The mathematical modelling of ligand arrangements in metal carbonyl clusters.

I. Sixteen, seventeen, and eighteen coordination for octahedral metal clusters

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Abstract

A mathematical model has been developed for the systematic calculation of the ligand arrangements in metal carbonyl clusters. The model is founded on the assumption that the ligand shell geometries are dependent upon: (a) the ligand–ligand repulsions, (b) the geometries of the metal cores and (c) the electronic interactions between the metal cores and the ligands. The agreement between minimum energy configurations and the structures determined by crystallography is good for nearly all small and medium sized metal carbonyl clusters $[M_x(CO)_y](x = 2$ to 7, $y = 8$ to 21). The model is described, together with the results of the calculations performed for the octahedral metal clusters systems $[M_6(CO)_{16}]$, $[M_6(CO)_{17}]$ and $[M_6(CO)_{18}]$. The presentation of the results is facilitated by use of a scheme that separates the minimum energy structures into groups according to the number and type of bridging ligands they contain.

Key words: Group 8; Group 9; Molybdenum; Cluster; Carbonyl; Molecular mechanics

1. Introduction

The calculation of the ligand position in mononuclear coordination complexes has been successfully achieved for a very large number of cases using an extended repulsion approach [1,2]. The method used was based on Valence Shell Electron Pair Repulsion (VSEPR) theory [3,4] in which the mutual repulsion of the electron pairs around an atom determines the relative positions of the ligands. The extended version takes into account the steric constraints imposed by chelating ligands and the distortions that can occur when the ligands are not all the same.

In metal carbonyl clusters $M_x(CO)_y$, simple electron counting rules can be used to predict the ratio of the number of metal atoms to carbonyl ligands [5,6]. There are, however, no general set of axioms for predicting the relative positions of the ligands on the surface of

metal atom clusters. This is primarily because the ligand positions are not controlled by metal cluster molecular orbitals [6]. A carbon monoxide ligand can bind to a metal core in a variety of modes. It can be terminally bound to a single metal atom or in a bridging position coordinated to two (double- or edge-bridging), or three (triple- or face-bridging) metal atoms. The bridges can be symmetrical, with equal distances to each bonded metal atom, or can have varying degrees of asymmetry. Bridges are most commonly observed in clusters in which the metal atoms are either first or second row transition metal elements.

Steric factors have long been understood to be highly important in determining the geometry of the carbonyl shell. Theoretical approaches include the close-packing arguments advanced by Johnson [7], the combined ligand–ligand repulsion and ligand–metal core packing technique adopted by Johnson and Benfield [8], and the surface force field or molecular mechanics model used by Lauher [9].

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The approach adopted in this work for the calculation of ligand stereochemistries can be considered to be a simplified molecular mechanics method [10]. The method lies midway between the Johnson and Lauher models in terms mathematical complexity of computational requirements. The approach is superior to previous attempts because of the ease of performing the calculations, the extendability of the method, and the good correlations with experimental data.

2. The theoretical model

2.1. Ligand–ligand repulsions

The mathematical model developed for the calculation of the stereochemical arrangement of carbonyl groups about a cluster of metal atoms is based on the minimisation of repulsion between the carbonyl groups. Ligand geometries are derived by the minimisation of the repulsion between all ligands where the interaction between any pair of ligands, u_{1-1}, is assumed to be simply a function of the distance, d_{1-1}, between the carbon atoms. The function is taken to be of the form of an inverse power relationship:

$$u_{1-1} \; \alpha \; d_{1-1}^{-n}$$

where the value of n used is six. It has been found that the results obtained are not strongly dependent on this value [1]. The total repulsion energy, U_{1-1} (tot.), is obtained by summing over all ligand–ligand interactions:

$$U_{1-1}(\text{tot.}) = \sum u_{1-1} = \sum a d_{1-1}^{-6}$$

where a is the proportionality constant. This method has been extensively used for mononuclear compounds [1].

2.2. The ligand shell

In the model, no attempt is made to calculate metal core geometries and so these must be introduced as fixed parameters. The metal polyhedra used in the calculations are taken to be as regular as possible, with idealised symmetries, and atom–atom distances equal to the averaged experimentally observed distances.

It is assumed that a carbonyl ligand can bond to any part of the metal polyhedron. The carbon atoms of carbon monoxide are thus constrained to lie on a two-dimensional non-spherical surface that envelops the entire metal core. The shape of this surface follows the smoothed-out contours of the metal atom unit in such a way that as a ligand swings from a terminal into a bridging position the metal–ligand bond distances increase to the degree that is observed experimentally. The surface is calculated by summing the distances from a ligand to each metal atom, raising to some

inverse power, p, and equating the sum to a constant, k, that is dependent on the size of the metal core:

$$\sum_i (M_i - C)^{-p} = k$$

The constant is typically in the range 0.010 to 0.025. The value of p needed to define the surface was determined by a least-squares fit of the calculated surface to the experimental surface in a series of molecules containing both bridging and terminal ligands. The average, equal to seven, was used in all calculations. In carbido-clusters, the carbide atoms were usually included in the surface calculation and weighted equally with the metal atoms.

2.3. Ligand-to-metal core interactions

Calculations based only on the minimisation of ligand–ligand repulsions with the carbonyls constrained to lie on the non-spherical surface will clearly return only one global minimum energy structure. In order to model structures that are stoichiometrically identical but with different ligand arrangements (for example, $[M_3(CO)_{12}]$, M = Os and Fe), it is necessary to be able to produce a range of minima which exhibit some correspondence with the experimentally observed structures. Such a range of minima is accessible if ligand to metal core interactions, capable of stabilising both terminal and bridging ligand positions, are introduced into the model.

