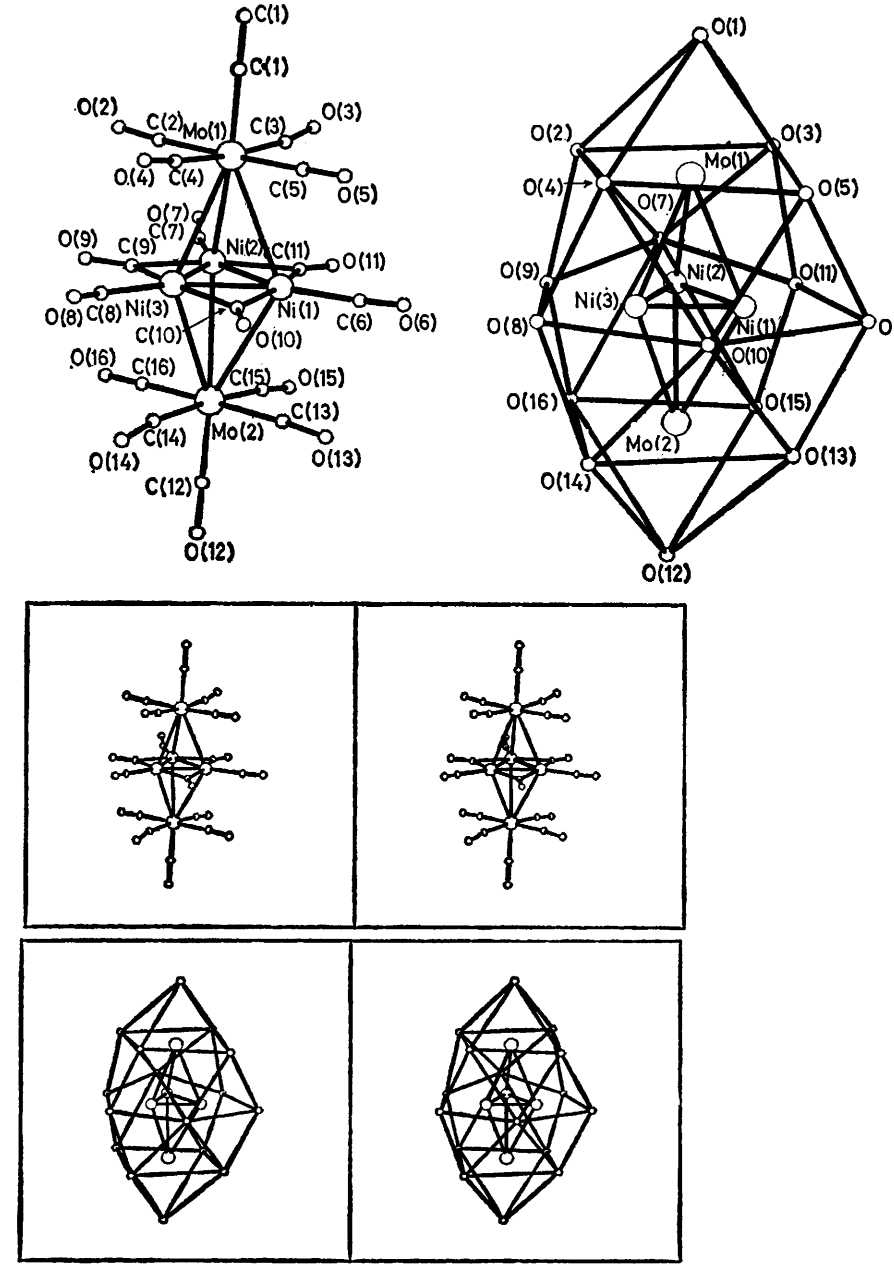


FIGURE 23 The structure of $[Mo_2Ni_3(CO)_{16}]^{2-}$ The anion $[W_2Ni_3(CO)_{16}]^{2-}$ has the same structure

