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The ligand polyhedral model: its application to carbonyl clusters containing thirteen carbonyl groups†

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The Ligand Polyhedral Model (LPM) has been applied to the series of carbonyl species $[Fe_4(CO)_{13}]^{2-}$, $[Fe_3Co(CO)_{13}]^-$, $[Ru_3Co(CO)_{13}]^-$, $[Ru_3Rh(CO)_{13}]^-$, $[Ru_3Ir(CO)_{13}]^-$, $[Os_3Ir(CO)_{13}]^-$ and $[Co_2Ru_2(CO)_{13}]$ containing thirteen carbonyl ligands. The model predicts that the 13-vertex polyhedra with the minimum energies are the face-capped icosahedron and edge-bridged icosahedron and that they are very close in energy. Polyhedra with next higher energies are the variously capped cubeoctahedra and capped anti-cubeoctahedra. In this sense these 13-vertex arrangements are clearly related to the polyhedra adopted by the 12-CO species $[Co_4(CO)_{12}]$ and $[Ir_4(CO)_{12}]$. Significantly, the structures of the carbonyl cluster anions $[Fe_4(CO)_{13}]^{2-}$, $[Fe_3Co(CO)_{13}]^-$, $[Ru_3Co(CO)_{13}]^-$, $[Ru_3Rh(CO)_{13}]^-$, $[Ru_3Ir(CO)_{13}]^-$ (one isomer), and $[Co_2Ru_2(CO)_{13}]$ all contain these capped icosahedra in line with prediction. These structures are discussed for clarity in terms of their close 12-CO relatives with an icosahedral CO shell with T or C_{3v} symmetry. Of special interest is the variety of orientations that the central, tetrahedral metal unit adopts within the capped icosahedron leading to the range of different structural forms observed experimentally. As anticipated, the anion $[Os_3Ir(CO)_{13}]^-$ and a second isomer of the anion $[Ru_3Ir(CO)_{13}]^-$ with a larger central metal core have a capped cubeoctahedral arrangement of thirteen CO ligands. The diverse range of structural types found for species containing thirteen carbonyl groups are readily understood in terms of the LPM. There is no other approach which so easily explains the observed structural types and isomeric forms seen.

Introduction

The Ligand Polyhedral Model (LPM) was first proposed in 1976[1] and was based on ideas derived from a consideration of the ligand polyhedral geometries adopted by a variety of inorganic cluster compounds. At that time it was applied to a wide range of binary carbonyls for which there was no simple understanding of the apparently complicated structures they adopt. This was the first time that such an analysis of carbonyl structures had been carried out and our proposal (the basis of the LPM) that the structures of these compounds are based on relatively simple geometric factors (*i.e.* metal polyhedron or polygon within CO polyhedra) was entirely new. The first full report of this work appeared in 1980[2–4] in which emphasis was placed on all binary carbonyl (both neutral and anionic) species. The extension of these ideas to the fluxional behaviour that many of these compounds exhibit, the different isometric forms they adopt and the pattern of carbonyl substitution reactions they undergo followed.

At the onset of the work in 1976 the challenge was to devise a means or model by which the various phenomena (the ground-state structure; the existence of isomers and the fluxional behaviour) could be better understood. We set out, if you wish, to devise a unifying approach to all these phenomena. The essence of the LPM stems from the realisation that the molecular structures of the binary carbonyls are the result of simply inserting one polyhedron (or polygon) within another. It was also important to realise that this may not give a single result and that the orientation of the central metal unit within the same polyhedron may vary and that the variations observed are symmetry related (see below). Of course we would expect that, given such small energy differences between one CO polyhedron and another and the different orientations that the metal unit may adopt within that polyhedron, the overall molecular structure would be sensitive to its environment within the crystal. In the case of anionically charged species this means a sensitivity to the nature of the cation present, and this is observed. Indeed much of the disorder experienced within carbonyl structures can be associated with these effects. The idea that the central metal unit is able to adopt different orientations within the carbonyl polyhedron also embraces the phenomenon of libration and this led to a clearer understanding of fluxional behaviour (especially in the solid), of isomer formation, and of the disorder frequently observed in the crystal.

In our work we initially took the view that the optimum CO polyhedra would be those with vertices lying on a sphere and in our consideration of larger co-ordination numbers (12 upwards) adopted the approach originally devised by Stone[5] to ascertain the available polyhedra and their relative energies. We immediately recognised the importance of the size of the CO ligand and chose a hard sphere model assuming the important contact distance as being that based on a sphere around the O atom. It is important to recognise (as has been touched on above) that the insertion of the metal unit into the CO polyhedron does not always lead to a unique solution and that structures arise simply as a consequence of the two geometries involved not chemistry! This is of enormous importance to the work considered in this paper which is specifically concerned with $(CO)_{13}$ species.