The first successful type of ligand-to-metal core potentials investigated were interactions between the centre of the metal–metal bonds and the ligands [10]. The interaction was taken to be the usual inverse sixth power expression. The total ligand-to-metal–metal bond repulsion energy, U_{1-mm}(tot.), is obtained by summing over all interactions. The total calculated energy for the ligand shell is the sum of the ligand–ligand and ligand-to-metal–metal bond interactions and is given by:

$$U(\text{tot.}) = U_{1-1}(\text{tot.}) + w U_{1-mm}(\text{tot.})$$

$$= \sum u_{1-1} + w \sum u_{1-mm}$$

where w is a weighting factor. The energies obtained in the calculations had no significance outside the context of the model, and so only this single weighting factor, w, is required.

Calculations with values of w of approximately 0.3 reproduce experimental structures containing only terminal carbonyls, such as those observed of osmium and rhenium clusters (where w needs to be approximately 0.3), whereas negative values of w, $w = 0.0$ to -0.04, stabilise ligands in bridging positions [10].

The weighted interaction between the centre of the metal–metal bonds and a ligand is understood to be an

empirical measure of the tendency of the ligand-to-bridge metal atoms. The parameter w is therefore termed the bridging parameter or bridging factor.

2.4. Method of calculation

The program for the stereochemical calculations converts a ligand starting approximation into a minimum energy structure using a numerical procedure based on the algorithm developed by Davidon [11]. For most systems, it is only the global minimum energy structure at each value of the bridging parameter that is of interest. It was found that the total energy function usually had a great many local minima the one obtained in a particular calculation being dependent upon the initial approximation used. Since there was no method for deciding if a given minimum is the absolute minimum, it was necessary to use a large number of initial approximations to be reasonably confident that the lowest energy structure had not been missed. For small clusters (with two to four metal atoms), between twenty and fifty calculations were sufficient and for medium sized clusters (with five to nine metal atoms) approximately two hundred calculations were often necessary.

3. Results and discussion

For each of the three high coordination numbers for the octahedral metal atom core (sixteen to eighteen carbonyl groups), the stereochemistry of the ligand shell was calculated at values of the bridging parameter ranging from 0.0 to −0.1 and at 0.3. Inspection of the final results revealed that the large number of global minimum energy structures obtained could be rationalised within a small conceptual framework. It was found that when only ligand–ligand repulsive potentials determined the ligand shell geometry ($w = 0.0$), the minimum energy arrangements obtained could best be described as approximate spherical ligand shells. That is, in each structure the ligands are approximately equidistant from the centre of the metal core and each nearest-neighbour ligand–ligand distance is similar. The incorporation of ligand-to-metal–metal bond repulsions into the calculations ($w = 0.3$) produced ligand arrangements that could be best regarded as distorted versions of the structures obtained at $w = 0.0$. In these structures, the distortions involved the rotation of ligands about each metal atom away from the metal polyhedral edges and faces.

When ligand-to-metal–metal bond attractive interactions were incorporated into the calculations (negative values of w), two types of structures were obtained. At small negative values of w (that is, weak ligand-to-metal core attractions), the lowest energy

structures were also distorted versions of the ligand arrangements calculated at $w = 0.0$. The distortions in these structures involved the formation of a small number of bridging ligands. For large negative values of w (that is, strong ligand-to-metal core attractions), the lowest energy structures obtained were of a very different type. In these configurations, there were ligands associated with every edge of the octahedral metal atom core.

A statistical comparison between calculated and observed structures was undertaken whenever the atomic coordinates of the experimental structures were available in the literature. The structures were compared by examining the root mean square (rms) or all metal–carbon bond lengths and angles. This method was preferred to comparisons of atomic positions because it avoided the difficulties of superimposing one structure upon another. As a general rule, a good fit returns values of rms (bond lengths) < 0.1 Å, rms (bond angles) < 4.0; an average fit gives values around 0.16 Å and 7.0; and finally a poor fit has the values over 0.25 Å and 12.0 for bond lengths and bond angles, respectively. Throughout all the calculations described below, it is the gross structure that is modelled rather than fine structure. Attention was directed mostly at the ligand connectivities for differentiating structures rather than at ligand coordinates. Thus, all of the rms values quoted do not represent the best fit of the observed and calculated results. This is especially true for the rms (bond lengths) figures. These numbers depend on the size of the metal core and the value of the surface constant used in the calculations. These parameters were kept constant in every set of experiments.

A simple terminology for describing the calculated structures is employed in this work. Each stereochemistry is assigned the form:

$$x\,T + y\,DB + z\,TB$$

where x is the number of terminal ligands, y is the number of double bridges and z is the number of triple bridges. For example, a structure with fourteen terminal, two doubly-bridging and two triply-bridging carbonyl ligands is reduced to $14T + 2DB + 2TB$. This method does not indicate asymmetric bridging, which must thus be made explicit when it is present.