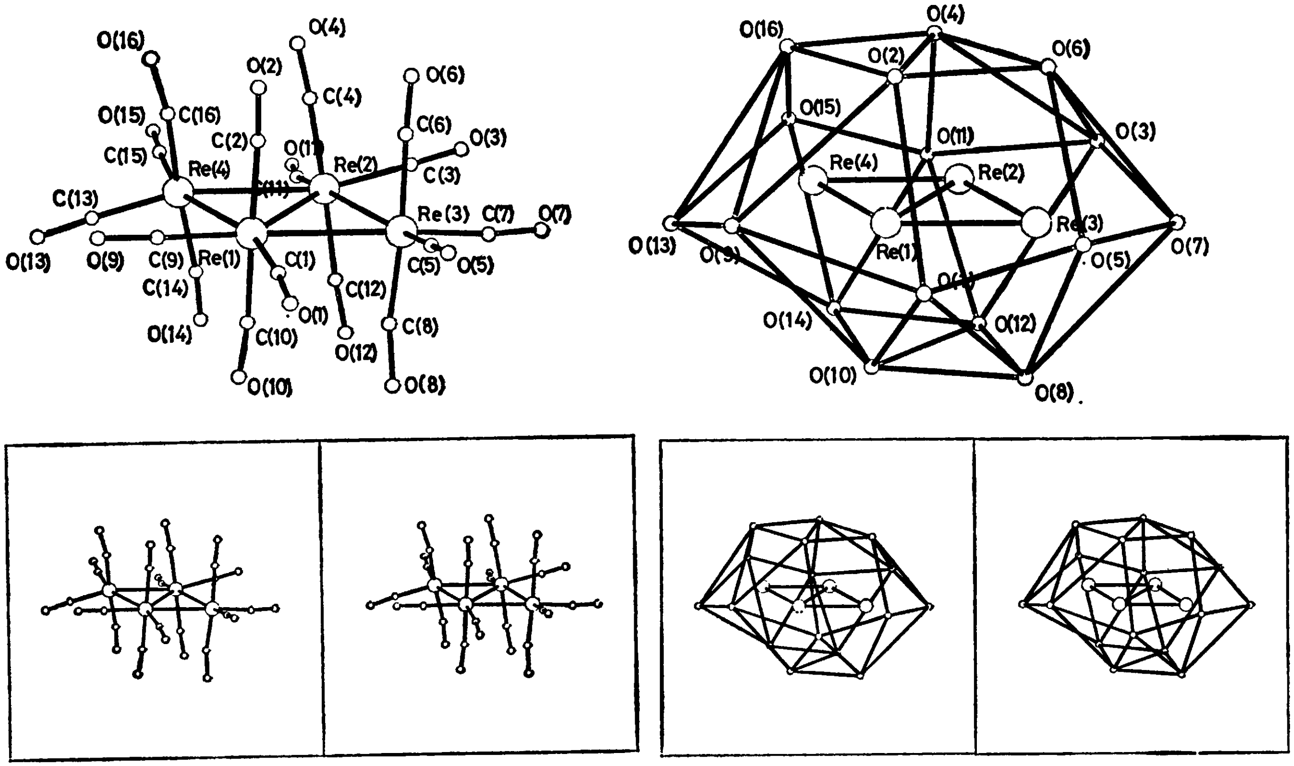


FIGURE 24 The structure of $[Re_4(CO)_{16}]^{2-}$

the iodo-derivatives $[Rh_6(CO)_{15}I]^-$ [49] and $[Os_5(CO)_{15}I]^-$ [50] are known. These structures are almost identical to those of the parent carbonyl molecules; the replacement of one CO group by the iodide ligand has very little effect on the rest of the ligand polyhedron.

