Metal Cluster Topology. 1. Osmium Carbonyl Clusters

R. BRUCE KING

Department of Chemistry, University of Georgia, Athens, Ga. 30602, U.S.A.

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Abstract

Important theoretical approaches to metal cluster bonding including the Wade–Mingos skeletal electron pair method, the Teo topological electron count, the King–Rouvray graph theory derived method, and Lauher's extended Hückel calculations are shown to agree in their apparent skeletal electron counts for the most prevalent metal cluster polyhedra including the tetrahedron, the trigonal bipyramid (both ordinary and elongated), square pyramid, octahedron, bicapped tetrahedron, pentagonal bipyramid, and capped octahedron. The graph theory derived method is used to treat osmium carbonyl clusters containing from five to eleven osmium atoms. In this connection most osmium carbonyl clusters can be classified into the following types: (1) Clusters exhibiting edge-localized bonding containing multiple tetrahedral chambers (e.g., $Os_5(CO)_{16}$, $Os_6(CO)_{18}$, $H_2Os_7(CO)_{20}$ and $HOs_8(CO)_{22}^-$); (2) Capped octahedral clusters derived from osmium carbonyl fragments of the type $Os_{6+p}(CO)_{19+2p}$ (p = 0, 1, 2, and 4) (e.g., $Os_6(CO)_{18}^{2-}$, $Os_7(CO)_{21}$, $Os_8(CO)_{22}^{2-}$, and $H_4Os_{10}(CO)_{24}^{2-}$). Other more unusual osmium carbonyl clusters such as the planar $Os_6(CO)_{17}[P(OCH_3)_3]_4$, the Os_9 cluster $[Os_9(CO)_{21}C_3H_2R]^-$, and the Os_{11} cluster $Os_{11}C(CO)_{27}^{2-}$ can also be treated satisfactorily by these methods. The importance of the number of ligands around isoelectronic Os_n systems in determining the cluster polyhedron is illustrated by the different cluster polyhedra found for each member of the following isoelectronic pairs: $HOs_6(CO)_{18}^-/H_2Os_6(CO)_{18}$. $Os_7(CO)_{21}/H_2Os_7(CO)_{20}$, $Os_8(CO)_{22}^{2-}/HOs_8(CO)_{22}^-$. The tendency for osmium carbonyl clusters frequently to form polyhedra exhibiting edge-localized rather than globally delocalized bonding relates to the facility for osmium carbonyl vertices to contribute more than three internal orbitals to the cluster bonding. In this way Wade's well-known analogy between boron hydride clusters and metal clusters, which assumes exactly three internal orbitals for each vertex atom, is frequently no longer followed in the case of osmium carbonyl clusters.

1. Introduction

During the past decade one of the most interesting areas of inorganic chemistry has been the chemistry of metal cluster compounds. The theory of the structure and bonding in such cluster compounds has also attracted considerable attention. A key aspect in the early development of this theory was the recognition of the close relationships between polyhedral boranes and carboranes on the one hand and transition metal clusters on the other hand [2]. This relationship also made relevant to transition metal cluster chemistry the earlier observation [3, 4] of certain magic numbers of skeletal electrons for stability of polyhedral boranes and carboranes, notably the requirement of $2n + 2$ skeletal electrons for deltahedral systems having n vertices. These observations were also supported by early LCAO-MO calculations by Hoffmann and Lipscomb on various boron hydride polyhedra [5, 6].

Subsequent theoretical work on metal cluster compounds has involved the development of mathematical justifications for the observed numbers of skeletal electrons in metal cluster compounds. A key topological idea in much of this work is the homeomorphism of cluster deltahedra to the sphere [7]. This idea provided the basis for both the graph theory derived approach of the author in collaboration with Rouvray [8] as well as the perturbed spherical shell theory of Stone [9]. Although it provides an elegant justification of the stability of $2n +$ 2 skeletal electrons for deltahedral systems, the perturbed spherical shell approach [9] appears to be cumbersome to apply to many of the more complicated metal cluster systems of current interest. The graph theory derived approach, on the other hand, has the advantage that its essential ideas can be applied to the understanding of the structure and bonding of even relatively complicated metal cluster systems. This approach, in fact, is relatively tractable to inorganic chemists since a detailed understanding of the underlying graph theory is not essential to application of the resulting ideas to cluster structure and bonding.

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Recently Teo [10, 11] has developed an alternative method for electron counting in polyhedral metal clusters based on topological ideas. Although there are no inconsistencies between our graph theory derived method and Teo's topological electron counting (TEC) method, our approach seems to offer the following advantages:

(1) In Teo's approach the determination of X, the missing antibonding cluster orbitals [10, 11], can give ambiguous results in certain cases. An exact value for X is necessary for the electron counting to give the correct answer.

(2) Our graph theory derived method [8, 12–14] provides some insight relative to the distribution of the total cluster electron counts between skeletal bonding within the cluster polyhedron and bonding to exopolyhedral ligands.

(3) Our graph theory derived method distinguishes between localized and delocalized bonding in cluster polyhedra.

This paper is the first of an anticipated series of papers intended to illustrate nontrivial applications of our graph theory derived method (GTD) to some of the more complicated actual cluster systems. This initial paper treats some of the more complicated known metal carbonyl clusters of osmium, which in many respects is a well behaved metal since osmium carbonyl vertices always have the favored 18-electron rare gas configuration and use the normal three internal orbitals for bonding in delocalized clusters. Osmium carbonyl clusters exhibit an interesting variety including a particularly large collection of electron-poor systems [15, 16] having capped triangular faces as well as a collection of ten-vertex systems containing a fragment of the face-centered cubic metal structure. Thus the osmium carbonyl clusters discussed in this paper provide excellent illustrations of the general principles for electron-poor capped deltahedra outlined in previous papers [8, 13].

2. Background

A key distinction in polyhedral metal cluster bonding is that between edge-localized bonding and (globally) delocalized bonding. Edge-localized bonding involves ordinary two-electron two-center bonds along each of the relevant polyhedral edges. Delocalized bonding combines surface bonding with a multicenter bond at the core of the polyhedron. Relevant to the choice between these two types of cluster bonding is the number of internal orbitals contributed by the vertex atoms, which is usually three [8, 13]. Matching the vertex degree or valency (number of edges meeting at the vertex in question) with the number of internal orbitals from that vertex leads to edge-localized bonding whereas a mismatch between the degree and number of internal orbitals from a given vertex leads to delocalization [13]. Since normal osmium carbonyl vertices contribute the usual three internal orbitals to a cluster polyhedron, polyhedral vertices of degree three generate pockets of edge-localization recognizable as tetrahedral chambers [8, 13]. Triangles (e.g., $Os_3(CO)_{12}$), tetrahedra, and polyhedra formed by fusing tetrahedra (e.g., the trigonal bipyramid of $Os_5(CO)_{16}$ from two fused tetrahedra and the bicapped tetrahedron of $Os_6(CO)_{18}$ from three fused tetrahedra) are thus built from a framework of edge-localized bonds with each vertex atom contributing a number of internal orbitals equal to its degree.

In contrast to these metal cluster systems having edge-localized bonding, a metal cluster system having globally delocalized bonding requires a polyhedron with a degree of at least four for each vertex if each vertex contributes the normal three internal orbitals to the cluster bonding. The simplest such polyhedron is the octahedron in which each vertex has degree four. Thus the smallest metal cluster system with globally delocalized bonding is the octahedron having six vertices. In general 'electron-precise' globally delocalized systems are based on polyhedra in which all faces are triangles and all vertices have degrees of at least four. Such polyhedra are conveniently called deltahedra. A deltahedral system with n vertices requires $2n$ electrons for n two-center surface bonds and two additional electrons for the n-center core bond for a total of $2n + 2$ skeletal electrons. Electron-rich systems having n vertices and more than $2n + 2$ skeletal electrons are based on polyhedra having all triangular faces except for one face with more than three edges for each electron pair in excess of $2n + 2$ electrons. In cases of electron-rich systems having two or more 'excess' electron pairs, fusion of the non-triangular faces can lead to a larger hole. The electron-rich systems correspond to the nido, arachno, and hypso systems in boron hydride chemistry [3] which have one, two, or three excess electron pairs, respectively. The non-triangular face(s) represent topological holes in the otherwise closed surface leading to interruptions in the delocalization. Electron-poor systems having n vertices and less than $2n + 2$ skeletal electrons are based on deltahedra with caps on one or more of the (triangular) faces. Such degree three vertex caps lead to tetrahedral chambers which may be recognized as 'pockets of localization'. The vertex atoms of the capped triangular faces of an electron-poor capped deltahedron use more than three internal orbitals, namely $3 + c$ internal orbitals where c is the number of capped triangular faces containing the vertex in question.

With these general considerations in mind it is instructive to compare the apparent skeletal electron counts obtained by our graph theory derived method

TABLE I. Comparison of apparent skeletal electron counts for common metal cluster polyhedra obtained using different theoretical approaches

Polyhedron	Shape parameters[a]									Apparent skeletal electron counts[b]			
	v	e	f	j_3	j_4	j_5	t	X	Z	Wade–Mingos SEP[c]	Teo TEC[d]	King–Rouvray GTD[e]	Lauher EHC[f]
Tetrahedron	4	6	4	4	0	0	1	0	0	12	12	12(L)	12
Trigonal bipyramid (ordinary)	5	9	6	3	2	0	2	0	3	12	12	12(L)	12
Trigonal bipyramid (elongated)[g]	5	7		2	1	(j_2 = 2)	0	2		h	16	16(D)	h
Square pyramid	5	8	5	4	1	0	0	0		14	14	14(D)	14
Octahedron	6	12	8	0	6	0	0	1		14	14	14(D)	14
Bicapped tetrahedron	6	12	8	2	2	2	3	0	6	12	12	12(L)	12
Pentagonal bipyramid	7	15	10	0	5	2	0	2		16	16	16(D)	h
Capped octahedron	7	15	10	1	3	3	1	1	3	14	14	14(D + L)	14

