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Metal cluster topology
14.* Fusion of octahedra in metal carbonyl clusters

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Abstract

Two metal carbonyl cluster octahedra can be fused by sharing a vertex to give an M_{11} cluster, by sharing an edge to give an M_{10} cluster, or by sharing a face to give an M_9 cluster. In a globally delocalized metal carbonyl cluster consisting of fused octahedra, vertices unique to a single octahedron use three internal orbitals, vertices of a face shared by two octahedra use four internal orbitals, vertices of an edge shared by two octahedra use five internal orbitals, and vertices of a face shared by two octahedra use six internal orbitals. Using this principle the iridium carbonyl clusters $Ir_9(CO)_{20}^{3-}$ and $Ir_{12}(CO)_{26}^{2-}$, constructed by face-sharing fusion of two and three octahedra, respectively, are seen to be electron- and orbital-precise and thus may be regarded as three-dimensional analogues of naphthalene and anthracene, respectively. These iridium carbonyl clusters are the second and third members of a homologous series $Ir_{3+3n}(CO)_{(21+11n)/2}$; the end member of this series is the polymer $[Ir_6(CO)_{11}]_n$ consisting of an infinite chain of octahedra sharing opposite faces. Other electron- and orbital-precise clusters constructed by the face-sharing fusion of two octahedra are the mixed metal derivative $Ir_3Ni_6(CO)_{17}^{3-}$ and the Ni_9 core in nickel clusters $Ni_{12}(CO)_{21}H_{4-n}^{n-}$; in the latter clusters the three symmetry-related edges of the central Ni_9 core are bridged by $Ni(CO)_2$ groups. The rhodium carbonyl clusters $Rh_9(CO)_{19}^{3-}$ and $H_2Rh_{12}(CO)_{25}$ both have two skeletal electrons less than their iridium carbonyl counterparts $Ir_9(CO)_{20}^{3-}$ and $Ir_{12}(CO)_{26}^{2-}$, respectively, and can both be regarded as missing a pair of core bonding electrons; this arises by interaction between the symmetric S^{σ} core molecular orbitals in adjacent face-fused octahedra in the rhodium clusters which raises the energy of one these orbitals to antibonding levels. The gold–nickel 'spiro' mixed cluster $Au_6Ni_{12}(CO)_{24}^{2-}$ consists of four Ni_3Au_3 octahedra which are fused by sharing each of the six gold vertices between two octahedra leading to overall T_d symmetry, this cluster as well as $Ru_{10}C_2(CO)_{24}^{2-}$ consisting of two edge-sharing octahedra are electron- and orbital-precise.

1. Introduction

Numerous polycyclic benzenoid hydrocarbons, of which naphthalene and anthracene are familiar examples, can be constructed by edge-sharing fusion of benzene rings (carbon hexagons). Similarly, metal carbonyl cluster polyhedra can be fused by sharing of edges or faces to give three-dimensional analogues of polycyclic aromatic hydrocarbons. The most extensive series of such metal carbonyl derivatives having multiple polyhedral cavities are obtained from metal octahedra; such structures can be viewed as pieces of an infinite three-dimensional bulk metal lattice. Indeed Teo [2] has shown that the Hume-Rothery rule [3] for electron counting in brasses can be extended to close-packed high nuclearity metal carbonyl clusters. Other aspects of the fusion of cluster polyhedra have been treated by Mingos [4–6] and by Slovokhotov and Struchkov [7].

In 1986 I discussed the fusion of octahedra in rhodium carbonyl clusters [8, 9]. Since that time a number of additional fused octahedral metal carbonyl clusters have been reported. Of particular interest are the iridium carbonyl clusters $Ir_9(CO)_{20}^{3-}$ [10] and $Ir_{12}(CO)_{26}^{2-}$ [11] which each have two more apparent skeletal electrons than their roughly isostructural rhodium analogues $Rh_9(CO)_{19}^{3-}$ and $H_2Rh_{12}(CO)_{25}$. In addition the novel 'spiro' cluster $Au_6Ni_{12}(CO)_{24}^{2-}$ has been reported [12]. This paper modifies and extends the earlier graph-theoretical and topological treatment of fused octahedra metal carbonyl clusters in light of these and related recent developments.