Results and discussion

In our earlier work we calculated the relative energies of suitable thirteen vertex polyhedra. As might be expected some polyhedra are very close in energy, *e.g.* the face-capped and

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† This paper is dedicated to the memory of Ron Snaith.

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edge-bridged icosahedra, whereas others, *e.g.* the various capped cubeoctahedron (C.O.) or capped anti-cubeoctahedra, (A.C.O.) are less stable. As observed for twelve vertex polyhedra the cavity size increases in going from the more favourable forms derived from the icosahedron to the less favourable derived from the C.O. and A.C.O. It follows that these less stable forms with larger cavities will be favoured by species with larger central metal units. When we first published our work in which we briefly considered $(CO)_{13}$ species we were hampered by the very few examples of such species available. Hence, we tended to concentrate on the twelve vertex case for which much data had been published, and also because of the highly symmetric forms available *e.g.* the icosahedron, the C.O. and the A.C.O. It is highly relevant to note the close relationship between the $(CO)_{12}$ and $(CO)_{13}$ cases and we shall use this relationship better to understand the available data.

In this work we have built on the crystallographic data available for salts of the $[Fe_4(CO)_{13}]^{2-}$ dianion and extended our studies to include the series of species $[Fe_3Co(CO)_{13}]^-$, $[Ru_3Co(CO)_{13}]^-$, $[Ru_3Rh(CO)_{13}]^-$, $[Ru_3Ir(CO)_{13}]^-$, $[Os_3Ir(CO)_{13}]^-$ and $[Co_2Ru_2(CO)_{13}]$. The available crystallographic data for these species have been examined and their CO polyhedra established. In addition, we have more carefully examined the predicted CO-polyhedral arrangements and discussed them in the light of the very extensive studies on a comprehensive range of different but clearly related $(CO)_{12}$ compounds. At the onset we would point out that our studies show that the structures observed experimentally are totally in line with the predictions of the LPM.

For the species containing the relatively smaller units (Fe_4, Fe_3Co, Ru_3Co and Ru_2Co_2) the lowest energy CO polyhedra (capped or bridged iscosahedra) are observed, whereas for the larger Os_3Ir the alternative and higher energy capped C.O. is observed. As with $[Rh_4(CO)_{12}]$, the species containing the Ru_3Rh appears anomalous with an icosahedral ligand shell rather than the expected (on the basis of ionic radii) cubeoctahedron environment. Clearly other factors must have a role to play here and are currently under investigation. This is the change anticipated as the size of the embraced metal unit increases. Furthermore, just as with $[Fe_3(CO)_{12}]$ (C_{2v} or D_3), $[Co_4(CO)_{12}]$ (C_{3v} or T), *etc.*, different isomeric forms which depend on the orientation of the tetrahedral metal unit within the thirteen CO polyhedron are observed, and good evidence for the librational motion of the metal tetrahedron within the CO polyhedron (or *vice versa*) has been found.

The 13-vertex polyhedra

The icosahedron has twenty triangular faces and thirty edges. Hence, there are twenty different ways of adding a face-cap, although of course in the absence of any central metal unit these lead to the same 13-vertex face-capped polyhedron. In a similar way, there are thirty different ways to edge-bridge the icosahedron.

Thirteen carbonyl species

If we now turn to real molecules we may consider the effect of capping known icosahedral species. For the species $[M_4(CO)_{12}]$ three principal structures are observed: the C_{3v} form, the postulated T form for $[Co_4(CO)_{12}]$, and the T_d form observed for $[Ir_4(CO)_{12}]$. In the two forms of $[Co_4(CO)_{12}]$ an icosahedral ligand arrangement is found whereas for $[Ir_4(CO)_{12}]$ it corresponds to a cubeoctahedron.

1. Addition of a cap to the $[M_4(CO)_{12}]$ structure with T symmetry and no bridges of any description. Imagine a structure of T symmetry produced when an M_4 tetrahedron is inserted into the icosahedron to produce, in chemical terms, a fully terminally bonded structure. This is the T structure suggested as the pivot in the low-energy fluxional behaviour of $[Co_4(CO)_{12}]$. The twentyfold degeneracy of the faces within the icosahedron is now removed and instead we have three different face-capping possibilities. There are four faces of one type (A) occupied by the four vertices of the internal tetrahedron leaving sixteen vacant faces. Of these sixteen empty faces, four (B) will sit above the four triangular faces of the central M_4 tetrahedron and the remaining twelve (C) above but are offset to the six edges of the same central tetrahedra. Thus, the twentyfold degeneracy of the original icosahedron is removed to give three sets of faces 4A + 4B + 12C. If we examine the consequence of face capping in a chemical sense the following structures emerge.