(*iv*) $[Mo_2Ni_3(CO)_{16}]^{2-}$ *and* $[W_2Ni_3(CO)_{16}]^{2-}$.[51] In these anions the metal clusters are elongated trigonal bipyramids. These markedly aspherical clusters are also heterometallic, and the widely differing electronic requirements of the nickel and molybdenum or tungsten atoms must impose severe restrictions on the pattern of metal–ligand bonding. Thus it is not surprising that the carbonyl configurations do not conform to the results of our simple calculations. The (CO)-polyhedra are a 1 : 4 : 6 : 4 : 1 arrangement (Figure 23), which is an unfavourably high-energy reference form (ideal $\sum_{i\neq j}\Omega_{ij}^{-6} = 79.220$); the real values of $\sum_{i\neq j}\Omega_{ij}^{-6}$ are also very high. Thus the optimisation of inter-ligand repulsions is of secondary importance in these two structures.

For $[Mo_2Ni_3(CO)_{16}]^{2-}$:

Radius of sphere fitted to oxygen atoms = 4.306 ± 16.76%

Real value of $\sum_{i\neq j}\Omega_{ij}^{-6} = 81.637$

For $[W_2Ni_3(CO)_{16}]^{2-}$:

Radius of sphere fitted to oxygen atoms = 4.298 ± 17.27%

Real value of $\sum_{i\neq j}\Omega_{ij}^{-6} = 81.898$

(*v*) $[Re_4(CO)_{16}]^{2-}$.[52] In this anion the Re_4 unit adopts a planar (rhombic) geometry. The reason for this is not entirely clear from electron counting schemes. However, taking this metal-cluster shape as a necessary starting point, it is apparent that the model of an isotropic metal unit enveloped by carbonyl groups distributed over the surface of a sphere does not apply to this species. It may be seen from Figure 24 that the disposition of the carbonyls is governed by the need to bond to the metal cluster. The deviation of the ligand polyhedron from sphericity is highlighted by the value of $R_O = 4.254$ Å ± 14.97%, for the radial distances of the oxygen atoms from the origin, and the real value of $\sum_{i\neq j}\Omega_{ij}^{-6}$ which is 108.18.

DISCUSSION

The Values of $\sum_{i\neq j}\Omega_{ij}^{-6}$.—It has been seen that in a number of the structures discussed above the carbonyl oxygen polyhedra have qualitatively the geometries of favourable polytopal forms, but the real values of $\sum_{i\neq j}\Omega_{ij}^{-6}$ are much higher than would be expected. An explanation must be sought if this is to be reconciled with the proposition that the CO ligands adopt a configuration which minimises non-bonded repulsions between them.

Firstly, the carbonyl polyhedra are naturally distorted as a consequence of the cluster shapes within them (as opposed to single, spherical atoms). This effect has recently been discussed by Churchill and Hutchinson [8] in their redetermination of the structure of $[Ir_4(CO)_{12}]$. They observed that certain triangular faces of the cuboctahedron of carbonyl oxygen atoms are significantly larger than others. This arises because the effect of a metal atom is to splay out the triangle of carbonyls within which it lies; triangular faces which do not accommodate a metal atom are correspondingly compressed. Thus, in almost every case, the real $\sum_{i\neq j}\Omega_{ij}^{-6}$ value for a carbonyl polyhedron can never attain the ideal value, but must always be somewhat higher. In a sum of inverse sixth powers of angles, it will require only a few of the many inter-ligand angles to deviate greatly from their ideal values to give a high total figure for $\sum_{i\neq j}\Omega_{ij}^{-6}$. In the real structures, the CO ligands do not lie exactly on the surfaces of spheres; the effect of unusually small angles Ω_{ij} (which cause the major contribution to $\sum_{i\neq j}\Omega_{ij}^{-6}$) may be alleviated in terms of interatomic *distance* (which is what really matters) by variation in the lengths of the radius vectors r_i.

More importantly though, these molecules consist of a cluster of heavy transition-metal atoms enveloped by carbonyl groups; the very nature of the *X*-ray diffraction experiment means that the positions of the carbonyl ligands can be determined with only relatively low precision. This is simply because a carbonyl group makes only a small contribution to the total electron density associated with the molecule. Most early crystal-structure determinations involved poor absorption corrections with the resultant uncertainties in light atomic positions appearing in the form of large thermal parameters; hence the carbonyl atom co-ordinates in many clusters are not accurately known. The uncertainties in the oxygen co-ordinates will be greatly magnified (by a factor of $\sqrt{6}$) on calculation of $\sum_{i\neq j}\Omega_{ij}^{-6}$. That this is so may be seen by comparing values for $\sum_{i\neq j}\Omega_{ij}^{-6}$ for the two sets of oxygen-atom co-ordinates in two dodecacarbonyls whose crystal structures have recently been redetermined with greater precision than before (Table 6). (These are simple, more precise, redeterminations, uncomplicated by disorder and pseudo-symmetry problems found in other dodecacarbonyls.)