[a] v = number of vertices; e = number of edges; f = number of faces; j_n = number of vertices of degree n (3, 4 or 5 as indicated), t = number of tetrahedral chambers; X = mixing antibonding orbitals in the TEC theory of Teo; $Z = 2e - 3v$ for the polyhedra with tetrahedral chambers corresponding to the total vertex degrees above three required for the GTD consideration of localized bonding in such polyhedra. [b] The papers on the TEC theory of Teo and the extended Hückel calculations of Lauher give the total electron counts of the cluster polyhedra rather than only the numbers of skeletal electrons. In order to obtain the apparent skeletal electron counts from their papers for comparison with the other theories, $12v$ electrons are subtracted from the total electron count numbers given in these papers in accord with the normal partition of the nine valence orbitals of the transition metal cluster vertex atoms into six external orbitals and three internal orbitals. [c] See refs. 17 and 18. [d] See refs. 10 and 11. [e] L = edge-localized bonding; D = globally delocalized bonding; D + L = globally delocalized deltahedron with a capped triangular face generating a tetrahedral chamber exhibiting edge-localized bonding. [f] These apparent skeletal electron count numbers are obtained by subtracting $12v$ from the cluster valence electron (CVE) counts resulting from the extended Hückel calculations of Lauher [19]. [g] This elongated trigonal bipyramid is found in clusters such as $[Ni_5(CO)_{12}]^{2-}$, $[Rh_5(CO)_{15}]^-$, and $[Ni_2M_2(CO)_{16}]^{2-}$ (M = Cr, Mo, and W). [h] These clusters are not treated explicitly by the indicated theories.

with those obtained by other methods. Table I shows that the results obtained by our graph theory derived method (GTD) are fully consistent with those obtained by Teo's topological electron count method (TEC) [10, 11] and the original Wade–Mingos skeletal electron pair method (SEP) [1, 17, 18] as well as the extended Hückel calculations (EHC) of Lauher [19]. These methods are applied as follows.

(1) Wade–Mingos Skeletal Electron Pair Method (SEP)

$2v$ Apparent skeletal electrons for capped deltahedra, $2v + 2$ apparent skeletal electrons for deltahedra (without tetrahedral chambers), $2v + 4$ apparent skeletal electrons for 'nido' polyhedra with one non-triangular faces, and 12 apparent skeletal electrons for the tetrahedron.

(2) Teo Topological Electron Count Method (TEC)

$12v$ electrons are subtracted from the total electron counts, N, in Teo's papers [10, 11] in order to convert his numbers to apparent skeletal electron counts. Alternatively, his cluster valence molecular orbital formula [10] can be converted to the following apparent skeletal electron count formula:

$$ASEC = 2(2v - f + 2 + X) \qquad (1)$$

Either method of obtaining apparent skeletal electron counts from Teo's total electron counts assumes that of the nine orbitals at each transition metal vertex, six are external orbitals and three are internal orbitals.

(3) Graph Theory Derived Method (GTD)

In this case it is necessary to distinguish between globally delocalized (D) and edge-localized (L) polyhedra. Treatment of globally delocalized polyhedra leads clearly to the same result as the SEP method. In the case of edge-localized polyhedra, a parameter Z measuring 'total vertex degrees in excess of three' must be considered in order to compare the results of the GTD method with other methods. This arises from the fact that for edge-localized polyhedra the number of internal orbitals for each vertex is equal to its degree rather than to the constant value of three. The parameter Z is simply obtained by the topological relationship $Z = 2e - 3v$ and is a generally useful 'correction factor' for comparing apparent skeletal electron counts obtained by methods assuming three internal orbitals from each vertex with those obtained by methods assuming variable numbers of internal orbitals from each vertex. The apparent skeletal electron count (*ASEC*) numbers listed in the GTD column in Table I for edge-localized polyhedra (L) can be simply obtained from the relationship

$$ASEC = 2e - 2Z = 6v - 2e \qquad (2)$$

A similar principle applies to capped deltahedra having a globally delocalized deltahedron with one or more adjoined edge-localized tetrahedral chambers such as the capped octahedron in Table I. In such cases each cap generates three new edge-localized bonds to the capping vertex but each vertex in the capped face uses an 'extra' internal orbital above three to form one of the edge-localized bonds to the capping vertex. Therefore each capped face of a deltahedron contributes three to the parameter Z but because of the three edge-localized bonds to the cap, the GTD apparent skeletal count for a capped deltahedron is the same as that of the corresponding uncapped deltahedron [8].

(4) Extended Hückel Calculations (EHC) of Lauher

Lauher's paper [19] like Teo's papers [10, 11] presents total electron count numbers for cluster polyhedra (CVE in Table II of Lauher's paper [19]) from which $12v$ electrons must be subtracted to convert them to apparent skeletal electron counts for comparison with the results of the various theoretical approaches.

In the comparisons of apparent skeletal electron counts for different metal cluster polyhedra in Table I, the following points relative to specific polyhedra should be noted.

(1) Tetrahedron

All of the theoretical methods give 12 apparent skeletal electrons in accord with two-center bonds along the six edges of the tetrahedron.

(2) Trigonal Bipyramid

For an ordinary trigonal bipyramid all theoretical methods lead to 12 apparent skeletal electrons even though some invoke delocalized bonding and others invoke localized bonding [10, 11]. An elongated version of the trigonal bipyramid with four more apparent skeletal electrons can be interpreted as having two less edges than the regular trigonal bipyramid. In the GTD method the regular trigonal bipyramid is interpreted to have edge-localized bonding and the elongated trigonal bipyramid is interpreted to have globally delocalized bonding. The bonding topology of the elongated trigonal bipyramid is discussed in more detail elsewhere [13, 14].

(3) Square pyramid

The square pyramid is the simplest example of an electron-rich nido polyhedron [3] with $2n + 4$ skeletal electrons.

(4) Octahedron

As noted above the octahedron is the simplest example of an unambiguously globally delocalized deltahedron.

(5) Bicapped Tetrahedron

In the GTD method 24 skeletal electrons are required for edge-localized bonding but there are six 'extra' internal orbitals (*i.e.*, $Z = 6$) arising from the two vertices of degree four and the two vertices of degree five (*i.e.*, $(2)(4 - 3) + (2)(5 - 3) = 6$) which provide 12 of these 24 skeletal electrons. Therefore, the apparent skeletal electron count for the bicapped tetrahedron arising from our GTD method for comparison with the other theories is $24 - 12 = 12$ in excellent agreement with the numbers obtained from the other theoretical approaches. This case is important for illustrating the 'apparent' nature of the apparent skeletal electron counts necessary in Table I .for comparison of the different theoretical approaches. In addition this case is important for the specific osmium carbonyl chemistry discussed in this paper in view of the bicapped tetrahedral geometry of the $Os_6(CO)_{18}$ cluster.

(6) Pentagonal Bipyramid

Next to the octahedron this is the simplest example of a globally delocalized deltahedron having $2n + 2$ skeletal electrons.

(7) Capped Octahedron

The capped octahedron is the simplest example of a capped globally delocalized deltahedron. For reasons noted above the apparent skeletal electron count of the capped octahedron is the same as that of its central octahedron.

As noted above the specific objective of this paper is to apply ideas from the graph theory derived approach to metal cluster structure and bonding in osmium carbonyl cluster systems. However, before considering specific systems, some points concerning electron counting will be considered. The distribution of carbonyl groups on the metal cluster framework is immaterial for electron counting since every carbonyl group found in osmium carbonyl chemistry whether it is terminal or bridging is a two-electron donor. Exceptional carbonyl groups analogous to the four-electron donor bridging carbonyl group $[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2Mn_2(CO)_5$ [20] or the six-electron donor bridging carbonyl group in $(C_5H_5)_3Nb_3(CO)_7$ [21] do not appear in osmium carbonyl chemistry. A μ_3-$Os(CO)_3$ fragment using the normal three internal orbitals is also a two-electron donor since six of the eight osmium(0) electrons are needed to fill the three external osmium orbitals not involved in bonding to the three external carbonyl groups. Similarly a μ_2-$Os(CO)_4$ fragment using two internal orbitals is also a two-electron donor. Thus for electron counting purposes edge-bridging μ_2-$Os(CO)_4$ units and face-bridging μ_3-$Os(CO)_3$ units may be regarded as equivalents of the two-electron donor bridging carbonyl groups μ_2-CO and μ_3-CO, respectively, thereby simplifying electron counting in complicated osmium carbonyl clusters. In the general case of an $Os(CO)_x$ vertex contributing s internal orbitals, the neutral osmium atom and the x carbonyl groups furnish 8 and $2x$ electrons, respectively, of which $2(9 - s)$ electrons are needed for the $9 - s$ external orbitals. This makes an $Os(CO)_x$ vertex contributing s internal orbitals a donor of $8 + 2x - 2(9 - s) = 8 + 2x - 18 + 2s = 2(s + x) - 10$ skeletal electrons.

3. Clusters of Five and Six Osmium Atoms

The cluster $Os_5(CO)_{16}$ has a trigonal bipyramidal structure [22] indicative of edge-localized bonding. It has 18 actual skeletal electrons according to the following skeletal electron counting scheme:

2 degree 3 $Os(CO)_3$ vertices in axial positions:	
$2[2(3 + 3) - 10] = (2)(2) =$	4 electrons
3 degree 4 $Os(CO)_3$ vertices in equatorial positions:	
$3[2(3 + 4) - 10] = (3)(4) =$	12 electrons
Extra CO group	2 electrons
Total skeletal electrons	18 electrons

These 18 skeletal electrons correspond to edge-localized bonding with a two-electron bond along each of the nine edges of the trigonal bipyramid. Subtraction of a total of 6 skeletal electrons for the fourth internal orbitals of each of the three equatorial osmium atoms in $Os_5(CO)_{16}$ from these actual skeletal electrons gives the 12 apparent skeletal electrons listed in Table I for the ordinary trigonal bipyramid. Thus erroneously considering $Os_5(CO)_{16}$ as a globally delocalized system leads fortuitously to a correct skeletal electron count after regarding $Os(CO)_3$ vertices as using three internal orbitals regardless of their position in the trigonal bipyramid:

5 degree 3 $Os(CO)_3$ vertices	10 electrons
Extra CO group	2 electrons
Total skeletal electrons	12 electrons

These 12 skeletal electrons would be considered to correspond to the $2n + 2$ skeletal electron required for a five-vertex globally delocalized system (*i.e*, $n = 5$). However, this correspondence is only fortuitous since consideration of a trigonal bipyramid as a delocalized rather than an edge-localized cluster contradicts principles that are necessary to explain the electron counts in other cluster systems.

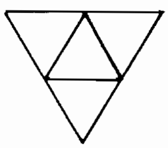
One such system is $Os_6(CO)_{18}$, whose Os_6 polyhedron is a bicapped tetrahedron [23], which may alternatively be regarded as three fused tetrahedra. This polyhedron, like the regular octahedron, has 6 vertices, 12 edges, and 8 faces. However, the bicapped tetrahedron has two vertices each of degrees 3, 4, and 5, whereas all six vertices of the octahedron have degree 4. The $Os_6(CO)_{18}$ cluster may be formulated as a 24 skeletal electron system using the following electron counting scheme:

2 degree 3 (capping) $Os(CO)_3$ vertices	4 electrons
2 degree 4 $Os(CO)_3$ vertices:	
$2[2(3 + 4) - 10] = (2)(4) =$	8 electrons
2 degree 5 $Os(CO)_3$ vertices:	
$2[2(3 + 5) - 10] = (2)(6) =$	12 electrons
Total skeletal electrons	24 electrons

These 24 electrons correspond to edge-localized bonding with a two-electron bond along each of the 12 edges of the bicapped tetrahedron. Subtracting a total of 12 skeletal electrons for the 'extra' internal orbitals of the osmium atoms at the two degree 5 vertices and the two degree 4 vertices from these 24 actual skeletal electrons gives the 12 apparent skeletal electrons listed in Table I for the bicapped tetrahedron. Thus, previous treatments [23] of $Os_6(CO)_{18}$ used the skeletal counting rules for a globally delocalized system which $Os_6(CO)_{18}$ is not. Under these rules $Os_6(CO)_{18}$ is a 12 skeletal electron system since each of the six $Os(CO)_3$ vertices is considered to donate two skeletal electrons. The bicapped tetrahedral rather than regular octahedral geometry of $Os_6(CO)_{18}$ can then be rationalized on the basis that $Os_6(CO)_{18}$ has only 12 skeletal rather than the 14 skeletal electrons (= (2)(6) + 2) required for a regular octahedron (with globally delocalized bonding). This simplified electron counting procedure is useful as a crude device for identifying electron-poor systems having less than $2n + 2$ skeletal electrons. However, the above more detailed electron counting for $Os_6(CO)_{18}$ can relate its skeletal electron count more precisely to a specific polyhedron system having tetrahedral chambers.

There are several examples of 14 skeletal electron Os_6 systems which formally may be obtained by adding two electrons to $Os_6(CO)_{18}$ [24]. The anions $Os_6(CO)_{18}^{2-}$ and $HOs_6(CO)_{18}^{-}$ have the regular octahedral Os_6 geometry expected for a 14 skeletal electron system (counting all six $Os(CO)_3$ vertices as normal vertices contributing three internal orbitals). The hydride $H_2Os_6(CO)_{18}$, although also electronically precise for a regular octahedron, instead adopts the geometry of a tetragonal pyramid (*i.e.*, distorted square pyramid) with an $Os(CO)_3$ cap on one of the triangular faces, *i.e.* $H_2Os_5(CO)_{15}[\mu_3\text{-}Os(CO)_3]$. The 14 skeletal electron count of $H_2Os_6(CO)_{18}$ is also correct for a square pyramid analogous to B_5H_9 where the 'extra' electron pair over $2n + 2 = 12$ for $n = 5$ corresponds to the single non-triangular face in the square pyramid (*i.e.*, the square base). The contrast between the octahedral Os_6 geometry in $Os_6(CO)_{18}^{2-}$ and $HOs_6(CO)_{18}^-$ and the capped tetragonal pyramid Os_6 geometry in $H_2Os_6(CO)_{18}$ probably relates to the steric requirements of the hydrogen atoms in $H_2Os_6(CO)_{18}$, which bridge opposite edges of the square base.

A rather different type of Os_6 cluster is represented by $Os_6(CO)_{17}[P(OCH_3)_3]_4$ which has the following planar Os_6 arrangement [25]:



The X-ray structure [25] shows that $Os_6(CO)_{17}[P(OCH_3)_3]_4$ can be regarded as $Os_3(CO)_9[\mu_2\text{-}Os(CO)_2[P(OCH_3)_3]_2]_2[\mu_2\text{-}Os(CO)_4]$. Since, as noted above, the μ_2-$Os(CO)_4$ unit and its substitution product μ_2-$Os(CO)_2[P(OCH_3)_3]_2$ are two-electron donors like bridging carbonyl groups, the cluster $Os_6(CO)_{17}[P(OCH_3)_3]_4$ becomes isoelectronic with $Os_3(CO)_{12}$, which, of course, is very stable. Note, however, that all of the carbonyl groups in $Os_3(CO)_{12}$ are terminal [26] in contrast to $Os_3(CO)_9[\mu_2\text{-}Os(CO)_2[P(OCH_3)_3]_2]_2[\mu_2\text{-}Os(CO)_4]$ in which the isoelectronic μ_2-$Os(CO)_2L_2$ (L = CO or $P(OCH_3)_3$) units are edge bridges. This is a good example of the greater tendency for $Os(CO)_2L_2$ units to function as bridges than their isoelectronic CO analogues.