2. Background

The chemical bonding topology in metal clusters can be represented by a graph G in which the vertices correspond to atoms or orbitals participating in the

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bonding and the edges correspond to bonding relationships. Previous papers [13–20] have shown that the energy parameter E_k for molecular orbital k is related to the eigenvalues x_k of the adjacency matrix A of G as follows:

$$E_k = \frac{\alpha + x_k \beta}{1 + x_k S} \tag{1}$$

In eqn. (1) α is the standard Coulomb integral, β is the resonance integral, and S is the overlap integral. Positive and negative eigenvalues, x_k, thus correspond to bonding and antibonding orbitals, respectively. The valence orbitals of the atoms in metal clusters may be partitioned into internal and external orbitals. Internal orbitals participate in the internal metal cluster skeletal bonding whereas external orbitals participate in the bonding to atoms or groups external to the metal clusters such as carbonyl groups in metal carbonyl clusters. A normal vertex atom in a metal cluster based on an isolated polyhedron, such as a globally delocalized deltahedron, uses three of its valence orbitals for internal orbitals.

The two extreme types of skeletal bonding in metal clusters may be called edge-localized and globally delocalized [13–15]. An edge-localized metal cluster has two-electron two-center bonds along each edge of the cluster polyhedron and is favored when the numbers of internal orbitals of the vertex atoms match the number of edges meeting at the vertex in question (called the *vertex degree*). Since normal vertex atoms in metal clusters use three internal orbitals for skeletal bonding, cluster polyhedra exhibiting pure edge-localized bonding normally have only degree three vertices. A globally delocalized cluster has a multicenter core bond in the center of the cluster polyhedron and is favored when the numbers of internal orbitals at the vertex atoms do not match the vertex degrees. Since all vertices of an octahedron have degree 4, octahedral metal carbonyl clusters are globally delocalized.

Globally delocalized deltahedral clusters with n vertices have $2n+2$ skeletal electrons with $2n$ of these electrons arising from the surface bonding and the remaining two electrons occupying the single bonding molecular orbital arising from the multicenter core bond [13–15]. Electron-rich polyhedra with n vertices and more than $2n+2$ apparent skeletal electrons have one or more non-triangular faces which may be regarded topologically as holes in the otherwise closed surface [13–15]. The electron richness of such systems arises from splitting the n-center core bond in the $2n+2$ skeletal electron globally delocalized system into a set of two or more bonds consisting of a multicenter core bond using fewer than n internal orbitals and one or more multicenter bonds located above the non-triangular faces. Electron-poor polyhedra with less than $2n+2$ apparent skeletal electrons have structures based on a central deltahedron having one or more capped faces to generate a tetrahedral chamber for each such capping relationship [13–15].

In connection with the extension of the graph-theory derived treatment of octahedral metal carbonyl clusters to larger metal carbonyl clusters consisting of fused octahedra, it is necessary to consider the properties of the multicenter core bonding orbital. Of particular significance is the fact that this multicenter core bonding orbital has no nodes thus corresponding to the fully symmetric A_{1g} representation in the case of the octahedron. This can be related to the use of the tensor surface harmonic theory for the treatment of [21–24] globally delocalized octahedral metal carbonyl clusters in which the octahedron is considered to be topologically homeomorphic [25] to the sphere. The unique internal orbitals used for the core bonding in a globally delocalized octahedral metal carbonyl cluster, which are sp hybrid orbitals [13–20], lead to core molecular orbitals described by the scalar spherical harmonics $\Theta(\theta)\Phi(\phi) = Y_{\mathrm{LM}}(\theta, \phi)$, which for an octahedron correspond successively to a single nodeless S^σ orbital (Y_{00}), the three uninodal P^σ orbitals (Y_{10}, Y_{11c}, Y_{11s}), and two of the five possible binodal D^σ orbitals. The single multicenter core bonding orbital thus is the nodeless S^σ orbital; the remaining P^σ and D^σ core molecular orbitals are antibonding orbitals. These core molecular orbitals are completely analogous in shape to the correspondingly labeled atomic s, p, and d orbitals.