(a) Addition of a face-cap to face A (containing a metal atom) leads to a structure with four carbonyl ligands attached to a single metal atom and, given the distortion of the icosahedron to accommodate this cap,‡ a structure with one terminal CO at the apical metal atom and three edge-bridge COs as shown in Fig. 1 is expected; this is observed for the three anions $[Fe_3Co(CO)_{13}]^-$, $[Ru_3Co(CO)_{13}]^-$, and $[Ru_3Rh(CO)_{13}]^-$.

(b) Alternatively, addition of a face-cap to one of the four faces B leads to a different structure with a triple-bridging ligand on one triangular face of the inner M_4 tetrahedron (and some distortion of the other CO ligands attached to the three M atoms of that same triangular face). This corresponds to the structure recently observed for the second isomeric form of the dianion $[Fe_4(CO)_{13}]^{2-}$ with twelve terminally bonded COs and one triply bonding CO ligand.

(c) Finally, addition of a face-cap to one of the twelve faces C results in a structure similar to that observed in 2 (below) except that the bridge would span a metal–metal edge rather than a face.

2. Addition of a cap to the C_{3v} structure observed for example in $[Co_4(CO)_{12}]$ with nine terminal ligands and three edge bridges in the basal plane. Consider now the capping of the $[Co_4(CO)_{12}]$ C_{3v} structure with nine terminal ligands and three edge-bridges in the basal plane. In this structure on insertion of the Co_4 unit the degeneracy of the twenty faces of the icosahedron is removed to produce six sets of faces A, B, 3C, 6D, 6E and 3F, a far more complicated picture than for type 1 (above). Face A is unique being occupied by the apical M atom of the internal tetrahedron, face B is also unique sitting beneath the M_3 basal plane. The remaining four sets of faces 3C, 6D, 6E and 3F follow automatically from that. Now consider the consequences of the adding of a face-cap to this structure.

(a) Addition of a cap to face A leads to a structure with four terminal CO groups on the apical atom M with some possible distortion of three terminal groups towards an asymmetric bridging environment. Since the remainder of the structure remains essentially unaltered there remain three edge-bridges in the basal plane.

(b) Addition of a cap to face B leads to a structure with one triple bridge sitting on the face opposite to the apical M atom. As in (a) the remainder of the structure remains essentially the same leading to an overall structure with one triple bridge and three edge-bridges as is observed for one form of the anion $[Fe_4(CO)_{13}]^{2-}$.

(c) Addition of a face cap to face C, D, E or F results in the formation of a bridge which may be considered to fall between an edge and a triple environment. This form does not appear to have been observed in any structure to date.

3. Addition of edge-bridges to the T and C_{3v} structures. Clearly similar arguments may be used in the addition of an edge-bridge to the icosahedral arrangement in both the T and C_{3v}