3.1. Sixteen coordination

The global minimum energy structures obtained for sixteen coordination are listed in Table 1. For values of $w = 0.0$ to 0.3, all ligands are terminal. Two *trans* metal atoms are coordinated to two ligands each and the remainder are coordinated to three ligands each. The ligands of the $M(CO)_2$ groups are staggered,
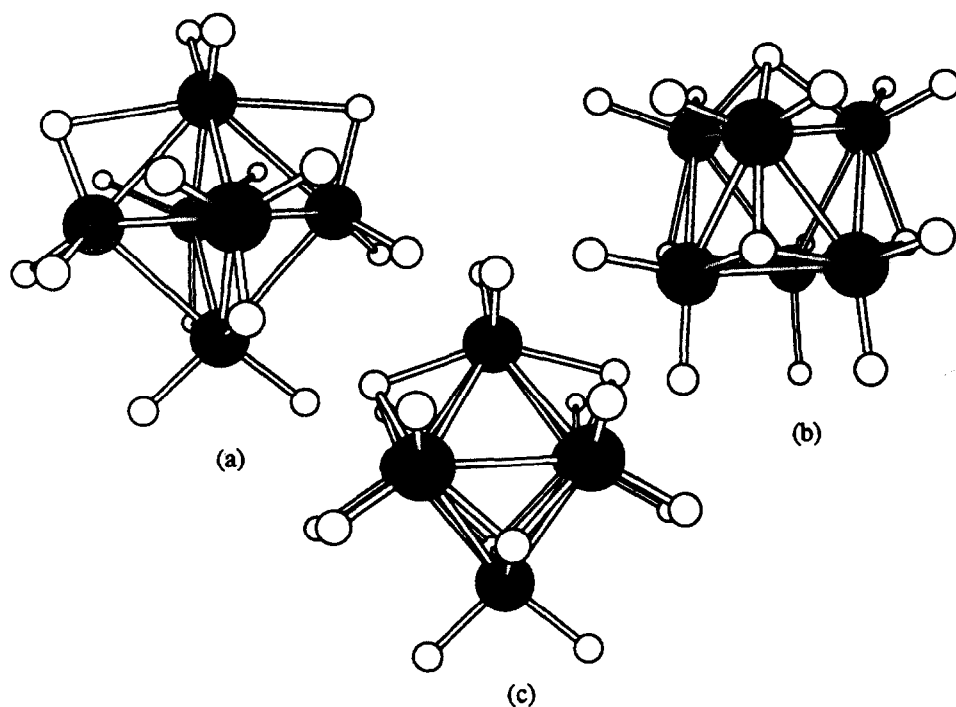
Fig. 1. The minimum energy structures for weak ligand to metal core attractive interactions for $[M_6(CO)_{16}]$. (a) 12T + 4DB ($w = -0.001$), (b) and (c) 12T + 4TB ($w = -0.01$).
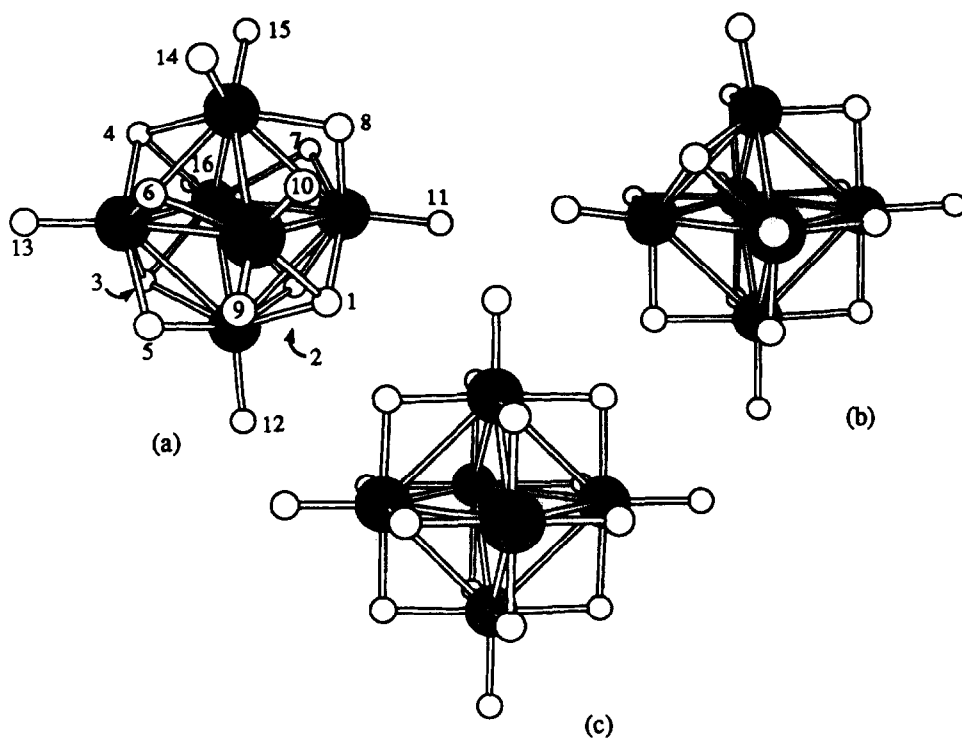

Fig. 2. The global minimum energy structures for strong ligand-to-metal core attractive interactions for $[M_6(CO)_{16}]$. (a) 8T + 4DB + 4TB ($w = -0.03$). (b) 6T + 9DB + 1TB ($w = -0.04$). (c) 4T + 12TB ($w = -0.01$).

TABLE 1. The global minimum energy structures calculated for sixteen ligands around the octahedron.

w	Structure
0.3	16T
0.0	16T
−0.001	12T+4DB
−0.002 to −0.026	12T+4TB
−0.027 to −0.034	8T+4DB+4TB
−0.035 to −0.050	6T+9DB+1TB
−0.051 to −0.100	4T+8TB

whereas in both *trans* M(CO)$_3$ pairs, the ligands are eclipsed. The symmetry of this structure is D_{2d}. The minimum energy structure obtained at the value of $w = 0.3$ is very similar to this arrangement. The structure, also of type 16T, has D_2 symmetry.