4. Clusters of Seven and Eight Osmium Atoms

The cluster $Os_7(CO)_{21}$ is shown to be a capped octahedron [27] and thus is best formulated as $Os_6(CO)_{18}[\mu\text{-}Os(CO)_3]$. The seven $Os(CO)_3$ units give $Os_7(CO)_{21}$ a total of 14 skeletal electrons in accord with the $2n + 2$ electron ($n = 6$) requirement for the central globally delocalized Os_6 octahedron.

The cluster $H_2Os_7(CO)_{20}$ is isoelectronic with $Os_7(CO)_{21}$ but does not form a related capped octahedral structure. Instead it forms a bicapped tetrahedral structure $Os_4(CO)_{10}[\mu_3\text{-}Os(CO)_3]_2[\mu_2\text{-}Os(CO)_4][\mu_3\text{-}H]_2$ with an edge-bridging μ_2-$Os(CO)_4$ group [21]. The electron counting in this system can be performed in the following manner analogous to that of $Os_6(CO)_{18}$ (see above):

2 degree 3 (capping) $Os(CO)_3$ vertices	4 electrons
3 degree 4 $Os(CO)_3$ vertices $2[2(3 + 4) - 10] = (2)(4) =$	8 electrons
2 degree 5 $Os(CO)_3$ vertices $2[2(3 + 5) - 10] = (2)(6) =$	12 electrons
1 μ_2-$Os(CO)_4$ group	2 electrons
2 hydrogen atoms: $(2)(1) =$	2 electrons
Deficiency of two CO groups from the above (*i.e.*, the above add up to 22 CO groups whereas $H_2Os_7(CO)_{20}$ has only 20 CO groups)	−4 electrons
Total skeletal electrons	24 electrons

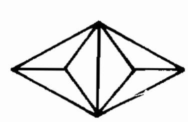
These 24 skeletal electrons correspond to edge-localized bonding with a two-electron bond along each of the 12 edges of the bicapped tetrahedron. The radically different structures of $Os_7(CO)_{21}$ and $H_2Os_7(CO)_{20}$ can relate to the different steric requirements of 21 ligands (CO groups) in the former case and 22 ligands (20 CO groups and 2 H atoms) in the latter case.

The two isoelectronic Os_8 clusters, namely $Os_8(CO)_{22}^{2-}$ and $HOs_8(CO)_{22}^-$, also have different structures which similarly can relate to the different steric requirements of 22 and 23 ligands surrounding the Os_8 cluster. The dianion $Os_8(CO)_{22}^{2-}$ is a bicapped octahedron [29] whereas the monoanion $HOs_8(CO)_{22}^-$ is a bicapped pair of edge-fused tetrahedra [30]. The electron counting in $Os_8(CO)_{22}^{2-}$ (*i.e.*, $Os_6(CO)_{16}[\mu_3\text{-}Os(CO)_3]_2^{2-}$) can be most readily visualized as follows realizing that the central Os_6 octahedron is a globally delocalized deltahedron using three internal orbitals from the vertex atoms:

6 $Os(CO)_3$ vertices	12 electrons
2 μ_3-$Os(CO)_3$ caps	4 electrons
−2 charge on dianion	2 electrons
Deficiency of two CO groups from the above (*i.e.*, the above add up to 24 CO groups whereas $Os_8(CO)_{22}^{2-}$ has only 22 CO groups)	−4 electrons
Total skeletal electrons	14 electrons

These 14 skeletal electrons are, of course, the correct $2n + 2$ ($n = 6$) number for the central Os_6 octahedron.

The geometry of the pair of edge-fused tetrahedra in $HOs_8(CO)_{22}^-$ can be represented as follows:



This polyhedral network thus has 11 edges, four degree 3 vertices, and two degree 5 vertices. Regarding $HOs_8(CO)_{22}^-$ as $HOs_6(CO)_{16}[\mu_3\text{-}Os(CO)_3]_2^-$ leads to the following electron counting scheme using edge-localized bonding for the Os_6 edge-fused tetrahedral pair:

2 degree 5 $Os(CO)_3$ vertices	
$2[2(3 + 5) - 10] = (2)(6) =$	12 electrons
4 degree 3 $Os(CO)_3$ vertices	8 electrons
2 μ_3-$Os(CO)_3$ caps	4 electrons
-1 charge on anion	1 electron
Hydrogen atom	1 electron
Deficiency of two CO groups from above	-4 electrons
Total skeletal electrons	22 electrons

These 22 skeletal electrons correspond to edge-localized bonding with a two-electron bond along each of the 11 edges of the edge-fused tetrahedral pair in accord with expectations.

Comparison of $Os_8(CO)_{22}^{2-}$ and $HOs_8(CO)_{22}^{-}$ indicates that the globally delocalized octahedron and the edge-localized edge-fused tetrahedral pair effectively have identical skeletal electron requirements. The globally delocalized octahedron requires $2n + 2 = 14$ skeletal electrons with each vertex using three internal orbitals. The edge-fused tetrahedral pair requires 22 skeletal electrons for two-electron bonds along each of the 11 edges. However, two of the six vertices of the edge-fused tetrahedral pair use five rather than three internal orbitals thereby increasing the apparent skeletal electron count of the system by eight corresponding to an electron pair for each 'extra' internal orbital above three for the two degree 5 vertex atoms. Thus four electron pairs (*i.e.*, eight electrons) which are non-bonding in an Os_6 octahedron become bonding in an Os_6 edge-fused tetrahedral pair so that a 14 skeletal electron Os_6 octahedron is isoelectronic with a 22 skeletal electron Os_6 edge-fused tetrahedral pair. Thus skeletal electron count alone will not distinguish between a globally delocalized octahedron and an edge-localized pair of edge-fused tetrahedra. However, the requirement of five internal orbitals for two of the six vertex atoms will make the pair of edge-fused tetrahedra unfavorable except for some of the heavy transition metals such as osmium.

5. A Cluster of Nine Osmium Atoms

As interesting Os_9 cluster $[Os_9(CO)_{21}C_3H_2R]^-$ ($R = H, CH_3$) has recently been characterized structurally [31]. This cluster may be regarded as a tetracapped Os_4C_3 pentagonal bipyramid with five additional face-bridging $Os(CO)_3$ groups. As expected from the requirement of d orbitals for atoms in capped faces [8], only the two Os_3 triangles of the central Os_4C_3 pentagonal bipyramid are capped and then one of the Os_3 faces of each cap is capped by another $Os(CO)_3$ cap. Thus there are two layers of caps in this structure. However, the $Os(CO)_3$ units are formally donors of two skeletal electrons regardless of their locations in the structure. Therefore this cluster may be regarded as $Os_4(CO)_6C_3H_2R_2[\mu_n\text{-}Os(CO)_3]^{5-}$ for electron counting purposes thereby providing the expected 16 skeletal electrons ($= 2n + 2$ where $n = 7$) for the central Os_4C_3 pentagonal bipyramid as follows:

4 $Os(CO)_2$ vertices of the pentagonal bipyramid	0 electrons
3 CH/CR vertices of the pentagonal bipyramid: $(3)(3) =$	9 electrons
5 bridging μ_n-$Os(CO)_3$ groups: $(5)(2) =$	10 electrons
-1 charge on anion	1 electron
Deficiency of 2 CO groups from the above (*i.e.*, the above add up to 23 CO groups rather than the 21 CO groups actually found in $[Os_9(CO)_{21}C_3H_2R]^-$):	-4 electrons
Total skeletal electrons	16 electrons

This is a good example of a cluster where a reliable electron count does not require understanding all of the details of a complicated structure.

An interesting feature of the above electron-counting scheme is that an $Os(CO)_2$ vertex using three internal orbitals contributes zero skeletal electrons. This conforms to the $2(s + x) - 10$ formula noted above (x is the number of carbonyl groups and s is the number of internal orbitals) and arises from the fact that the eight electrons from the osmium(0) atoms are all needed for non-bonding pairs in the four external orbitals not used by the two CO groups.

6. Clusters of Ten and Eleven Osmium Atoms

A series of isoelectronic clusters of ten osmium atoms is known in which a central Os_6 octahedron has four faces capped by μ_3-$Os(CO)_3$ groups so that no two capped faces share an edge. These Os_{10} clusters include the carbides $Os_{10}C(CO)_{24}^{2-}$ [32] and $HOs_{10}C(CO)_{24}^{-}$ [33] in which a carbon atom is in the center of the Os_6 octahedron as well as $H_4Os_{10}(CO)_{24}^{2-}$ [34] lacking such an interstitial carbon atom. The skeletal electron counting is similar, of course, for all of these isolectronic Os_{10} systems as illustrated below for $Os_{10}C(CO)_{24}^{2-}$ (*i.e.*, $Os_6C(CO)_{12}[\mu_3\text{-}Os(CO)_3]_4^{2-}$):

6 $Os(CO)_2$ vertices	0 electrons
4 μ_3-$Os(CO)_3$ caps	8 electrons
1 interstitial carbon atom	4 electrons
-2 charge on anion	2 electrons
Total skeletal electrons	14 electrons

The observed 14 skeletal electrons are in accord with expectations for the central globally delocalized Os_6 octahedron.

The clusters $Os_6(CO)_{18}^{2-}$, $Os_7(CO)_{21}$, $Os_8(CO)_{22}^{2-}$, and $H_4Os_{10}(CO)_{24}^{2-}$ may all be regarded as derivatives of a homologous series of clusters of the type $Os_{6+p}(CO)_{19+2p}$ formed by capping a central Os_6 octahedron with p μ_3-$Os(CO)_3$ caps where p is 0, 1, 2, and 4, respectively. The maximum number of such μ_3-$Os(CO)_3$ caps on a central Os_6 octahedron is likely to be 4 (*i.e.*, $0 \leqslant p \leqslant 4$) since otherwise some vertices of the central Os_6 octahedron would need six internal orbitals: three for the globally delocalized bonding in the central Os_6 octahedron and three for localized bonds to μ_3-$Os(CO)_3$ caps. Steric considerations concerning the orientations of the maximum nine (= one s orbital, three p orbitals, and five d orbitals) valence orbitals of an osmium vertex suggest that five might be the maximum possible number of internal orbitals which can be contributed by a surface atom of an osmium polyhedron. This suggests that the Os_{10} polyhedron found in $Os_{10}C(CO)_{24}^{2-}$, $HOs_{10}C(CO)_{24}^{-}$ and $H_4Os_{10}(CO)_{24}^{2-}$ is the largest Os_{6+p} polycapped octahedron which can be formed by capping a total of p faces of a central Os_6 octahedron with μ_3-$Os(CO)_3$ groups. Clusters based on more than ten osmium atoms are therefore likely to exhibit structural features other than capped Os_6 octahedra.