TABLE 6

Molecule	Real $\sum_{i\neq j}\Omega_{ij}^{-6}$ (1st crystal-structure determination)	Real $\sum_{i\neq j}\Omega_{ij}^{-6}$ (2nd crystal-structure determination)	Ref.
$[Ru_3(CO)_{12}]$	26.049	25.472	53, 16
$[Os_3(CO)_{12}]$	27.011	26.006	54, 15

It is significant that in molecules with a high degree of crystallographically imposed symmetry {such as $[Co_6(CO)_{14}]^{4-}$} which have fewer independent carbonyl-atom co-ordinates, agreement between real and ideal values of $\sum_{i\neq j}\Omega_{ij}^{-6}$ is much closer.

Thirdly, the effect of crystal-packing forces on the molecular structures should not be overlooked. These forces are difficult to quantify, or even to analyse qualitatively, but can be quite large in magnitude. Finally, it should be noted that the large, symmetric polyhedra defined by the carbonyl groups have shapes inconsistent with the requirements of translational symmetry;[28] they must therefore become distorted in order to fill space efficiently in the crystal. This is particularly important in neutral species.

When these factors are borne in mind, we feel that the high values of $\sum_{i \neq j} \Omega_{ij}^{-6}$ in some real structures do not present too great a problem.

Conclusion.—It has been shown that the structures of the majority of transition-metal-cluster carbonyl species, including the distribution of edge- and face-bridging carbonyls, may be rationalised in terms of a simple model. This model postulates that the carbonyl ligands pack in space in such a manner as to minimise the non-bonded repulsions between themselves. The ways in which this may be achieved are found by calculation of repulsion potentials between points on the surface of a sphere. Although this presupposes that the metal cluster to be enveloped by the ligand polyhedron is reasonably spherical in shape, so that sensible metal–carbonyl bonding distances may be maintained, the success of the model for a range of metal-cluster geometries as diverse as the triangle, tetrahedron, trigonal bipyramid, and octahedron is noteworthy.

The carbonyl polyhedra observed enveloping these cluster shapes are among the two or three most favourable forms for each number of vertices, as indicated by our very simple calculations based purely on the optimisation of ligand–ligand repulsions. Forms of unfavourably high repulsion energy occur only when the metal-atom cluster is markedly aspherical {as in $[Re_4(CO)_{16}]^{2-}$}, and/or heterometallic {as in $[Mo_2Ni_3(CO)_{16}]^{2-}$}. Some other aspherical clusters, such as $[Rh_6C(CO)_{15}]^{2-}$, possess carbonyl geometries resembling favourable forms, but which are quantitatively very distorted. Calculations (not presented here) on polyhedra with fewer vertices show that the model also works for carbonyls which possess two metal atoms.

Work is continuing on the model, and as more crystal-structure determinations of cluster carbonyls are carried out, it may be tested further. In particular, an investigation into its use to rationalise the structures of carbonyl hydrides will be made. The hydride ligand may sometimes possess a stereochemical bulk similar to that of a carbonyl group, and sometimes appears not to represent a vertex of the ligand polyhedron at all. A number of carbonyl hydride structure determinations are being carried out by *X*-ray and neutron methods {for example, $[Os_3H_2(CO)_{10}]$[55] and $[Ru_4H_4(CO)_{12}]$[56]} by various researchers, and sufficient data should shortly be available to enable a systematic study to be made.