For weak ligand to metal core attractions, two minima were obtained. The corresponding structures are illustrated in Fig. 1. The 12T + 4DB structure, with D_{2d} symmetry, contains four extremely asymmetric double bridges (with metal–carbon bond lengths of 1.749 Å and 2.485 Å) and is very similar to the structure calculated at the value of $w = 0.0$. The ligand polyhedron of the 12T + 4TB structure, which has T$_d$ symmetry, is also similar with each metal atom identically attached to two terminal ligands and two symmetrical triple bridges. This structure is obtained from the 12T + 4DB structure by a simple concerted rotation of the entire ligand shell (or metal core) by 45 around its C_2 axis. This relationship can be seen by comparing Fig. 1a and c.

Strong ligand to metal core attractions generated two types of ligand packing, over values of the bridging parameter ranging from −0.03 to −0.1. The structures

are shown in Fig. 2. One minimum energy structure contained a large number of triply-bridging ligands, with double bridges in close proximity to the remaining uncapped faces of the metal atom polyhedron. This is the 8T + 4DB + 4TB structure, which has C_2 symmetry. In Fig. 2a, the triple bridges are ligands numbered 1 to 4, the double bridges are numbered 5 to 8, and the remainder are all terminal.

The other minimum energy structures obtained for strong attractions contain large numbers of symmetrical double bridges. Two structures were obtained and these are illustrated in Fig. 2b and c. The 6T + 9DB + 1TB structure has C_{3v} symmetry and the 4T + 12DB ligand arrangement has D_{4h} symmetry.

The clusters [Rh$_6$(CO)$_{16}$], [FeRh$_5$(CO)$_{16}$]$^-$ (two crystal structure determinations have been considered for this anion), [Fe$_2$Rh$_4$(CO)$_{16}$]$^{2-}$, [Ir$_6$(CO)$_{16}$], [RuRh$_5$(CO)$_{16}$]$^-$, and [Co$_6$(CO)$_{16}$] have all been found to have the 12T + 4TB ligand configuration [12–18]. Only the coordinates for the Ir$_6$ and RuRh$_5$ clusters were available, and both showed a very good agreement with the calculated results. For the Ir$_6$ cluster, rms (bond lengths) = 0.17 Å and rms (bond angles) = 4.8° and for the RuRh$_5$ cluster, rms (bond lengths) = 0.18 Å and rms (bond angles) = 5.2°.

As well as the red isomer of [Ir$_6$(CO)$_{16}$] described above, there is a black isomer which has two distinct molecules in the unit cell [16], both of which are close to the calculated 12T + 4DB configuration with some distortion towards the 12T + 4TB arrangement [19]. The crystal structure of [RhFe$_5$C(CO)$_{16}$]$^-$ has been found to possess the same 12T + 4TB geometry [14]. Two structure determinations have been carried out for [Ru$_6$C(CO)$_{16}$]$^{2-}$. In the first of these, involving the Ph$_4$As$^+$ cation, the ligand geometry is again 12T + 4TB
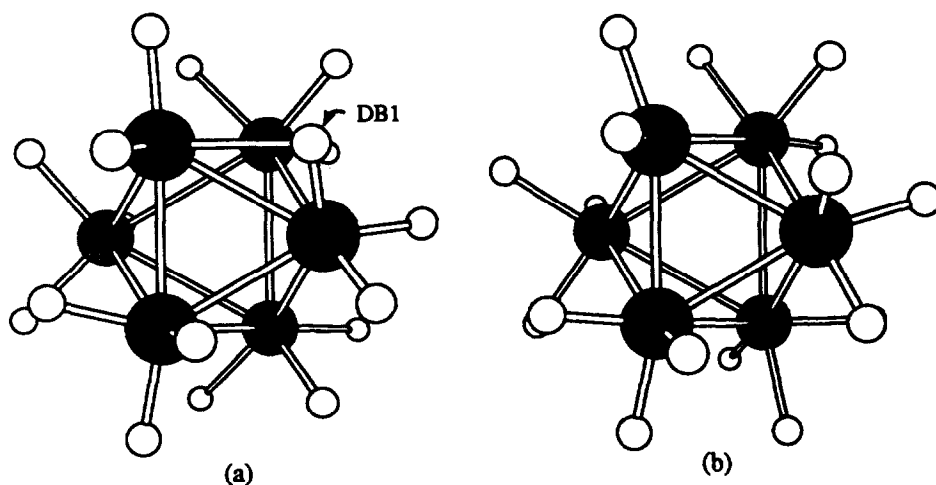

Fig. 3. Some global minimum energy structures for the [M$_6$(CO)$_{17}$] system. (a) 16T + 1DB ($w = 0.0$). (b) 17T ($w = 0.3$).

TABLE 2. The global minimum energy structures calculated for seventeen ligands around the octahedron.

w	Structure
0.3	17T
0.0 to -0.004	16T + 1DB
-0.005	15T + 2DB
-0.006 to -0.019	13T + 1DB + 3TB
-0.020 to -0.022	9T + 8DB
-0.023 to -0.039	6T + 11DB
-0.040 to -0.100	5T + 12DB

[20]. With the $N(CH_3)_4^+$ cation [21] the ligand arrangement was described as 13T + 3DB, although the difference between this structure and the calculated 12T + 4TB structure is small. Coordinate analysis gave: rms (bond lengths) = 0.06 Å and rms (bond angles) = 4.7°. A similar structure was observed for $[Fe_6C(CO)_{16}]^{2-}$ which was again reported as 13T + 3DB [22], rms (bonds lengths) = 0.12 Å and rms (bond angles) = 3.7°.

