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Metal Cluster Topology.
2. Gold Clusters*

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Abstract

Previously developed methods for the treatment of polyhedral boranes, carboranes, and metal clusters are extended to the treatment of gold clusters, which present a variety of new problems. In most cases gold atoms in such cluster compounds do not employ the usual 9-orbital sp^3d^5 spherical bonding orbital manifold. Instead almost all non-tetrahedral gold clusters consist of a center gold atom surrounded by a puckered polygonal belt of peripheral gold atoms generally with one or more additional peripheral gold atoms in distal positions above and/or below the belt. The peripheral gold atoms in such clusters use a 7-orbital spd^5 cylindrical bonding orbital manifold, but their residual two orthogonal antibonding p orbitals can receive electron density from the filled d orbitals of adjacent peripheral gold atoms through $d\sigma \rightarrow p\sigma^*$ and/or $d\pi \rightarrow p\pi^*$ backbonding leading to bonding distances between adjacent peripheral gold atoms. Centered gold clusters can be classified into either spherical or toroidal clusters depending upon whether the center gold atom uses a 9-orbital sp^3d^5 spherical bonding orbital manifold or an 8-orbital sp^2d^5 toroidal bonding orbital manifold, respectively. The topology of the core bonding in gold clusters is generally not that of the K_n complete graph found in other clusters but instead mimics the topology of the polyhedron formed by the surface atoms. This apparently is a consequence of the poor lateral overlap of the cylindrical spd^5 manifolds of the peripheral gold atoms. Examples of non-centered gold clusters treated in this paper include the squashed pentagonal bipyramidal $Au_7(PPh_3)_7^+$ and the edge-fused bitetrahedral $(Ph_3P)_4Au_6[Co(CO)_4]_2$ which may be regarded as a 'perauraethylene' in which the six cluster gold atoms correspond to the six atoms of ethylene including a double bond between the two gold atoms corresponding to the two ethylene carbon atoms.

1. Introduction

The previous paper of this series [1] treats in detail the bonding topology of osmium carbonyl clusters. This paper presents an analogous treatment of gold clusters [2, 3] Although such gold clusters have been previously studied by Mingos [4, 5] this paper represents the first attempt to present the bonding topology of gold clusters in terms analogous to those used in previous papers [6, 7] on polyhedral boranes and carboranes as well as clusters of central transition metals and post-transition elements [8]. Gold clusters are particularly interesting for the following reasons: (1) Gold is an excellent example of a heavy element where relativistic effects [9] appear to be important in its chemical bonding. (2) Gold clusters contain topological features not found in clusters of other transition metals. Thus gold is the only metal forming cluster compounds which can be interpreted as being homeomorphic to the torus rather than the sphere. I anticipated the existence of toroidal clusters back in 1972 [10] but the primitive nature of metal cluster chemistry and the underlying theory at that time made it impossible to guess how one might obtain such toroidal clusters.

2. Gold Vertices

The general features of our topological treatment of metal clusters have been discussed in detail elsewhere [6–8]. In order to apply this treatment to gold clusters, it is first necessary to understand some special features of gold vertices in cluster polyhedra. These features derive from some principles outlined by Evans and Mingos [11].

The accessible spd orbital manifold of most transition metals consists of 9 orbitals (sp^3d^5) and has spherical geometry with equal extent in all three dimensions, where the geometry of an orbital manifold relates to contours of the sum $\Sigma\psi^2$ over all orbitals in the manifold. Filling this accessible spherical spd orbital manifold with electrons from

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either the central metal atom or its surrounding ligands results in the familiar 18-electron configuration of the next rare gas.

A specific feature of the chemical bonding in some systems containing the late transition metals observed by Nyholm [12] 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. If one p orbital is so shifted to become antibonding, then the accessible spd orbital manifold contains only 8 orbitals (sp^2d^5) and has the geometry of a torus or doughnut. The 'missing' p orbital is responsible for the hole in the doughnut. This toroidal sp^2d^5 orbital manifold can bond only in the two dimensions of the plane of the ring of the torus. Filling this sp^2d^5 manifold of 8 orbitals with electrons leads to the 16-electron configuration found in square planar complexes of the d^8 late transition metals such as Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III). The locations of the four ligands in these square planar complexes can be considered to be points on the surface of the torus corresponding to the sp^2d^5 manifold.