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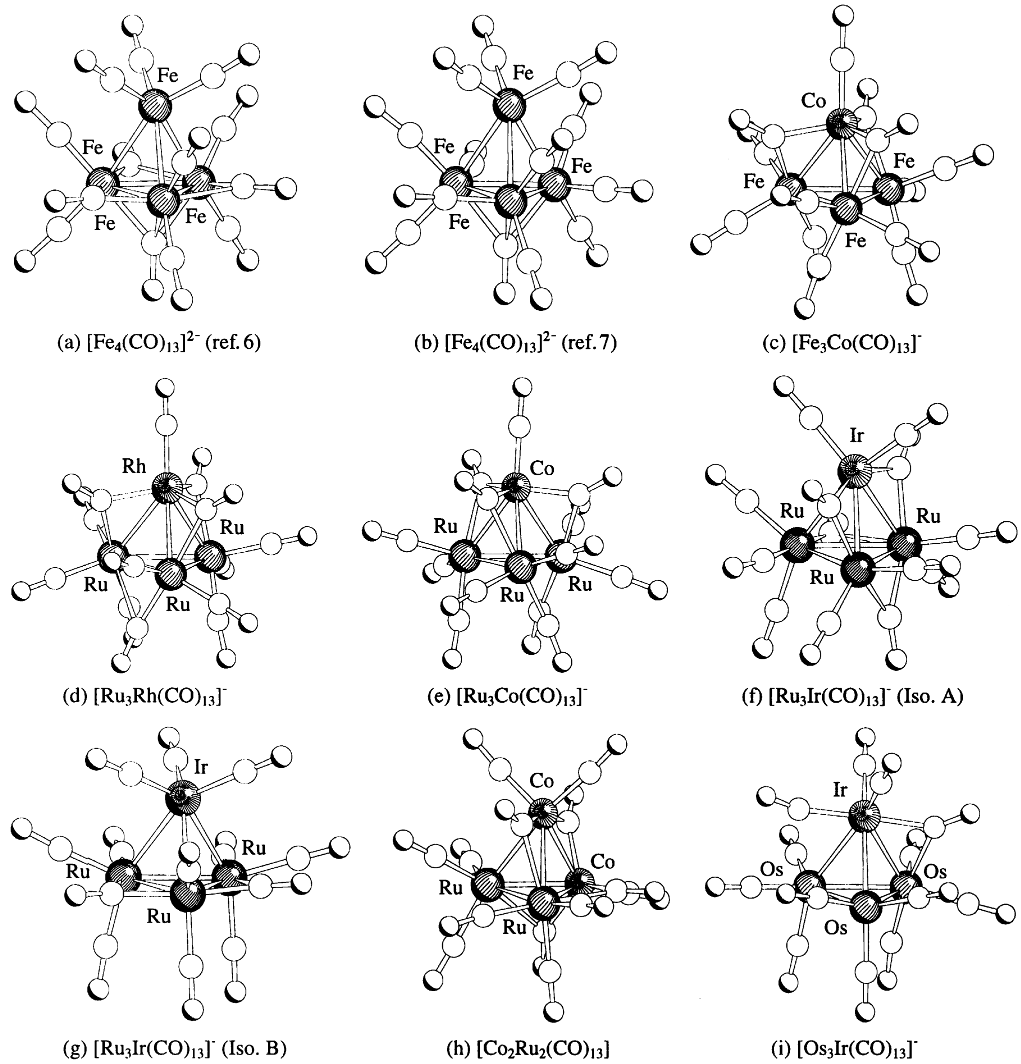
‡ In each case it is of importance to recognise that the addition of a face-cap or an edge-bridge will modify the overall structure of the parent icosahedra. For example, addition of the face-cap brings about an expansion of the capped face as the polyhedron attempts to achieve spherical symmetry.



(a) $[Fe_4(CO)_{13}]^{2-}$ (ref. 6) (b) $[Fe_4(CO)_{13}]^{2-}$ (ref. 7) (c) $[Fe_3Co(CO)_{13}]^-$

(d) $[Ru_3Rh(CO)_{13}]^-$ (e) $[Ru_3Co(CO)_{13}]^-$ (f) $[Ru_3Ir(CO)_{13}]^-$ (Iso. A)

(g) $[Ru_3Ir(CO)_{13}]^-$ (Iso. B) (h) $[Co_2Ru_2(CO)_{13}]$ (i) $[Os_3Ir(CO)_{13}]^-$

Fig. 1 Molecular structures of: (a) $[Fe_4(CO)_{13}]^{2-}$,[6] (b) $[Fe_4(CO)_{13}]^{2-}$,[7] (c) $[Fe_3(Co(CO)_{13}]^-$, (d) $[Ru_3Rh(CO)_{13}]^-$ (e) $[Ru_3Co(CO)_{13}]^-$, (f) $[Ru_3Ir(CO)_{13}]^-$ (isomer A), (g) $[Ru_3Ir(CO)_{13}]^-$ (isomer B), (h) $[Co_2Ru_2(CO)_{13}]$ and (i) $[Os_3Ir(CO)_{13}]^-$.

forms of $[M_4(CO)_{12}]$ species. We shall not go into them here. However, the edge-bridged icosahedron is found in the compound $[Co_2Ru_2(CO)_{13}]$ leading, as predicted, to a structure with four edge-bridges (see Fig. 3a). In this case we believe, as we have argued previously, that the symmetry of the internal metal unit plays a dominant role in deciding between two closely related polyhedra (the edge-bridged and face-capped icosahedron).

We shall not develop these ideas further in this paper preferring instead to discuss the full geometric considerations in a full paper devoted to the topic. Finally, a few examples of capped C.O. and A.C.O. are known (see below). Again, depending on the symmetry of the embraced metal unit, a variety of different structural forms will emerge. At this stage it is sufficient to say that, in these fundamental polyhedra, capping may occur on any of the eight triangular or six square faces, and hence structures derived from $[Ir_4(CO)_{12}]$ are obtained.