3.2. Seventeen coordination

The minimum energy structures obtained for seventeen coordination are listed in Table 2. For ligand–ligand repulsions only ($w = 0.0$), the structure contains

sixteen terminal groups and one semi-bridging ligand (with metal–carbon bond lengths of 1.756 Å and 2.473 Å) (Fig. 3a). In this arrangement (which has no symmetry), each metal atom is attached to three ligands. The geometry obtained when ligand-to-metal bond repulsions were included in the calculations is very similar. This stereochemistry is of the 17T type and also contains no symmetry (Fig. 3b).

The inclusion of weak ligand-to-metal core attractions in the calculations generated three global minimum energy structures (Fig. 4). In each of these structures, the ligand packing is similar to that found in the $w = 0.0$ calculated structure. The 15T + 2DB configuration (which has no symmetry), can be obtained from the 16T + 1DB configuration by the conversion of a terminal ligand into a weakly semi-bridging group (with metal–carbon bond lengths of 1.772 Å and 2.469 Å) and by increasing the symmetry of the original bridge (metal–carbon bond lengths of 1.845 Å and 2.037 Å). The 13T + 1DB + 3TB structure (which has no symmetry) and the 9T + 8DB structure (which has C_2 symmetry) are related to one another by a simple concerted rotation of the ligand shell around the metal core. The numbering scheme used in Fig. 4b and c illustrates the relationship between the 13T + 1DB + 3TB and 9T +
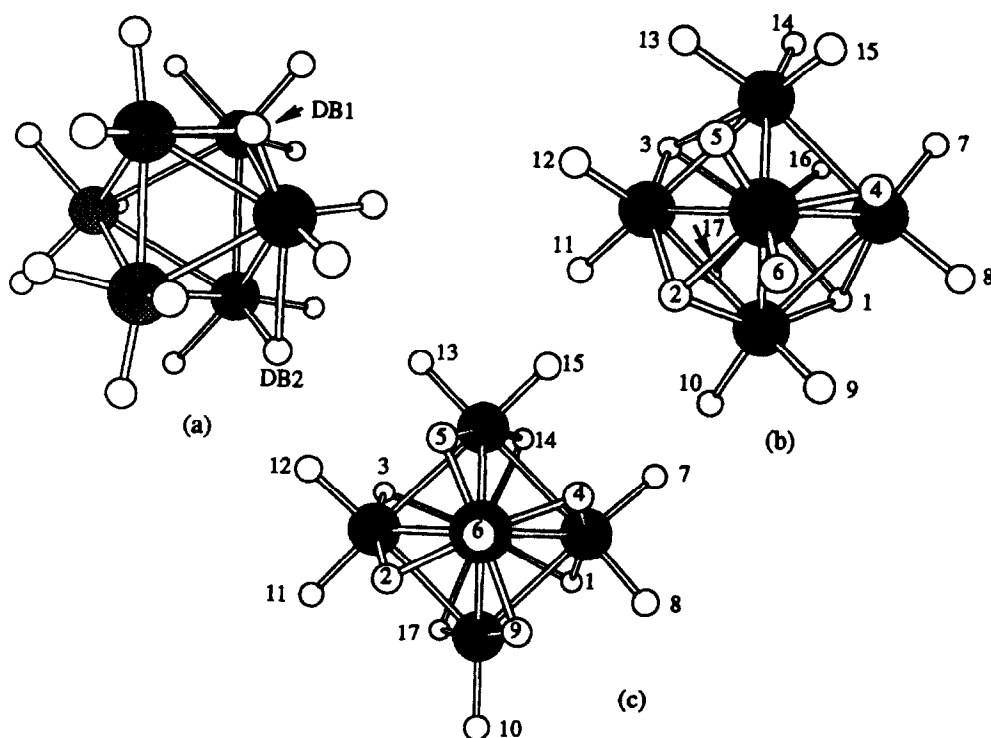

Fig. 4. The minimum energy structures for weak ligand-to-metal core attractive interactions for $[M_6(CO)_{17}]$. (a) 15T + 2DB ($w = -0.005$). (b) 13T + 1DB + 3TB ($w = -0.01$). (c) 9T + 8DB($w = -0.02$).
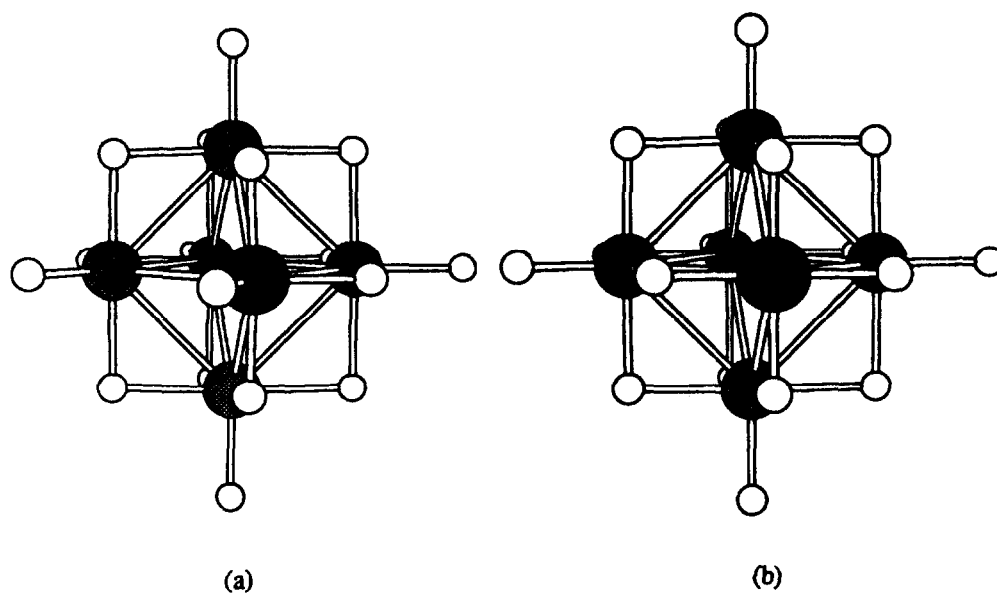
(a)   (b)