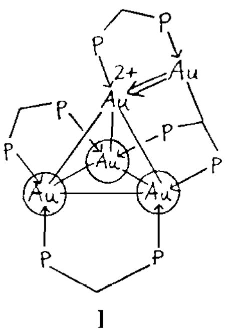
In some systems containing the late 5d transition and post-transition metals such as platinum, mercury, thallium, as well as gold, the subject of this paper, two of the outer p orbitals are raised to antibonding energy levels [21]. This leaves only one p orbital in the accessible spd orbital manifold, which now contains 7 orbitals (spd^5) and has cylindrical geometry extending in one axial dimension much farther than in the remaining two dimensions. Filling this spd^5 manifold with electrons leads to the 14-electron configuration found in two-coordinate linear complexes of d^{10} metals such as Pt(0), Ag(I), Au(I), Hg(II), and Tl(III). The raising of one or particularly two outer p orbitals to antibonding levels has been attributed to relativistic effects [9].

Thus to an initial approximation the spd^5 orbital manifold of an L → Au or X–Au vertex (L = tertiary phosphine or isocyanide ligand; X = halogen or pseudohalogen) in a polyhedral gold cluster may be regarded as having a pair of linear sp hybrids. One of these hybrids, corresponding to the unique internal orbital in our previously discussed bonding models [6–8], points towards the center of the polyhedron and thus can participate in the core bonding discussed in the earlier papers. The other sp hybrid corresponds to the external orbital in our bonding models [6–8] and overlaps with the bonding orbital from the external L or X ligand. In this initial approximation the five d orbitals of the gold vertex are essentially non-bonding and are filled with electron pairs thereby using 10 of the 11 valence electrons of a neutral gold atom. As a result of this the L → Au and X–Au vertices are donors of one and zero skeletal electrons, respectively. In this initial approximation an L → Au vertex functions much like a hydrogen atom. In fact some recent gold transition metal carbonyl chemistry [13] is similar to metal carbonyl hydride chemistry but with R_3PAu units replacing hydrogen atoms. Furthermore, the binuclear derivative [14] $(C_6H_5)_3P \rightarrow Au{-}Au \leftarrow P(C_6H_5)_3$ may be regarded as an analogue of dihydrogen, H–H, as well as the mercurous halides, X–Hg–Hg–X, with which it is isoelectronic.

An important difference between an L → Au vertex and a hydrogen atom is the two empty orthogonal p orbitals of the L → Au vertex, namely the two p orbitals that are not used for the sp hybrid mentioned above. These are the p orbitals which are raised to antibonding levels as noted above so that they are not contained in the spd^5 cylindrical manifold of bonding orbitals. These empty p orbitals correspond to the twin internal orbitals in our earlier bonding models [6–8] and, although devoid of electrons in the initial approximation, are appropriately oriented for surface bonding. Such surface bonding in these gold clusters can involve overlap between a filled d orbital of a gold vertex and an empty p orbital of an adjacent gold vertex and thus can be viewed as an unusual example of $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding depending upon the symmetry of the overlap. Such bonding has been suggested by Dedieu and Hoffmann [15] for closely related Pt(0)–Pt(0) dimers on the basis of extended Hückel calculations. This type of surface bonding (like, for example, $d\pi \rightarrow p\pi^*$ backbonding in metal carbonyls) does not affect the electron bookkeeping of the gold cluster but accounts for the bonding rather than non-bonding distances between adjacent gold vertices in gold clusters.