Future neutron diffraction studies of cluster carbonyls will provide more accurate atomic co-ordinates for their carbonyl atoms, so that the ligand polyhedra may be characterised in more detail. The problem of co-ordinate uncertainty in *X*-ray structural determinations becomes particularly acute when there are six or more second- or third-row transition-metal atoms in the cluster; this together with the very large number of reference forms for larger ligand polyhedra has prevented systematic analysis of the 18-carbonyl clusters of Ru_6 and Os_6. It has been stated that it is in these larger clusters that ligand–ligand repulsions may assume their greatest importance.[18]

We recognise that the method of using the real value of $\sum_{i \neq j} \Omega_{ij}^{-6}$ as a single number to indicate the degree to which a carbonyl polyhedron deviates from its idealised form is not entirely satisfactory, as it relies upon the characterisation of the polyhedral forms by inspection. More reliable information about the extent of deviation from idealised geometry may be obtained by considering the dihedral angles between adjacent pairs of faces of the ligand polyhedron.

It has been found that, for co-ordination numbers up to ten,[26–28,57] at least some of these angles are particularly sensitive to distortion, and give an accurate indication of both its nature and degree. Calculations of these dihedral angles in real carbonyl polyhedra are being carried out, to afford a more informative test of the model described in this work. However, the large number of faces possessed by 12—16-vertex polyhedra makes the results of such calculations difficult to interpret.

A number of other points are worthy of mention. (i) In spaces between CO spheres three types of hole are commonly observed: triangular, butterfly, and square planes. The size of these holes follows the order triangle < butterfly < square plane. It follows that occupancy of triangular holes will have the effect of bringing the metal atoms closer together than occupancy of, say, the plane. As a consequence, for a given $(CO)_n$ polyhedron small metal atoms *will tend to* occupy triangular holes whereas larger metal atoms *will tend to* occupy butterfly or planar holes.

This effect is demonstrated in the species $[Rh_6(CO)_{16}]$ and $[Fe_6C(CO)_{16}]^{2-}$ (see above). If we consider mixed metal clusters, *e.g.* $[Fe_2Ru(CO)_{12}]$ or $[RhCo_3(CO)_{12}]$, the larger metal ion *i.e.* Ru or Rh will occupy the larger holes. Thus the observation that CO bridges are associated with the lighter metal ions in $[Fe_2Ru(CO)_{12}]$[58] but the heavier ion in $[RhCo_3(CO)_{12}]$[59] (a contradiction in terms of electronic arguments) is easily understood since in each case the heavier atom occupies the larger butterfly hole in the icosahedron.

(ii) The change from bridged to non-bridged structures as the electron density of the cluster is increased either by anionic charge or by the substitution of CO by tertiary phosphines is usually attributed to the ability of CO bridges to function as better π acceptors than the terminally bound ligand.[13,60] This is possibly true but in general terms comparison is usually made between neutral and anionic carbonyls with different numbers of CO ligands, *e.g.*, $[Co_6(CO)_{16}]$, and $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ and, for the reasons discussed above, such comparisons are not valid. For a correct comparison, species with the same numbers of CO groups should be examined and we find, for example, that neither $[Os_6(CO)_{18}]$ [9] nor $[Os_6(CO)_{18}]^{2-}$ [61] contain CO bridges, and that in the isoelectronic series $[Co_2(CO)_8]$,[62] $[CoFe(CO)_8]^-$,[63] and $[Fe_2(CO)_8]^{2-}$,[63] an increase in negative charge is accompanied by a *decrease* in the number of carbonyl bridges. The effect of ligand substitution should also be more carefully examined. Substitution of one carbonyl ligand in $[Ir_4(CO)_{12}]$ by a phosphine like $PMePh_2$ shifts the ground-state structure from the non-bridged T_d form to the *quasi*-$[Co_4(CO)_{12}]$ form (C_{3v}) with three edge-bridging groups.[64] This is taken to be the effect of increased electron density on the cluster. But substitution of one, two, or three CO groups in $[Ru_3(CO)_{12}]$ does not produce a CO-bridged structure; [65] very little supporting evidence for the above supposition. We believe that a complete description of such structural phenomena will include greater recognition of the steric effects of carbonyl ligands than has previously been the case.*

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* *Note added at proof:* Several cluster carbonyls have been determined very recently.