Fig. 5. The minimum energy structures for strong ligand-to-metal core attractive interactions for [M$_6$(CO)$_{17}$]. (a) 6T + 11DB (w = -0.03). (b) 5T + 12DB (w = -0.04).

8DB geometries. A similar type of rearrangement relates the 15T + 2DB and 13T + 1DB + 3TB structures.

Strong ligand-to-metal core attractions gave two new structures, both based on packing with twelve double bridges (Fig. 5). The 6T + 11DB configuration has C_{2v} symmetry and the 2T + 12DB configuration has C_{4v} symmetry.

Three seventeen-coordinate metal carbonyl clusters have known structures: [Ru$_6$C(CO)$_{17}$], [HRu$_6$B(CO)$_{17}$] and [MoFe$_5$C(CO)$_{17}$] and [MoFe$_5$C(CO)$_{17}$]$^{2-}$ [23–25]. Each of these structures is related to the calculated 16T + 1DB structure. The ruthenium carbidocluster

contains sixteen terminal and one doubly-bridging ligand and is very similar to the calculated structure. The ruthenium hydride cluster has the same connectivities, although it appears slightly distorted at two neighbouring M(CO)$_3$ sites. This suggests the hydride ligand may be bridging these two metal atoms. The iron–molybdenum mixed metal cluster consists of fifteen terminal and two doubly-bridging carbonyls. The bridges do not span the same edges as in the calculated 15T + 2DB structure. The experimental ligand arrangement can be obtained from the calculated 16T + 1DB structure simply by joining the molybdenum atom
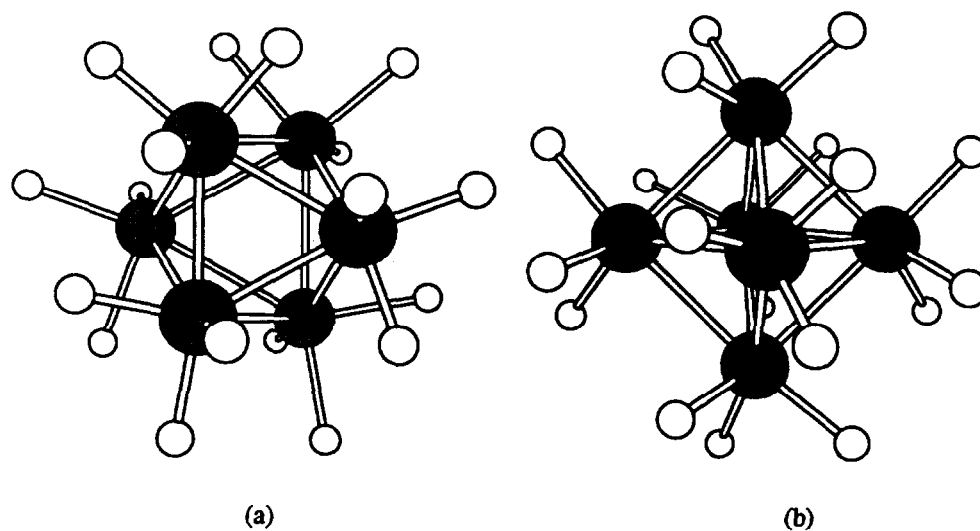

(a)   (b)