The following other points concerning capped Os_6 octahedra are of interest:

(1) The tetracapped octahedra in the Os_{10} clusters mentioned above have T_d symmetry and represent a fragment of the face-centered cubic lattice [35] found in many metals. Thus the face-centered cubic lattice may be regarded as a network of 14-vertex octacapped octahedra, *i.e.*, the Os_{10} tetracapped octahedra with four added caps on each of the four uncapped octahedral faces. Here, however, the analogy between these Os_{10} polyhedra and face-centered cubic metals ends since the four tetrahedral chambers in the Os_{10} polyhedra have edge-localized bonding whereas the bonding in free metals, including the face-centered cubic ones, is fully delocalized leading to features such as Fermi surfaces [36] which are not found in these finite molecular clusters.

(2) Os_9 clusters based on tricapped octahedra do not seem to be known. However, such clusters should be possible and would be based on a tricapped octahedral $Os_9(CO)_{25}$ (*i.e.*, $Os_{6+p}(CO)_{19+2p}$ for p = 3). Possible stoichiometries for such Os_9 clusters include $Os_9C(CO)_{22}^{2-}$ and $H_4Os_9(CO)_{22}^{2-}$.

The above considerations suggest new structural principles for clusters containing more than ten osmium atoms. The only structurally characterized such clusters appear to be $Os_{11}C(CO)_{27}^{2-}$ [16] and its copper derivative $[Os_{11}C(CO)_{27}Cu(NCCH_3)]^-$ [37]. These clusters are based on a central Os_7 4-capped trigonal prism with a carbon atom in the center and with four of the six triangular faces capped by μ_3-$Os(CO)_3$ groups. The skeletal electrons for $Os_{11}C(CO)_{27}^{2-}$ (*i.e.*, $Os_7C(CO)_{15}[\mu_3\text{-}Os(CO)_3]_4^{2-}$) can be counted as follows:

7 $Os(CO)_2$ vertices	0 electrons
extra CO group	2 electrons
interstitial carbon atoms	4 electrons
4 μ_3-$Os(CO)_3$ caps	8 electrons
−2 charge on anion	2 electrons
Total skeletal electrons	16 electrons

The observed 16 electrons correspond to the $2n + 2$ skeletal electrons expected for a globally delocalized Os_7 polyhedron. However, the observed Os_7 polyhedron is not the pentagonal bipyramid found in $B_7H_7^{2-}$ [38] but instead is a 4-capped trigonal prism which is not a deltahedron since it has two rectangular faces. In this case the deviation from a deltahedral structure for a $2n + 2$ skeletal electron system is probably a consequence of the volume requirements of the interstitial carbon atom in the center of the polyhedron. An interstitial atom requires a larger polyheral volume leading in some cases to fewer edges than found in the otherwise expected deltahedron. A similar situation is found in rhodium carbonyl chemistry where the peripheral Rh_{12} polyhedron in the rhodium-centered clusters $[Rh_{12}(CO)_{24}(Rh)H_{5-x}]^{-x}$ ($x = 2$ or 3) [39, 40] is not an icosahedron or other deltahedron but instead has six rectangular and eight triangular faces even though it has the 26 skeletal electrons ($26 = 2n + 2$ for $n = 12$) required for a globally delocalized deltahedral system.

7. Conclusion

The known chemistry of osmium carbonyl clusters containing five or more metal atoms indicates that osmium carbonyl vertices always have the favored 18-electron rare gas configuration in contrast to some of the later transition metals such as platinum and gold where 16 and even 14-electron configurations are found. Furthermore, edge-localized bonding relative to globally delocalized bonding appears to be more frequently found in osmium carbonyl clusters than in clusters of other transition metals leading to the following consequences:

(1) The abundance of osmium carbonyl clusters based on fused tetrahedra or containing tetrahedral chambers.

(2) The limitation of globally delocalized polyhedra to the octahedron in osmium carbonyl derivatives having six to ten osmium atoms. In other words

clusters containing n osmium atoms where $7 \leqslant n \leqslant 10$ use at least $n-6$ of the osmium atoms as caps leading frequently to structures based on central octahedra having various numbers of capped faces.

(3) The occurrence of a structure (namely that of $HOs_8(CO)_{22}^-$) based on an edge-localized pair of edge-fused tetrahedra even though the system has the correct number of electrons for an alternative structure based on a globally delocalized center octahedron. Related to this phenomenon is the observation of a partially localized capped tetragonal pyramid structure for $H_2Os_6(CO)_{18}$ which has the correct number of electrons for a globally delocalized octahedral structure.

The tendency for osmium carbonyl clusters to form polyhedra exhibiting edge-localized rather than globally delocalized bonding relates to the facility for osmium carbonyl vertices to contribute more than three internal orbitals to the cluster bonding. In this manner osmium carbonyl clusters differ most greatly from boron hydride clusters in which the availability of only s and p orbitals to the vertex boron atoms limit the number of internal orbitals to three. Thus Wade's well-known analogy [1] between boron hydride clusters and transition metal clusters is frequently no longer followed in the case of osmium carbonyl clusters.

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