The fusion of globally delocalized metal carbonyl cluster octahedra can occur by sharing of a vertex, an edge, or a face (Fig. 1). A pair of vertex-sharing octahedra (Fig. 1(a)) has a total of 11 vertices among which the single shared vertex has degree 8. A normal vertex shared by two octahedra can be assumed to use six internal orbitals, namely three for the skeletal bonding in each octahedron sharing the vertex in question. A pair of edge-sharing octahedra (Fig. 1(b)) has a total of 10 vertices among which the two vertices of the shared edge have degrees 7. The vertices of the shared edge can be assumed to use five internal orbitals, namely one for the core bonding in each of the octahedra, two for the usual type of surface bonding, and one for a two-center two-electron bond along the shared edge. A pair of face-sharing octahedra (Fig. 1(c)) has a total of 9 vertices among which the three vertices of the shared face have degrees 6. The vertices of the shared face can be assumed to use four internal orbitals, namely one for the core bonding in each of the octahedra and two for the usual type of surface bonding.

The general approach for considering skeletal bonding models for a given metal cluster calculates the number of available skeletal electrons required to fill the bonding

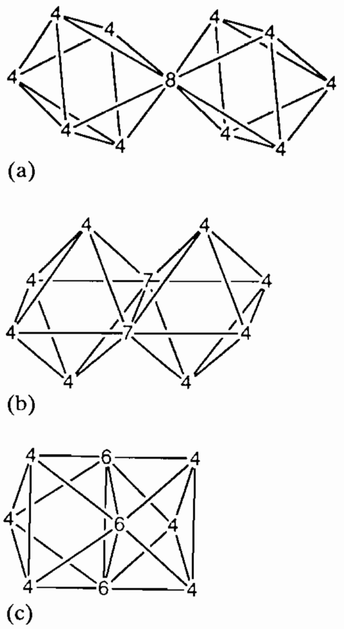

Fig 1. Three ways of fusing two octahedra: (a) vertex-sharing, (b) edge-sharing, (c) face-sharing. The vertices are labelled according to their degrees.

molecular orbitals for various cluster shapes and bonding topologies. Delocalized bonding topologies for isolated deltahedra are evaluated using apparent skeletal electron counts which assume that transition metal vertices use the normal three internal orbitals and have the favored 18-electron rare gas electronic configurations. In the case of metal carbonyl clusters constructed from fused metal octahedra, vertices of a face, vertices of an edge, and a single vertex shared by two octahedra are assumed to use four, five and six internal orbitals, respectively, as noted above. Metal carbonyl groups, whether terminal or bridging, are donors of two skeletal electrons except in the very rare cases of bridging carbonyl groups in which the carbon–oxygen multiple bond or the oxygen atom as well as the carbon atom participates in the bonding to the transition metal skeleton. Such 'anomalous' bridging carbonyl groups which are partially bonded to the metals through oxygen atoms are not found in the compounds discussed in this paper.

3. Face-sharing fusion of octahedra: three-dimensional iridium and nickel carbonyl cluster analogues of naphthalene and anthracene

The Ir_9 skeleton of the iridium carbonyl cluster $Ir_9(CO)_{20}^{3-}$ (Fig. 2(a)) [10] consists of two fused octahedra sharing a face and therefore can be regarded as a three-dimensional analogue of naphthalene. Its skeletal electrons and orbitals can be counted as follows:

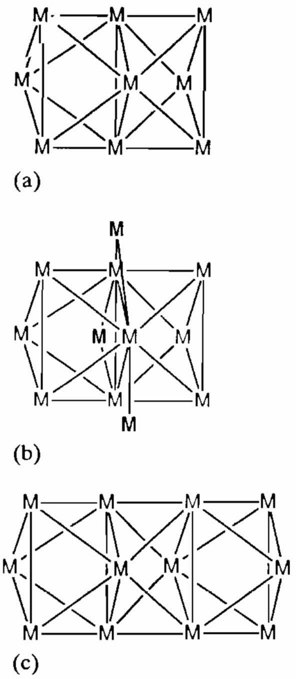

Fig. 2 Face-sharing fusion of two and three octahedra: (a) two octahedra sharing a face in the M_9 units of the three-dimensional naphthalene analogues $Ir_9(CO)_{20}^{3-}$ and $Rh_9(CO)_{19}^{3-}$, (b) the M_9 bioctahedron with three additional edge-bridging metal atoms (in bold face) as found in $Ni_{12}(CO)_{21}H_{4-n}^{n}$ derivatives: (c) three octahedra sharing faces in the 'linear' M_{12} units of the three-dimensional anthracene analogues $Ir_{12}(CO)_{26}^{2-}$ and $H_2Rh_{12}(CO)_{25}$.

(*a*) *Sources of skeletal electrons and orbitals*:

6 $Ir(CO)_2$ vertices belonging to one octahedron and therefore using three internal orbitals	6 electrons	18 orbitals
3 $Ir(CO)_2$ vertices in the face shared by two octahedra and therefore using four internal orbitals	9 electrons	12 orbitals
'Extra' two CO groups: (2)(2) =	4 electrons	
−3 charge on ion	3 electrons	
Total available skeletal electrons and orbitals	*22 electrons*	*30 orbitals*

(*b*) *Uses of skeletal electrons and orbitals*:

Six-center core bonds in each of the two octahedra	4 electrons	12 orbitals
Surface bonds for the Ir_9 bioctahedron: (2)(9) =	18 electrons	18 orbitals
Total skeletal electrons and orbitals required	*22 electrons*	*30 orbitals*

Thus the electrons and orbitals required for globally delocalized bonding in bioctahedral $Ir_9(CO)_{20}^{3-}$ correspond exactly to those available so that this cluster may be regarded as electron- and orbital-precise. Also note that the isostructural nine-vertex mixed metal bioctahedral derivative [26] $Ir_3Ni_6(CO)_{17}^{3-}$ is isoelectronic with $Ir_9(CO)_{20}^{3-}$ and thus is likewise electron- and orbital-precise.

The twelve-vertex nickel clusters of the type $Ni_{12}(CO)_{21}H_{4-n}^{n-}$ (Fig. 2(b)) [27] can also be regarded as three-dimensional naphthalene analogues with three $Ni(CO)_2$ bridges across the edges of the face common to a pair of octahedra similar to the two octahedra in $Ir_9(CO)_{20}^{3-}$ discussed above. The three edge-bridging $Ni(CO)_2$ groups in $Ni_{12}(CO)_{21}H_{4-n}^{n-}$ use two nickel valence orbitals to bond to the central Ni_9 bioctahedron leaving seven orbitals of the nine-orbital nickel sp^3d^5 manifold, which are exactly filled by the ten nickel valence electrons and four electrons from the two carbonyl groups. The edge-bridging $Ni(CO)_2$ groups thus act as zero skeletal electron donors and do not provide any *skeletal* orbitals since the orbitals linking these edge-bridging $Ni(CO)_2$ groups to the bioctahedral Ni_9 core are external orbitals. The electrons and orbitals in $Ni_{12}(CO)_{21}H_2^{2-}$ can then be counted as follows:

(*a*) *Sources of skeletal electrons and orbitals*:

6 $Ni(CO)_2$ vertices at the 'ends' belonging to one octahedron and therefore using three internal orbitals	12 electrons	18 orbitals
3 $Ni(CO)_2$ vertices in the face shared by the two octahedra and therefore using four internal orbitals	12 electrons	12 orbitals
3 edge-bridging $Ni(CO)_2$ groups	0 electrons	0 orbitals
'Deficiency' of 3 CO groups	−6 electrons	
2 H atoms	2 electrons	
−2 charge on ion	2 electrons	
Total available skeletal electrons and orbitals	*22 electrons*	*30 orbitals*

(*b*) *Uses of skeletal electrons and orbitals*:

Six-center core bonds in each of the two octahedra	4 electrons	12 orbitals
Surface bonds for the central Ni_9 bioactehedron	18 electrons	18 orbitals
Total skeletal electrons and orbitals required	*22 electrons*	*30 orbitals*

Using this electron- and orbital-counting scheme the electrons and orbitals required for globally delocalized bonding in the central Ni_9 bioctahedron in $Ni_{12}(CO)_{21}H_2^{2-}$ correspond exactly to those available so that the $Ni_{12}(CO)_{21}H_{4-n}^{n-}$ clusters are electron- and orbital-precise.

The Ir_{12} skeleton of the iridium carbonyl cluster $Ir_{12}(CO)_{26}^{2-}$ (Fig. 2(c)) [11] consists of three fused iridium octahedra sharing faces and can therefore be regarded as a three-dimensional analogue of anthracene. Its skeletal electrons and orbitals can be counted as follows:

(*a*) *Sources of skeletal electron and orbitals*:

6 $Ir(CO)_2$ vertices belonging to one octahedron and therefore using three internal orbitals	6 electrons	18 orbitals
6 $Ir(CO)_2$ vertices belonging to faces shared by two octahedra and therefore using four internal orbitals	18 electrons	24 orbitals
'Extra' two CO groups: (2)(2) =	4 electrons	
−2 charge on ion	2 electrons	
Total available skeletal electrons and orbitals	*30 electrons*	*42 orbitals*

(*b*) *Uses of skeletal electrons and orbitals*:

Six-center core bonds in each of the three octahedra:	6 electrons	18 orbitals
Surface bonds for the Ir_{12} trioctahedron (2)(12) =	24 electrons	24 orbitals
Total skeletal electrons and orbitals required	*30 electrons*	*42 orbitals*

Again the skeletal electrons and orbitals required for globally delocalized bonding in trioctahedral $Ir_{12}(CO)_{26}^{2-}$ correspond exactly to those available so that this cluster is electron- and orbital-precise.

These iridium carbonyl clusters may be considered as derivatives of the second and third members ($n = 2$, 3) of a homologous series of the type $Ir_{3+3n}(CO)_{(21+11n)/2}$ if the negative charges on the ions are replaced by a corresponding number of carbonyl groups (i.e. one CO group corresponds to a −2 charge). The initial member of this series ($n = 1$) is the known [28] $Ir_6(CO)_{16}$ containing an Ir_6 octahedron; the structurally characterized dianion [29] $Ir_6(CO)_{15}^{2-}$ also has a closely related structure. The limiting member of the series (i.e. $n \rightarrow \infty$) would be the neutral polymer $[Ir_6(CO)_{11}]_n$ or the polymeric ion $[Ir_3(CO)_5]_n^{n-}$ consisting of an infinite chain of fused iridium octahedra sharing faces. The skeletal electrons and orbitals in $[Ir_6(CO)_{11}]_n$ can be counted as follows:

(*a*) *Source of skeletal electrons and orbitals*:

6 $Ir(CO)_2$ vertices all in faces shared by two octahedra and therefore using four internal orbitals	18 electrons	24 orbitals
'Deficiency' of one CO group (−1)(2) =	−2 electrons	
Total available skeletal electrons and orbitals	*16 electrons*	*24 orbitals*

(*b*) *Use of skeletal electrons and orbitals*

Six-center core bonds in the Ir_6 octahedron of the $Ir_6(CO)_{11}$ unit	2 electrons	6 orbitals
Half of two six-center core bonds in adjacent octahedra	2 electrons	6 orbitals
Surface bonds in the Ir_6 octahedron	12 electrons	12 orbitals
Total skeletal electrons and orbitals required	*16 electrons*	*24 orbitals*

In this electron- and orbital-counting scheme the following should be noted:

(1) All of the $Ir(CO)_2$ vertices are parts of faces shared by two octahedra and thus each contribute four internal orbitals.

(2) Each $Ir_6(CO)_{11}$ building block contains an octahedral cavity and must furnish half of the skeletal electrons and orbitals for core bonding in the two adjacent octahedral cavities sharing faces with the central octahedral cavity. Thus the skeletal electrons and orbitals in an $Ir_6(CO)_{11}$ building block must be sufficient for $1+\frac{2}{2}=2$ six-center octahedral core bonds.

The $[Ir_6(CO)_{11}]_n$ polymer is thus seen to be electron- and orbital-precise.

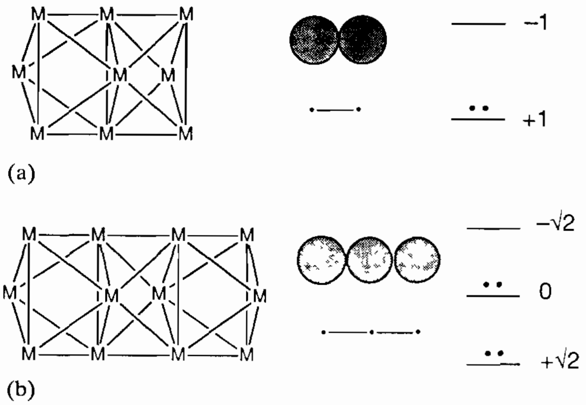

Fig. 3. Interaction between the symmetric S^σ core molecular orbitals in (a) two- and (b) three face-sharing fused octahedra showing the metal framework structure, the interacting S^σ molecular orbitals, the octahedral interaction graph, and the corresponding energy levels arising from the spectrum of the octahedral interaction graph. (a) Naphthalene analog: $Rh_9(CO)_{19}{}^{3-}$; (b) anthracene analog: $H_2Rh_{12}(CO)_{25}$.