Fig. 6. Two views of the all terminal structure for the [M$_6$(CO)$_{18}$] system (w = 0.0).
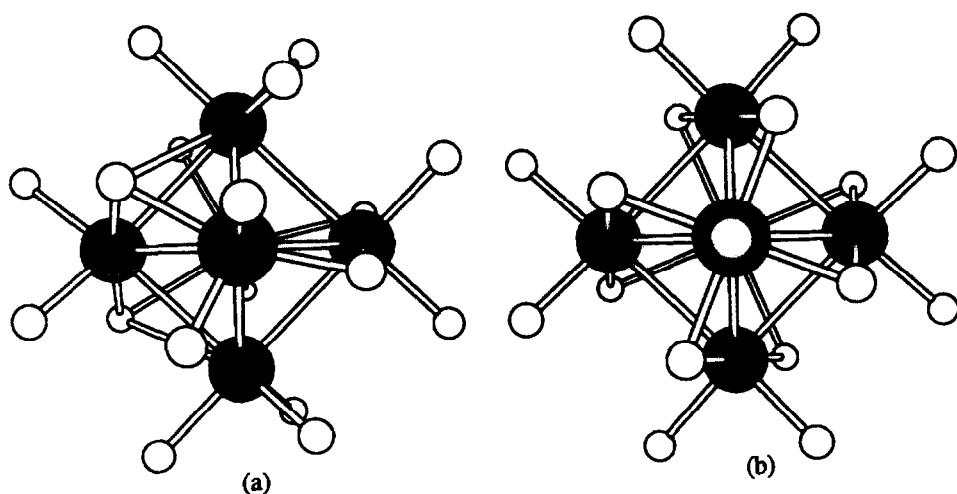
Fig. 7. The minimum energy structures for weak ligand-to-metal core attractive interactions for $[M_6(CO)_{18}]$. (a) 14T + 2DB + 2TB ($w = -0.015$). (b) 10T + 8DB ($w = -0.02$).
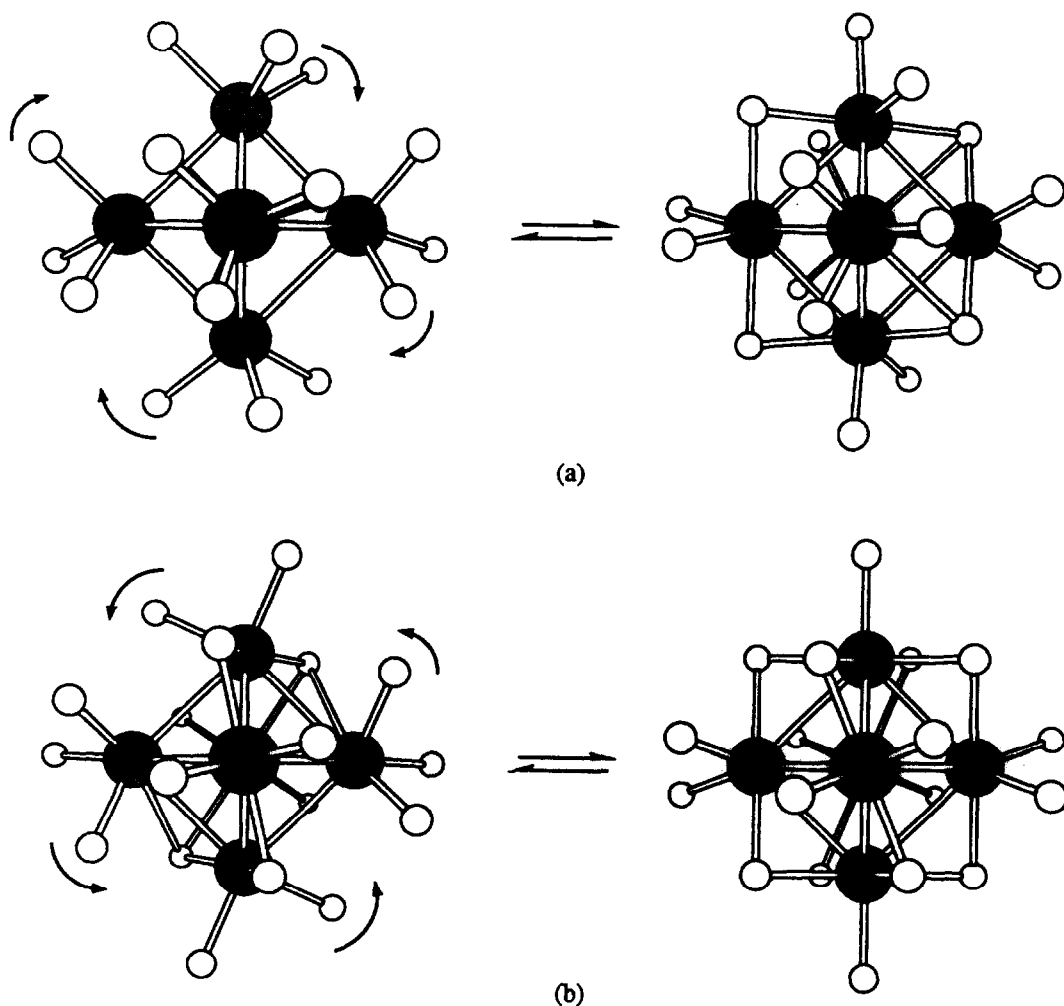

Fig. 8. The ligand shell rotations relating the 18T, 14T + 2DB + 2TB and 10T + 8DB structures. (a) The 18T to 14T + 2DB + 2TB conversion. (b) The 14T + 2DB + 2TB to 10T + 8DB conversion.

TABLE 3. The global minimum energy structures calculated for eighteen ligands around the octahedron.

w	Structure
0.3	18T
0.0 to −0.0013	18T
−0.014 to −0.016	14T + 2DB + 2TB
−0.017 to −0.047	10T + 8DB
−0.048 to −0.100	6T + 12DB

to a nearby ligand and rotating two $M(CO)_3$ groups by approximately 20°.

3.3. Eighteen coordination

The global minimum energy structures calculated for eighteen coordination for the octahedron are listed in Table 3. The minimum energy structure obtained for values of w greater than −0.013 is illustrated in Fig. 6. In this stereochemistry of type 18T (with D_3 symmetry), each metal atom is identically coordinated by three terminal ligands. The structure resides in a reasonably deep potential energy well. Plots of the angular coordinates of the ligands as a function of w reveal that the ligand positions remain comparatively constant over large variations in the value of the bridging parameter.