3. Gold Clusters Based on Tetrahedra

Metal clusters built from tetrahedra generally have edge-localized bonding [1, 6–8] and tetrahedral gold clusters are no exception to this rule. Let us examine, for example, the Au_5 cluster of bis(diphenylphosphino)methane [16], $[Au_5(Ph_2PCH_2PPh_2)_3(Ph_2PCHPPh_2)]^{2+}$, which can be represented schematically as follows:



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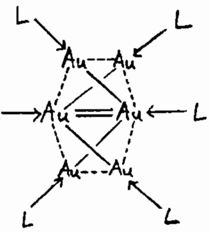
In this Au_5 cluster four of the five gold atoms form a tetrahedron. The three basal gold atoms (circled in the diagram) have the favored 18-electron rare gas electronic configuration since they each receive four electrons from the two phosphorus atoms and three additional electrons from bonds to three other gold atoms (*i.e.*, $11 + 4 + 3 = 18$). These three basal gold atoms thus have the spherical sp^3d^5 manifold of bonding orbitals. The external gold atom in this Au^5 cluster is sp hybridized with a 14-electron spd^5 bonding manifold similar to that in the numerous mononuclear LAuX derivatives. Transmission of electron density from the filled d orbitals of this external gold atom to the empty p orbitals of the apical gold atom can give the apical gold atom a reasonable electronic configuration.

The shapes of Au_6 clusters illustrate some interesting points. An octahedral $[(R_3P)_6Au_6]^{n+}$ requires only two skeletal electrons for the single bonding orbital from the 6-center bond at the core of the Au_6 octahedron. Since each R_3PAu vertex contributes one skeletal electron, *n* must be 4 for an octahedral Au_6 cluster of this type. For this reason it is not surprising that the known [17] Au_6 cluster, $[(C_6H_5)_3P]_4Au_6[Co(CO)_4]_2$, which has four skeletal electrons when counted as an octahedron, does not have octahedral Au_6 geometry. Note that in $[(C_6H_5)_3P]_4Au_6[Co(CO)_4]_2$ the $Co(CO)_4$ unit functions like a pseudohalide so that an $Au-Co(CO)_4$ vertex is electronically equivalent to an Au–X vertex in terms of skeletal electron contribution to the gold cluster.

The actual geometry of $[L_6Au_6]^{2+}$ or the isoelectronic $L_6Au_6X_2$ derivatives (*i.e.*, $L = (C_6H_5)_3P$ and $X = Co(CO)_4$ in the example above) is that of a pair of edge-fused tetrahedra which may be represented as follows:



II

After making due allowances for the differences between heavy gold atoms and light carbon and hydrogen atoms, it is reasonable to regard these Au_6 derivatives as 'perauraethylenes.' Thus the six gold atoms in structure **II** may be classified into two types: (a) the four outer gold atoms not involved in the Au=Au double bond and corresponding to the hydrogen atoms of ethylene; (b) the two inner gold atoms which form the Au=Au double bond and which therefore, correspond to the carbon atoms of ethylene. However, the possibility of $d\sigma \rightarrow p\sigma^*$ and/or $d\pi \rightarrow p\pi^*$ bonding with gold atoms but not with carbon and/or hydrogen atoms leads to significant differences in the Au_6 geometry of perauraethylenes and the C_2H_4 geometry of ethylene itself.

In order to do the electron bookkeeping in this perauraethylene structure the 11 edges of the pair of edge-fused tetrahedra must be classified into the following three types:

(1) The single edge between the inner gold atoms which is common to both tetrahedra. This corresponds to the Au=Au double bond. The length of this edge in $[(C_6H_5)_3P]_4Au_6[Co(CO)_4]_2$ is relatively short (2.66 Å) [17] in accord with the idea of a double bond.

(2) The four solid edges in structure **II** which correspond to a σ bond between an outer gold atom and an inner gold atom. Each outer gold atom forms one of these bonds and each inner gold atom forms two of these bonds. These bonds correspond to the C–H bonds in ethylene. In $[(C_6H_5)_3P]_4Au_6[Co(CO)_4]_2$ these edges are relatively long (2.77–2.81 Å) [17] in accord with single bond character.