4. Face-sharing fusion of octahedra in rhodium carbonyl clusters: 'Missing' multicenter core bonds

Rhodium, like iridium, forms an Rh_9 cluster consisting of two fused octahedra sharing a triangular face (Fig. 2(a)) corresponding to 'three-dimensional naphthalene' and an Rh_{12} cluster consisting of three fused octahedra sharing triangular faces (Fig. 2(c)) corresponding to 'three-dimensional anthracene'. However, the stoichiometries of these rhodium carbonyl clusters, namely $Rh_9(CO)_{19}{}^{3-}$ [30] and $H_2Rh_{12}(CO)_{25}$ [31], each correspond to two skeletal electrons less than the corresponding iridium carbonyl clusters discussed above with the same metal skeletons, namely $Ir_9(CO)_{20}{}^{3-}$ and $Ir_{12}(CO)_{26}{}^{2-}$. These rhodium carbonyl clusters are no longer electron- and orbital-precise in the sense used in the previous section.

This difference in skeletal electron counts between analogous rhodium and iridium clusters can be rationalized by the presence of much stronger interactions between the six-center core bonding orbitals in adjacent octahedra in the rhodium clusters relative to the corresponding iridium clusters. The electron counting scheme outlined in the previous section for both $Ir_9(CO)_{20}{}^{3-}$ and $Ir_{12}(CO)_{26}{}^{3-}$ both assume insignificant interoctahedral interaction between the fully symmetric six-center S^σ core orbitals in adjacent octahedra so that all three of these S^σ core orbitals remain bonding and thus accommodate electron pairs. However, strong interoctahedral interaction between these normally bonding S^σ molecular orbitals can raise the energy of one of these S^σ orbitals to antibonding levels so that it no longer accommodates an electron pair. Such interoctahedral interactions, which are expected to be stronger for Rh_6 octahedra than for the larger Ir_6 octahedra, thus can lower the favored apparent skeletal electron count by two. Interoctahedral interactions can be represented by an *interoctahedral interaction graph* in which the vertices represent octahedral cavities and two vertices are connected by an edge if the corresponding octahedra share a face.

Figure 3 illustrates the interactions between the S^σ orbitals in the fused octahedral clusters. In the case of the two face-sharing fused octahedra in $Rh_9(CO)_{19}{}^{3-}$ (Fig. 3(a)) the octahedral interaction graph consists of two vertices connected by a single edge, which has the two eigenvalues $+1$ and -1. The -1 eigenvalue can correspond to an antibonding orbital if the interoctahedral interaction is sufficiently strong as it appears to be in $Rh_9(CO)_{19}{}^{3-}$ in accord with its electron count suggesting that the collection of core orbitals in the two octahedral cavities can accommodate only two rather than four electrons. In the case of the three face-sharing fused octahedra in $H_2Rh_{12}(CO)_{25}$ the octahedral interaction graph consists of a chain of three vertices, which has the three eigenvalues $+\sqrt{2}$, 0, and $-\sqrt{2}$. Again the $-\sqrt{2}$ eigenvalue can correspond to an antibonding orbital so that the collection of core orbitals in the three octahedral cavities accommodates only four rather than six electrons.

5. Edge-sharing fusion of octahedra

Edge-sharing fusion of octahedra (Fig. 1(b)) is found in the cluster $Ru_{10}C_2(CO)_{24}{}^{2-}$ [32]. Its skeletal electrons and orbitals can be counted as follows:

(*a*) *Sources of skeletal electrons and orbitals*:

8 $Ru(CO)_2$ vertices belonging to one octahedron and therefore using three internal orbitals	0 electrons	24 orbitals
2 $Ru(CO)_2$ vertices belonging to the edge shared by the two octahedra and therefore using five internal orbitals	8 electrons	10 orbitals
4 'extra' CO groups: (4)(2) electrons =	8 electrons	
2 interstitial carbon atoms (2)(4) electrons =	8 electrons	
−2 charge on ion	2 electrons	
Total available skeletal electrons and orbitals	*26 electrons*	*34 orbitals*

(*b*) *Uses of skeletal electrons and orbitals*:

10 Ru–Ru surface bonds (10)(2) =	20 electrons	20 orbitals
1 Ru–Ru bond along the shared edge	2 electrons	2 orbitals
Six-center core bonds in each of the two octahedra	4 electrons	12 orbitals
Total skeletal electrons and orbitals required	*26 electrons*	*34 orbitals*

Thus the electrons and orbitals required for globally delocalized bonding in $Ru_{10}C_2(CO)_{24}^{2-}$ correspond exactly to those available so that this cluster is electron- and orbital-precise. The published [8, 9] electron-counting scheme for $Ru_{10}C_2(CO)_{24}^{2-}$ is wrong since the −2 charge on the ion was not considered.