The incorporation of weak ligand to metal core attractions in the calculations generated two new minimum energy structures, both of which contain the kind of packing observed in the 18T structure described above. These structures are illustrated in Fig. 7. In the 14T + 2DB + 2TB configuration (which has C_2 symmetry), each metal atom is bonded to four ligands. In the 10T + 8DB configuration (which has D_4 symmetry), four of the metal atoms have four ligands attached (two terminal and two bridging groups) and the other

two metal atoms have five ligands attached (one terminal and four bridging groups). The 14T + 2DB + 2TB ligand arrangement can be obtained from the 18T structure by a simple rotation of the entire ligand shell around the metal core. This transformation is depicted in Fig. 8a. The same kind of process relates the 10T + 8DB configuration and the 14T + 2DB + 2TB structure (Fig. 8b).

For strong ligand-to-metal core attractions, a structure containing six equivalent terminal and twelve symmetrical doubly-bridging ligands was found to be of lowest energy. The structure, which has O_h symmetry, is illustrated in Fig. 9. With this stereochemistry, each metal atom is identically coordinated to one terminal and four bridging groups.

Many experimentally observed structures possess the 18T calculated geometry. The ligand arrangements in $[Os_6(CO)_{18}]^{2-}$ and $[Ru_6H(CO)_{18}]^-$ (in which the hydride is at the centre of the metal core) [26,27], almost exactly match the calculated stereochemistry. The structures of the hydride clusters $[HOs_6(CO)_{18}]^-$, $[H_2Ru_6(CO)_{18}]$ and $[H_2Re_6C(CO)_{18}]^{2-}$, which each contain eighteen terminal carbonyls, are again very similar [26,28–30]. The differences in the experimental and calculated ligand positions in these three cases can be attributed to the hydrogen atoms. A statistical comparison (with the w = 0.3 minimum energy structure) could only be carried out for the osmium hydride cluster, rms(bond lengths) = 0.16 Å and rms(bond angles) = 15.4°.

The $[Ru_6(CO)_{18}]^{2-}$ cluster [31] has the calculated 14T + 2DB + 2TB structure. Comparison of experimental and calculated results yielded rms(bond lengths) = 0.16 Å and rms(bond angles) = 6.6°. The
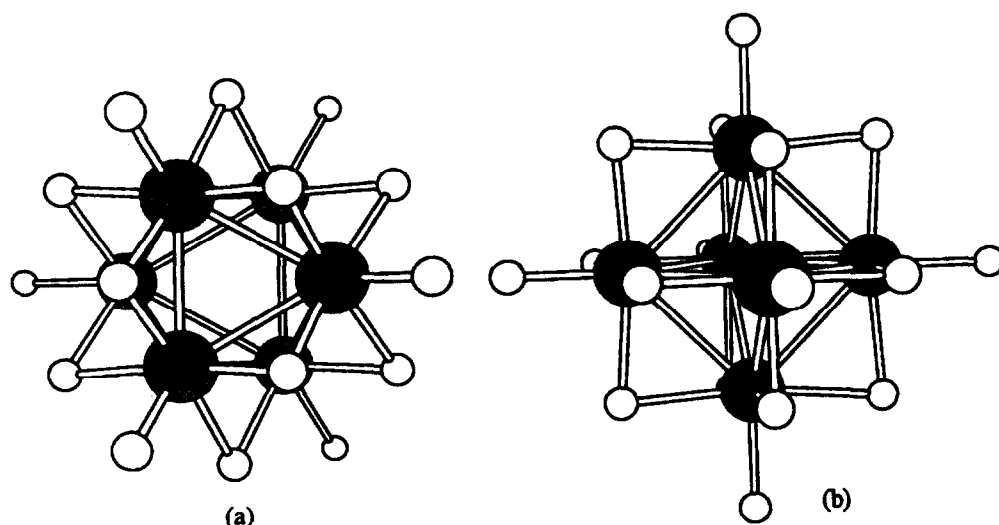

(a)   (b)

Fig. 9. Two views of the minimum energy structure for strong ligand-to-metal core attractive interactions for $[M_6(CO)_{18}]$, 6T + 12DB (w = −0.05).

successful modelling of this complex structure demonstrates that the approach is very efficient at reproducing the experimentally observed ligand arrangements in sterically crowded systems.

4. Conclusions

The important features of the observations include:

(i) For ligand–ligand repulsions only ($w = 0.0$), the minimum energy structures obtained consisted of terminal ligands and sometimes extremely asymmetric doubly-bridging groups. The structures were described throughout as perturbed spherical ligand shells. In this respect, they closely resemble the geometries obtained when y points are fixed to the surface of a sphere and forced to repel one another according to an inverse power law similar to that used in the model.

(ii) When ligand-to-metal–metal bond repulsions were included in the calculations ($w = 0.3$), the structures obtained consisted of terminal ligands only. The geometries were shown to be distorted versions of the perturbed spherical ligand shells calculated at the value of $w = 0.0$. The distortions were found to involve the rotation of ligands about each metal atom away from the metal polyhedral edges. Increasing the magnitude of w above 0.3 in the calculations simply results in greater rotations away from the metal–metal edges and a tighter grouping of the ligands in each $M(CO)_n$ fragment.

(iii) When weak ligand-to-metal core attractive interactions were incorporated into the calculations (that is, small negative values of the bridging parameter), many different structures were obtained. They were all found to be best described in terms of distorted versions of the minima obtained for no attractive interactions. The distortions, involving the formation of a small number of bridging ligands, were observed to be of two types. The first type involved the rotation of some of the ligands towards metal polyhedral edges (and sometimes towards faces), thereby generating bridging groups. The second type involved the concerted rotation of the entire ligand shell around the metal core.

(iv) The minimum energy structures obtained at the value of $w = -0.1$ contained twelve doubly-bridging ligands. Many examples of this structure are know for halide and hydroxo ligands [32].

Acknowledgement

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