(3) The six dotted edges in structure **II** which correspond to $d\sigma \rightarrow p\sigma^*$ and/or $d\pi \rightarrow p\pi^*$ bonds between gold atoms. Analogous bonds are not possible in ethylene because of the lack of d orbitals leading, as noted above, to major differences in the Au_6 geometry from the C_2H_4 geometry of ethylene. The topology of these six dotted edges is that of a hexagon. Furthermore, when an inner gold atom is involved in this $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding, the inner gold atom is the one using the p orbitals. Since each inner gold atom forms two such bonds, the inner gold atoms effectively have the 18-electron rare gas electronic configuration corresponding to spherical sp^3d^5 manifolds of bonding orbitals. Also the bonds in $[(C_6H_5)_3P]_4Au_6[Co(CO)_4]_2$ corresponding to the dotted edges in structure **II** have variable lengths owing to different amounts of $d\sigma \rightarrow p\sigma^*$ and/or $d\pi \rightarrow p\pi^*$ bonding [17]. The four dotted edges from an outer to an inner gold atom have single bond length (2.77–2.81 Å) whereas the two dotted edges connecting a pair of outer gold atoms are much shorter (2.62 Å) suggesting an unusual double bond ($Au \rightleftarrows Au$) formed by a pair of $d\pi \rightarrow p\pi^*$ bonds in opposite directions.

The four σ-bonds between the outer gold atoms and the inner gold atoms (solid edges in structure **II**) use d orbitals of the inner gold atoms as described above. Alternatively they may be regarded as effectively adding d orbitals to the linear sp hybrid. This makes all four skeletal electrons of the $L_6Au_6{}^{2+}$ or $L_4Au_6X_2$ system available for the Au=Au bond between the inner gold atoms.

4. Centered Gold Clusters

An important class of gold clusters containing n gold atoms consists of a single central gold atom surrounded by $n-1$ peripheral gold atoms [2, 3]. The peripheral gold atoms all have a cylindrical spd^5 manifold of bonding orbitals and can be divided into the following two types:

(1) Belt gold atoms which form a puckered hexagonal or octagonal belt around the center gold atom.

(2) Distal gold atoms which appear above or below the belt gold atoms. The topology of the centered gold clusters can be considered to be either spherical or toroidal depending on whether the center gold atom uses a spherical sp^3d^5 manifold or a toroidal sp^2d^5 manifold of bonding orbitals.

A recent note by Mingos and co-workers [5] appears to be the first to point out the fundamental distinction between spherical and toroidal gold clusters. Also centered gold clusters, especially those of spherical topology, can be regarded as 'porcupine compounds' since the central gold atom corresponds to the body of the porcupine and the peripheral gold atoms (with cylindrical geometry as noted above) correspond to the quills [18].

The following features of centered gold clusters make their systematics very different from that of other metal cluster compounds such as those discussed in previous papers of this series [6–8]:

(1) The volume enclosed by the peripheral gold atoms must be large enough to contain the center gold atom. Thus the volume of a cube of eight peripheral gold atoms is not large enough to contain a ninth central gold atom without some distortion. Therefore centered cube gold clusters of the stoichiometry $Au_9L_8^+$ such as $Au_9(PPh_3)_8^+$ (ref. 19) are distorted from the ideal O_h symmetry to lower symmetry such as D_3. However, the volume of an icosahedron of 12 peripheral gold atoms is large enough to contain a thirteenth central gold atom without any distortion. The peripheral gold polyhedron of a spherical centered gold cluster containing fewer than 13 total gold atoms is generally based on an undistorted icosahedral fragment which has a large enough volume for the center gold atom.

(2) The overlap topology of $n-1$ unique internal orbitals of the peripheral gold atoms at the core of a centered Au_n cluster is not that of a K_{n-1} complete graph as in other globally delocalized metal clusters [6–8]. Instead the overlap topology of the unique internal orbitals of the peripheral gold atoms corresponds to the polyhedron formed by the peripheral gold atoms. This presumably relates to the sharper focus of the cylindrical 7-orbital spd^5 manifold of the peripheral gold atoms relative to that of the spherical 4-orbital sp^3 and 9-orbital sp^3d^5 manifolds of the vertex atoms in the clusters discussed in the earlier papers [6–8]. Thus the number of positive eigenvalues of the graphs corresponding to the peripheral gold polyhedra relates to the number of bonding orbitals in the centered gold cluster.