Species examined in this work

We have investigated the polyhedra formed by the thirteen carbonyl ligands in the range of species $[Fe_4(CO)_{13}]^{2-}$,[6,7] $[Co_2Ru_2(CO)_{13}]$,[8] $[Ru_3Ir(CO)_{13}]^-$,[9] $[Ru_3Rh(CO)_{13}]^-$,[10] $[Ru_3Co(CO)_{13}]^-$,[11] $[Os_3Ir(CO)_{13}]^-$,[12] and $[Fe_3Co(CO)_{13}]^-$ [13] (see Fig. 1).

Icosahedron-based geometries. The complex $[Fe_4(CO)_{13}]^{2-}$ is the only species for which a discussion of its structure in LPM terms has been reported.[3] We argued that the 'best' CO polyhedron for a 13-CO system is the edge-bridged icosahedron and the second best is the face-capped icosahedron. However, the energy difference between these two forms is small. In the molecular structure of $[Fe_4(CO)_{13}]^{2-}$ the thirteen CO ligands adopt a face-capped icosahedron, with the unique vertex corresponding to the unique triply bridging carbonyl of the cluster [three other carbonyl ligands being μ_2-bridged, and the remaining nine ligands bonding in a terminal mode, see Fig. 1(a)].[6] A recent structural reinvestigation of this complex has reported the existence of a second isomeric form for $[Fe_4(CO)_{13}]^{2-}$, in which the unique triply bridging carbonyl is retained, and the remaining twelve carbonyl ligands are terminal [see Fig. 1(b)].[7] In both cases, the ligand polyhedron is the face-capped icosahedron. The difference in structure arises from the change in orientation of the Fe_4 tetrahedron, related by rotation of the internal tetrahedron through the unique C_3 axis. The structures of $[Ru_3Co(CO)_{13}]^-$, $[Fe_3Co(CO)_{13}]^-$, and $[Ru_3RhCO)_{13}]^-$ are also based on a face-capped icosahedron. Unlike $[Fe_4(CO)_{13}]^{2-}$, these display three μ_2-bridging carbonyls (all bonded to the heterometal) and no triply bridged CO (see Figs. 1(c)–(e).[11] This difference in structure may also be seen in terms of the relative orientation of the inner M_4 tetrahedron within the same capped icosahedron of CO ligands. It follows from our discussions above that there are four possible orientations of the tetrahedron within the face-capped icosahedron. These can be divided into two sets; in one the "capping" ligand

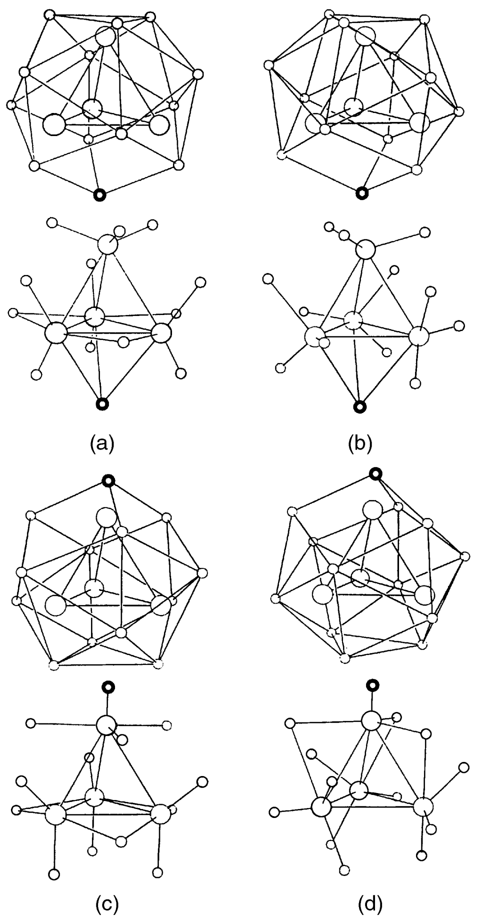


Fig. 2 Molecular structures of the four possible isomers (a)–(d) of $[M_4(CO)_{13}]^{n-}$ with face-capped icosahedral geometry (the capping ligand is represented by a solid circle) depicted in terms of the ligand polyhedral model (above) and localised bond theory (below).

is coordinated to a vertex of the tetrahedron, whereas in the other it is coordinated to one of its faces (see Fig. 2 and also above).

Similar behaviour had previously been reported for $[Ru_6C(CO)_{16}]^{2-}$.[14,15] The structures of $[Ru_3Co(CO)_{13}]^-$, $[Fe_3Co(CO)_{13}]^-$, and $[Ru_3RhCO)_{13}]^-$ are based on the inverted *T* structure (see Fig. 2(d)). The heterometal often corresponds to the vertex of the metal tetrahedron close to the cap. Such an orientation might be favoured in order to align the C_3 axis of the M_3M' unit with that of the CO shell. It should be noted that the M–Co vectors are similarly short in the homologous series $[M_3Co(CO)_{13}]^-$ (M = Fe or Ru), with a mean M–Co distance of 2.62 Å for M = Ru and 2.48 Å for M = Fe), despite the size of the metal tetrahedron being greater for M = Ru than for Fe. Such data reflect the fact that the size of the CO polyhedral shell is similar in both cases. In this case therefore it would appear that the interligand carbonyl interactions are the dominant factor in the choice of geometry of the CO shell polyhedron rather than the metal–carbonyl (M–CO) interactions.

The neutral cluster $[Co_2Ru_2(CO)_{13}]$ (see Fig. 3a) adopts a different CO-polyhedral geometry to those described above. One cobalt atom is coordinated to three bridging and one terminal carbonyl ligand, while the other is attached to two asymmetric CO bridges and two terminal ligands. In LPM terms the CO shell forms the edge-capped icosahedron, rather than the previously described face-capped icosahedron. The preference of M_4 and M_3M' derivatives toward the face-capped icosahedron, over the slightly less energetically demanding edge-capped icosahedron, may be dictated by symmetry considerations. The symmetry of the metal tetrahedron with a principal C_3 axis best matches that of the capped icosahedron, whereas with the M_2M_2' unit (Co_2Ru_2) the principal axis is C_2 and better suited to match with the C_2 axis of the edge-bridged icosahedron.

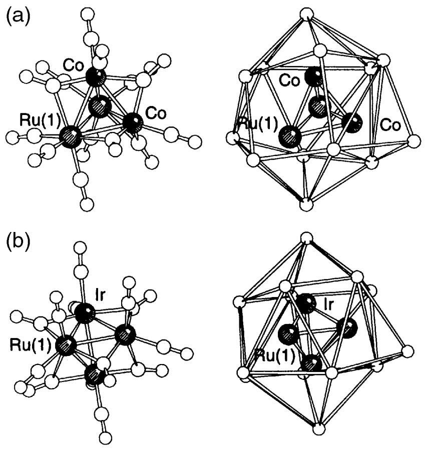


Fig. 3 Molecular structures of: (a) $[Co_2Ru_2(CO)_{13}]$ and (b) $[Ru_3Ir(CO)_{13}]^-$ (isomer A), depicted in terms of the ligand polyhedral model and localised bond theory.

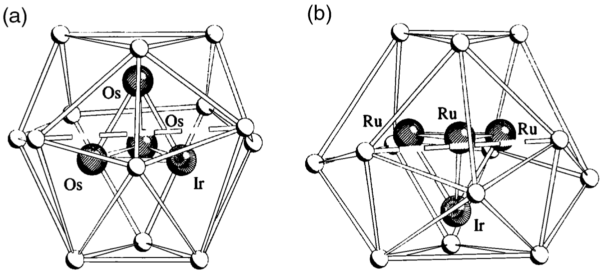


Fig. 4 Molecular structures of $[M_3Ir(CO)_{13}]^-$ depicted in terms of the ligand polyhedral model (**4a**, $[Os_3Ir(CO)_{13}]^-$; **4b** $[Ru_3Ir(CO)_{13}]^-$ (isomer B)).

The edge-bridged icosahedral structure is also found for one of the two known isomeric structures of $[Ru_3Ir(CO)_{13}]^-$ [Fig. 3(b), isomer A], which displays five bridging and eight terminal carbonyl ligands, with the heteroatom bearing two ligands of each type. This structure is related to that described for $[Co_2Ru_2(CO)_{13}]$, but differs in the orientation of the tetrahedron inside the cavity (see Fig. 3). The two forms are interconverted by rotation of the tetrahedron along a pseudo-C_3 axis by about 60°, which passes in the case of $[Ru_3Ir(CO)_{13}]^-$ through the Ru(1) atom and the centre of the opposite face $IrRu_2$. For $[Co_2Ru_2(CO)_{13}]$ this axis passes through Ru(1) and the centre of the opposite face Co_2Ru.