6. Delocalized spiro clusters: $Au_6Ni_{12}(CO)_{24}^{2-}$

In two-dimensional spiro carbon compounds constructed from vertex-sharing carbocyclic rings, the carbon vertex shared between the two rings is bonded to four other carbon atoms and thus must be sp^3 hybridized. For this reason this carbon atom does not have any orbitals available for delocalization. However, in the three-dimensional analogues of spiro compounds in which two octahedra share a vertex (e.g. Fig. 1(a)) globally delocalized derivatives are possible since the vertex common to both octahedra has orbitals which can participate in the delocalisation.

Simple examples of M_{11} metal carbonyl clusters constructed from two octahedra sharing a vertex appear to be unknown. However, a more complicated but symmetrical example of a delocalized metal spiro cluster is $Au_6Ni_{12}(CO)_{24}^{2-}$ (Fig. 4) [12]. The structure of this cluster, which has high T_d symmetry, consists of four Ni_3Au_3 octahedra joined by sharing each of the six gold atoms between two adjacent Ni_3Au_3 octahedra so that alternate faces of the central Au_6 octahedron are capped by Ni_3 triangles. Each of the gold atoms in $Au_6Ni_{12}(CO)_{24}^{2-}$ can be assumed to provide six internal orbitals, namely three to each of the Ni_3Au_3 octahedra of which they are members. The octahedral interaction graph in $Au_6Ni_{12}(CO)_{24}^{2-}$ is the K_4 complete graph corresponding to the edges of a regular tetrahedron but the distance between the core molecular S^σ orbitals in the Ni_3Au_3 octahedra is much too far for any interaction between them as postulated in the rhodium carbonyl clusters depicted in Fig. 3 and discussed above. The following scheme can be used for counting electrons and orbitals in $Au_6Ni_{12}(CO)_{24}^{2-}$:

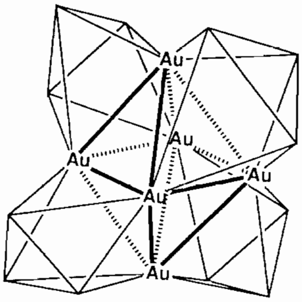

Fig. 4. The metal framework in $Au_6Ni_{12}(CO)_{24}^{2-}$. The unlabeled vertices are nickel vertices and the edges of the central Au_6 octahedron are depicted in wider lines for clarity

(*a*) *Sources of skeletal electrons and orbitals*:

12 $Ni(CO)_2$ vertices belonging to one octahedron and therefore using three internal orbitals	24 electrons	36 orbitals
6 Au vertices shared between two octahedra and therefore using six internal orbitals	30 electrons	36 orbitals
−2 charge on ion	2 electrons	
Total available skeletal electrons and orbitals	*56 electrons*	*72 orbitals*

(*b*) *Uses of skeletal electrons and orbitals*:

One six-center core bond in each of the four Ni_3Au_3 octahedra	8 electrons	24 orbitals
Six surface bonds in each of the four Ni_3Au_3 octahedra	48 electrons	48 orbitals
Total skeletal electrons and orbitals required	*56 electrons*	*72 orbitals*

Note the following in this bonding scheme for $Au_6Ni_{12}(CO)_{24}^{2-}$.

(1) Each of the four Ni_3Au_3 octahedra contains a six-center core bond but the central Au_6 octahedron does not contain a multicenter core bond.

(2) Six of the eleven valence electrons of a bare gold atom with six internal orbitals are required for its $9-6=3$ external orbitals leaving $11-6=5$ skeletal electrons from each gold vertex.

Using this electron- and orbital-counting scheme the rather complicated cluster $Au_6Ni_{12}(CO)_{24}^{2-}$ is thus seen to be electron- and orbital-precise.

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