(3) The center gold atom has 11 valence electrons. All but one of these electrons are needed to fill its five d orbitals. The remaining electron is in its spherically symmetric s orbital which is the orbital of the center gold atom overlapping with the unique internal orbitals of the cylindrical spd^5 manifold of the peripheral gold atoms. This overlap lowers the energy of the lowest (fully symmetric) cluster bonding orbital without adding any new bonding orbitals. The center gold atom is thus a donor of one skeletal electron.

(4) Mingos and co-workers [5] have observed a $12p+16$ electron rule for toroidal centered gold clusters and a $12p+18$ electron rule for spherical centered gold clusters where $p=n-1$ is the number of peripheral gold atoms. These numbers count not only the skeletal electrons but the 10 electrons needed to fill the five d orbitals of each peripheral gold atom and the 2 electrons needed for one bond from each peripheral gold atom to an external L or X group. The $12p$ terms in Mingos' total electron numbers thus correspond to non-skeletal electrons involving only the peripheral gold atoms leaving 16 or 18 electrons for a center gold atom with toroidal or spherical geometry, respectively. This corresponds exactly to the number of electrons required to fill the 8-orbital toroidal sp^2d^5 manifold of the 9-orbital spherical sp^3d^5 manifold, respectively. This thus indicates that the recent ideas of Mingos and co-workers [5] are fully consistent with the ideas in this paper. Subtracting 10 from the 16 or 18 electrons allocated to the center gold atom for the five d orbitals of the center gold atom leaves 6 or 8 skeletal electrons for toroidal or spherical gold clusters, respectively.

(5) Consider L to be a 2-electron donor ligand (*i.e.*, tertiary phosphines or isocyanides) and X to be a 1-electron donor ligand (*i.e.*, halogen, pseudohalogen, $Co(CO)_4$, etc.). Then the above considerations give centered toroidal clusters the general formula $Au_nL_yX_{n-1-y}^{(y-5)+}$ and centered spherical clusters the general formula $Au_nL_yX_{n-1-y}^{(y-7)+}$.

Table I summarizes the following properties of centered gold clusters and related systems:

(1) The symmetry point group of the cluster ignoring any asymmetry in the external ligands.

(2) The numbers of gold atoms of various types. A centered gold cluster necessarily has one center gold atom but the uncentered pentagonal bipyramidal cluster [20] $[(C_6H_5)_3P]_7Au_7^+$ is also listed in Table I for comparison purposes. The positions of the distal gold atoms are specified where $x_1(C_3)$ means a distal atom on a C_3 axis, $2x_1(C_3)$ means a distal atom above and below the belt on a C_3 axis, $x_1(123)$