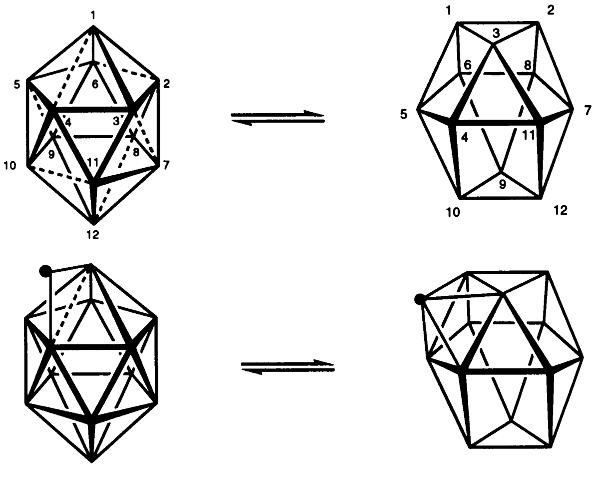
Cubeoctahedron-based geometries. The notable exception to the capped-icosahedral geometry of the CO envelope in $[M_4(CO)_{13}]^{n-}$ is $[M_3Ir(CO)_{13}]^-$ (Fig. 4(a), M = Os,[12] and Fig. 4(b), Ru,[9] in isomer B), in which a cubeoctahedral based geometry is observed. This geometry may be described as two staggered triangular faces separated by a puckered heptagonal central layer.

In the series of calculated best 13-vertex polyhedra the first capped cubeoctahedron ranks fifth in order of energy, preceded by the four different capped icosahedron geometries.[3] Given the larger size of the cavity, the capped-cubeoctahedral arrangement is expected to become more favourable in the presence of larger metals. In the series $[M_4(CO)_{13}]^{n-}$ the cubeoctahedron is found only in the structures that bear a third-row element, while all the lighter congeners (with M belonging to either the first or second row) adopt a capped-icosahedral ligand shell. There are two possible ways of face-capping, *i.e.* on a triangular face or on a square face. The structures depicted in Fig. 4 can be derived form the cubeoctahedron by capping a square face. The alternative geometry has been found for the carbide derivatives

$[M_4C(CO)_{13}]$ (M = Fe or Ru), where a triangular face has been capped.[16,17]

Fluxional rearrangements. The fluxional behaviour observed for $[M_4(CO)_{12}]$ species may be considered in two parts. First is the libration (on reorientation) of the M_4 tetrahedron within the icosahedral ligand envelope. This is the *low energy process* and occurs through a transition state (complementary geometry) of *T* symmetry. Second is the interconversion of the icosahedral ligand through an anti-cubeoctahedral complementary geometry. This is a *higher energy process*, and clearly at higher temperatures both occur. In our view similar processes will occur for systems containing thirteen ligands, and from the discussion above it is clear that the central M_4 unit may adopt a variety of orientations within the face capped icosahedron.

In this work the case of $[Ru_3Ir(CO)_{13}]^-$ provides further evidence on the nature of the fluxional rearrangements of carbonyl clusters. The single-crystal X-ray diffraction analysis of a salt of this anion reveals the presence of the two isomers A and B in the unit cell (see Fig. 1(f) and 1(g)). The co-crystallisation of an icosahedron-based and a cubeoctahedron based structure is a well documented phenomenon for dodecacarbonyl cluster derivatives of general formula $[M_4(CO)_{12-n}L_n]$,[18–21] and has been rationalised in terms of a low energy fluxional process, which is at the root of the solid state dynamic behaviour of such complexes.[22] We believe that a similar phenomenon is taking place for $[Ru_3Ir(CO)_{13}]^-$: the two isomers observed for this compound in the solid state are the expression of a facile interconversion reaction between an edge-bridged icosahedron and a face-capped cubeoctahedron. In solution, even at −120 °C, only a singlet is observed for the thirteen carbonyl ligands indicating that the fluxional process occurs at a lower temperature.[9] Scheme 1 shows the known mechanism of interconversion between an icosahedron and a cubeoctahedron,[18] and a possible analogous mechanism of interconversion between an edge-bridged icosahedron and a face-capped cubeoctahedron. The known interconversion of an icosahedron into a cubeoctahedron involves the breaking of six edges of the icosahedron (dotted in Scheme 1) to yield the square faces of the cubeoctahedron.[18] In the case of the edge-bridged icosahedron, one edge (dotted in Scheme 1) is already stretched along this soft mode of vibration indicating conversion into the face capped cubeoctahedron (with a capped square and five other non-capped square faces).



Scheme 1 Proposed interconversion of an edge-bridged icosahedron into a face-capped cubeoctahedron.