For n = 13. In $[CoRu_3(CO)_{13}]^-$ the ligand polyhedron is the 1 : 3 : (3) : 3 : (3) face-capped icosahedral form, with a repulsion energy approximating well to the ideal value.[66] The metal-atom tetrahedron is oriented within this polyhedron so that the unique capping carbonyl vertex lies over the apex of the metal cluster, whereas in $[Fe_4(CO)_{13}]^{2-}$ it spans the base. Thus the two structures differ in their distribution of terminal and bridging carbonyls. This may arise from the unequal sizes of the two metal clusters, or from a preference of the apical cobalt atom in the heterometallic cluster for a particular site in the (CO)–polyhedron.

$$\text{For } [CoRu_3(CO)_{13}]^-\text{: } R_0 = 3.998\ \text{Å} \pm 9.39\%$$
$$\text{Real} \sum_{i\neq j} \Omega_{ij}^{-6} = 28.334$$

For n = 14.—The crystal structure of $[Co_6C(CO)_{14}]^-$ has been published.[67] In this paramagnetic cluster the 'extra' (87th) electron appears to occupy an antibonding orbital localised along one edge of the metal-atom octahedron, elongating this edge and splaying out the adjacent carbonyls. As a result, the (CO)-polyhedron appears irregular, with a high real repulsion energy.

$$\text{For } [Co_6C(CO)_{14}]^-\text{: } R_0 = 4.275 \pm 5.96\%$$
$$\text{Real} \sum_{i\neq j} \Omega_{ij}^{-6} = 53.331$$

For n = 15.—The structure of $[Co_6N(CO)_{15}]^-$ has been published.[68] Atomic co-ordinates are not available, but the cluster's structure is very similar to that of the isoelectronic $[Rh_6C(CO)_{15}]^{2-}$.

In $[Co_6H(CO)_{15}]^-$ the octahedral metal cluster contains an interstitial hydride, located by neutron diffraction.[69] There are ten terminal, one symmetrically bridging, and four asymmetrically bridging carbonyls. The (CO)-polyhedron is rather irregular, most closely resembling a 2 : (2) : 7 : 2 : (2) form in which the equatorial plane of seven vertices has undergone considerable puckering. This form does not bear an obvious symmetry relationship to the metal cluster. In terms of $\sum_{i\neq j} \Omega_{ij}^{-6}$ though, the optimum value for a 15-vertex polyhedron is approached quite closely. This neutron study emphasises the effect of co-ordinate uncertainty in *X*-ray determined structures (see above).

$$\text{For } [Co_6H(CO)_{15}]^-\text{: } R_0 = 4.221 \pm 4.85\%$$
$$\text{Real} \sum_{i\neq j} \Omega_{ij}^{-6} = 51.569$$

For n = 16.—Two independent *X*-ray determinations of $[Ru_6C(CO)_{16}]^{2-}$ have been completed. In $[NMe_4]_2[Ru_6C(CO)_{16}]$, space group $P2_1/c$ the anion is isostructural with its iron analogue.[70] In $[AsPh_4]_2[Ru_6C(CO)_{16}]$, space group Pn, there are four

$$R_0 = 4.488\ \text{Å} \pm 4.18\%$$
$$\text{Real} \sum_{i\neq j} \Omega_{ij}^{-6} = 74.385$$

fairly symmetrical bridging carbonyls which correspond to the three asymmetric bridges and one non-linear terminal carbonyl in the $[Fe_6C(CO)_{16}]^{2-}$ structure.[71] The ligand polyhedron is different, a 2 : (2) : 8 : 2 : (2) form of very high real repulsion energy.

$$R_0 = 4.580\ \text{Å} \pm 4.69\%$$
$$\text{Real} \sum_{i\neq j} \Omega_{ij}^{-6} = 118.69$$

The influence of the counter ion on cluster carbonyl structures has previously been demonstrated in $[W_2H(CO)_{10}]^-$.[72]

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