TABLE I. Shapes of gold clusters with polygonal belts

Cluster	Reference	Cluster symmetry[a]	Number of gold atoms			Eigenvalue signs[b]			Symmetry factoring
			Center	Belt	Distal	+	0	–	
(a) Pentagonal belt									
$Au_7(PPh_3)_7{}^+$	20	D_{5h}	0	5	$2x_1(C_5)$	3	0	4	$2^3 1$
(b) Hexagonal belt: Toroidal									
$Au_7L_6{}^+$	unknown	D_{3d}	1	6	0	3	0	3	1^6
$Au_8(PPh_3)_7{}^{2+}$	24	C_s	1	6	$x_1(123)$	3	0	4	31^4
$Au_9(PPh_3)_8{}^{3+}$	25	D_{2h}	1	6	$2x_1(123,456)$	3	0	5	21^6
$Au_9(SCN)_3(PCx_3)_5$[c]	26	C_{2v}	1	6	$2x_1(123,345)$	3	0	5	$2^2 1^4$
$Au_{10}Cl_3(PCx_2Ph)_6{}^+$[c]	5	C_{3v}	1	6	$3x_1(123,345,561)$	3	2^-	4	21^7
(c) Hexagonal belt: Spherical									
$Au_8(PPh_3)_8{}^{2+}$	27	C_{3v}	1	6	$x_1(C_3)$	3	1	3	21^5
$Au_9(PPh_3)_8{}^+$	19	O_h[d]	1	6	$2x_1(C_3)$	4	0	4	1^8
$Au_{11}I_3(PPh_3)_7$	28	C_{3v}	1	6	$x_3x_1(C_3)$	4	0	8	$42^2 1^2$
$Au_{13}Cl_2(PMe_2Ph)_{10}{}^{3+}$	29	I_h	1	6	$2x_3(C_3)$	4	0	8	$2^3 1^6$
(d) octagonal belt: Toroidal									
$Au_9[P(C_6H_4OMe\text{-}p)_3]_8{}^{3+}$	30	D_{4d}	1	8	0	3	2^-	3	$2^2 1^4$

[a] The designation of cluster symmetry considers only the gold atoms. Symmetry reductions arising from non-equivalence of external groups are ignored. [b] These columns refer to the numbers of positive (+), zero (0), and negative (–) eigenvalues of the characteristic polynomial of the graph formed by the peripheral gold atoms. The designation 2^- in the 0 column means two zero eigenvalues which become negative when certain non-nearest neighbor gold–gold interactions are considered (see text). [c] Cx = cyclohexyl. [d] The known example of this cluster type, $Au_9(PPh_3)_8{}^+$, is distorted from the ideal O_h symmetry of the regular cube to D_3 symmetry.

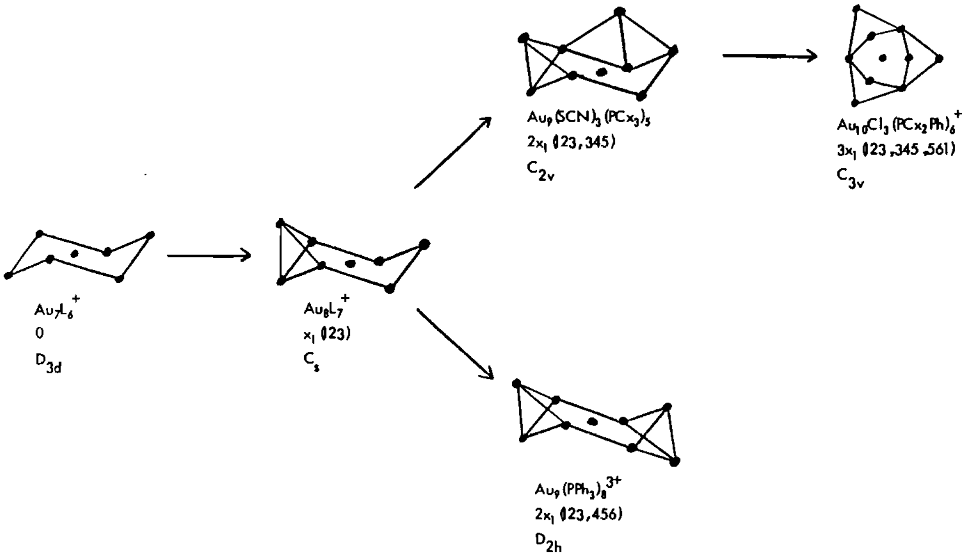


Fig. 1. Shapes of the toroidal gold clusters with hexagonal belts listed in Table I. The gold atoms are represented by heavy dots. Under each structure are listed the molecular or ionic formula, the designations of the locations of the distal peripheral gold atoms, and the idealized symmetry point group of the gold cluster.

means a distal atom connected to belt atoms 1, 2, and 3, x_3 means a set of 3 distal atoms above or below the belt atoms so situated as not to destroy the rotational symmetry, etc. