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Metal cluster topology
16. Macropolygons and macropolyhedra in coinage metal iron carbonyl cluster anions and related compounds ☆

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Abstract

The diamagnetic copper–iron carbonyl cluster anions $Cu_3[Fe(CO)_4]_3^{3-}$, $Cu_5[Fe(CO)_4]_4^{3-}$ and $Cu_6[Fe(CO)_4]_4^{2-}$ with triangular, butterfly and tetrahedral structures, respectively, have the expected electron counts for a large iron macropolygonal or macropolyhedral network with Fe–Cu–Fe edges containing a smaller copper polygonal or polyhedral network which is the line graph of the iron network. Similarly, the paramagnetic silver–iron carbonyl cluster anion $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$ with an outer Fe_8 macrocube and an inner Ag_{12} cuboctahedron has the expected electron count for an outer diamagnetic $Ag_{12}[Fe(CO)_4]_8^{4-}$ unit encapsulating a neutral paramagnetic silver atom in accord with its ESR spectrum.

Keywords: Metal cluster topology; Macropolygons; Macropolyhedra; Iron complexes; Metal complexes; Cluster complexes

A previous paper of this series [2] discusses important topological features of transition metal clusters containing mercury vertices. Such clusters are characterized by structures containing linear M–Hg–M units (M = transition metal) and include transition metal–mercury clusters containing so-called macropolygons or macropolyhedra with edges consisting of nearly linear M–Hg–M units. More recently, related clusters have been prepared containing likewise nearly linear M–M′–M units in which M is a transition metal and M′ is a coinage metal such as copper or silver. This paper extends the previous treatment [2] to coinage metal iron carbonyl anion clusters constructed from macropolygonal or macropolyhedral networks with Fe–M′–Fe edges (M′ = Cu, Ag) and typically $Fe(CO)_4$ vertices such as the triangular cluster [3] $Cu_3[Fe(CO)_4]_3^{3-}$, the butterfly cluster [3] $Cu_5[Fe(CO)_4]_4^{3-}$, the tetrahedral cluster [4] $Cu_6[Fe(CO)_4]_4^{2-}$, and the paramagnetic centered cubic cluster [5] $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$. Such clusters are obtained from various reactions of Cu(I) or Ag(I) compounds with the $Fe(CO)_4^{2-}$ dianion. Many aspects of the coinage metal environments in such clusters are similar to those in the coinage metal alkyls, aryls and alkynyls discussed in a recent paper [6].

A specific feature of the chemical bonding in some structures containing the coinage metals (Cu, Ag, Au), mercury, and other post-transition elements observed by Nyholm [7] as early as 1961 is the shifting of one or two of the outer p orbitals to such high energies that they no longer participate in the chemical bonding and the accessible spd valence orbital manifold is no longer spherical (isotropic). In the structures of interest in this paper, two of the outer p orbitals of the coinage metal atoms are raised to antibonding energy levels leaving one p orbital in the accessible spd orbital manifold, which now contains seven orbitals (spd^5) and has cylindrical geometry extending in one axial dimension much further than in the remaining two dimensions [6]. Filling this seven-orbital spd^5 manifold with electrons leads to the 14-electron configuration found in two-coordinate linear complexes of d^{10} metals including the coinage metals Cu(I), Ag(I) and Au(I), as well as Hg(II). In the compounds discussed in this paper the two-coordinate coinage metal atoms are directly bonded to two adjacent transition metal atoms (generally iron) leading to approximately linear M–M′–M units (M = transition metal, M′ = coinage

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☆ For Part 15 see Ref. [1]. This paper is dedicated to György Bor in recognition of his pioneering work in both metal carbonyl chemistry and metal cluster chemistry.

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metal) bearing a formal negative charge on the coinage metal atom so that a linear uninegative M–Cu(I)$^-$–M or M–Ag(I)$^-$–M unit is isoelectronic with the neutral linear M–Hg–M units found in the transition metal–mercury clusters discussed in the previous paper [2]. The linear M–M′–M units can form the edges of large polygons or polyhedra, which can conveniently be called macropolygons or macropolyhedra, respectively, and which have the transition metals, M, at their vertices. The p orbitals of the coinage metals which are raised to antibonding levels in these linear M–M′–M units can participate in $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding to adjacent similar coinage metal atoms. Such bonding was suggested some years ago by Dedieu and Hoffmann [8] for Pt(0)–Pt(0) dimers on the basis of extended Hückel calculations. This type of $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding like, for example, the $d\pi \rightarrow p\pi$ backbonding in metal carbonyls, does not affect the electron bookkeeping in the coinage metal clusters but accounts for bonding rather than non-bonding distances between adjacent coinage metal vertices in such clusters. In the metal clusters discussed in this paper this $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding between adjacent coinage metal atoms leads to coinage metal polygons or polyhedra in which the edges are direct M′–M′ bonds between the coinage metals M′. The coinage metal iron carbonyl cluster anion structures discussed in this paper thus contain both transition metal macropolygons or macropolyhedra with linear M–M′–M edges and coinage metal polygons or polyhedra with M′–M′ edges. The graph of the polygon or polyhedron formed by the coinage metal vertices is the line graph of the graph of the macropolygon or polyhedron formed by the transition metal vertices. In this context the line graph L(G) of a graph G is constructed by taking the edges of G as vertices of L(G) and joining two vertices in L(G) when the corresponding edges in G have a common vertex [9].

The iron carbonyl vertices of the coinage metal iron carbonyl clusters discussed in this paper are always $Fe(CO)_4$ units, which are of two types, namely divalent (degree 2) $Fe(CO)_4$ vertices forming two Fe–M′ bonds and trivalent (degree 3) $Fe(CO)_4$ vertices forming three Fe–M′ bonds. In order for the iron atoms in these $Fe(CO)_4$ vertices to have the favored 18-electron noble gas configuration, the divalent $Fe(CO)_4$ vertices must be formally neutral and the trivalent $Fe(CO)_4$ vertices must bear a formal +1 charge (Fig. 1).

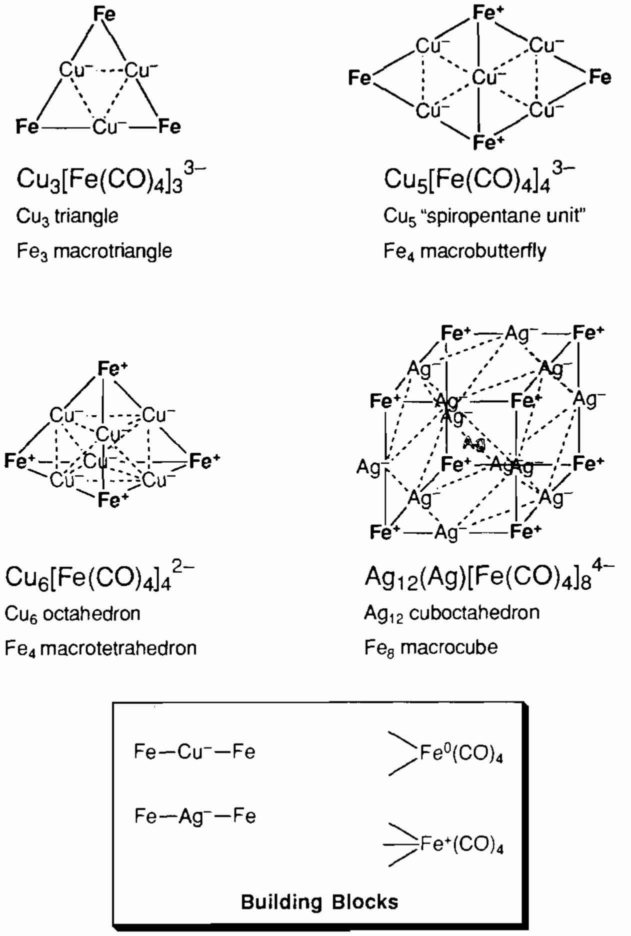

Fig. 1. The metal skeletons of the coinage metal iron carbonyl clusters discussed in this paper.

The metal skeletons of the known mixed coinage metal–iron carbonyl cluster anions with Fe–M′–Fe edges are depicted in Fig. 1. In all cases the charge on the cluster anion is the algebraic sum of −1 for each coinage metal, M′, in the Fe–M′–Fe edges, zero for a bivalent $Fe(CO)_4$ group, and +1 for a trivalent $Fe(CO)_4$ group (Fig. 1). The large silver–iron carbonyl anion cluster unit $Ag_{12}[Fe(CO)_4]_8^{4-}$ containing an Fe_8 macrocube with Fe–Ag–Fe edges is found in the cluster anion $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$, in which a thirteenth silver atom is located in the center of the cluster [5]. The twelve silver atoms at the edge midpoints of the Fe_8 macrocube form a cuboctahedron, which is the line graph of the cube. Since the outer $Ag_{12}[Fe(CO)_4]_8^{4-}$ unit has the expected closed-shell −4 charge arising from the algebraic sum of the formal −1 charges on the twelve Ag atoms and the formal +1 charges on the eight trivalent $Fe(CO)_4$ vertices, the 'central' silver atom in $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$ is formally neutral, i.e. Ag^0. The observed ESR signal [5] in $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$ indicates strong coupling of the unpaired electron with the central Ag atom but only loose coupling with the peripheral Ag atoms in accord with the dissection of $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$ into a closed-shell outer $Ag_{12}[Fe(CO)_4]_8^{4-}$ unit with no unpaired electrons and a central Ag^0 atom on which the unpaired electron mainly resides. This interpretation of the structure and bonding in $Ag_{12}(Ag)[Fe(CO)_4]_8^{4-}$ resolves the problem of its 'extra' nine electrons relative to the predictions of most theories mentioned in the original paper on this cluster and suggests the use of the

$Ag_{12}[Fe(CO)_4]_8^{4-}$ unit to encapsulate other reactive neutral atoms besides Ag^0 in its cuboctahedral cavity.

A few mixed coinage metal–transition metal clusters other than iron carbonyl derivatives are known which have polygonal or polyhedral structures containing M–M′–M edges (M = transition metal, M′ = coinage metal). The very hydrogen-rich cluster [10] $Cu_6[Re(PPh_3)_2H_6]_4^{2+}$ contains a similar metal core to the $Cu_6[Fe(CO)_4]_4^{2-}$ cluster discussed above. The observed +2 charge on this cluster is consistent with the six Cu atoms each with a −1 formal charge and the four trivalent $Re(PPh_3)_2H_6$ vertices each with the +2 formal charge required for the favored 18-electron noble gas configuration. The neutral triangular cluster [11] $[HC(PPh_3)_3Ag_3]Ag_3[Fe(CO)_4]_3$ is closely related to $Cu_3[Fe(CO)_4]_3^{3-}$ with the three L→Ag units in the $[HC(PPh_3)_3Ag_3]$ group of neutral $[HC(PPh_3)_3Ag_3]Ag_3[Fe(CO)_4]_3$ providing the 'extra' three electrons which arise in the related $Cu_3[Fe(CO)_4]_3^{3-}$ from the −3 ionic charge.

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