The degree of fluxionality of metal carbonyl cluster derivatives is known to be linked not only to the relative orientations of the metal and CO polyhedra (discussed above) but also to the relative stability of the CO-envelope geometry.[22] The maximum stability occurs only when two conditions are met: *i.e.* (i) all M–CO interactions and (ii) all CO–CO interactions are the same. In geometrical terms this translates to the two following conditions: all vertices lie on a sphere and all faces are deltahedra. Such conditions are found only in three cases: the tetrahedron, the octahedron and the icosahedron.[22] The presence of an edge-bridge or face-cap in $[M_4(CO)_{13}]^{n-}$ derivatives is sufficient to break the inherent stability of the parent icosahedral shell. In the case of $[Ru_3Ir(CO)_{13}]^-$, for example, the existence of the two forms in the crystalline state is evidence of the ease of interconversion, or, if you wish, to the relative instability of the edge-bridged icosahedron.

Conclusion

We have shown that the ligand polyhedral model can readily be extended to clusters of general formula $[M_4(CO)_{13}]^{n-}$. In particular, unlike the localised bond approach, the model offers a simple description of the different structures displayed and the relationship between them. The structural features of these thirteen carbonyl species may be explained in terms of two central tenets of the LPM: (i) interligand repulsion minimisation, and (ii) symmetry matching of the CO-shell polyhedron with the inner metal polyhedron, which embraces the idea of relative orientations of the central metal unit with the CO shell. We have also proposed a potential mechanism by which the fluxional isomerism within two different structural forms of $[M_4(CO)_{13}]^{n-}$ may occur. In particular, the interconversion between capped-icosahedral- and capped-cubeoctahedral-based structures is easily visualised and understandable in terms of the ligand polyhedral model. Fluxionality within these systems will, like $[Fe_4(CO)_{12}]$ and $[Co_4(CO)_{12}]$, be determined by the ability of the inner metallic cluster unit to undergo librational motion and the CO polyhedron to undergo polyhedral interconversion.

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References

1 B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.*, 1976, 211.
2 R. E. Benfield and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1978, 1554.
3 R. E. Benfield and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1980, 1743.
4 R. E. Benfield and B. F. G. Johnson, *Transition Met. Chem.*, 1981, **6**, 131.
5 A. J. Stone, personal communication.
6 R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 1966, **88**, 4847.
7 G. Van Buskirk, C. B. Knobler and H. D. Kaesz, *Organometallics*, 1985, **4**, 149.
8 E. Roland and H. Vahrenkamp, *Chem. Ber.*, 1985, **118**, 1133.
9 G. Süss-Fink, S. Haak, V. Ferrand and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1997, 3861.
10 A. Fumagalli, M. Banchi, M. C. Malatesta, G. Ciani, M. Moret and A. Sironi, *Inorg. Chem.*, 1998, **37**, 1324.
11 P. C. Steinhardt, W. L. Gladfelter, A. D. Harley, J. R. Fox and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 332.
12 G. Süss-Fink, S. Haak, V. Ferrand and H. Stoeckli-Evans, *J. Mol. Catal.*, 1999, **143**, 163.
13 C. P. Horwitz, E. M. Holt and D. F. Shriver, *Organometallics*, 1985, **4**, 1117.
14 J. S. Bradley, G. B. Ansell and E. W. Hill, *J. Organomet. Chem.*, 1980, **184**, C33.
15 B. F. G. Johnson, J. Lewis, S. W. Sankey, K. Wong, M. MacPartlin and W. J. H. Nelson, *J. Organomet. Chem.*, 1980, **191**, C3.
16 J. S. Bradley, G. B. Ansell, M. E. Leonowicz and E. W. Hill, *J. Am. Chem. Soc.*, 1981, **103**, 4968.

17 A. G. Cowie, B. F. G. Johnson, J. Lewis and P. Raithby, *J. Organomet. Chem.*, 1986, **306**, C63.
18 B. F. G. Johnson, Y. V. Roberts, E. Parisini and R. E. Benfield, *J. Organomet. Chem.*, 1994, **478**, 21.
19 D. Braga, C. E. Anson, A. Bott, B. F. G. Johnson and E. Marseglia, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3517.
20 B. F. G. Johnson and Y. V. Roberts, *Polyhedron*, 1993, **12**, 977.
21 B. F. G. Johnson and Y. V. Roberts, *Inorg. Chim. Acta*, 1993, **205**, 175.
22 B. F. G. Johnson and E. A. Quadrelli, manuscript in preparation.
23 E. Keller, SCHAKAL 92, program for the graphic representation of molecular and crystallographic models, University of Freiburg, 1992.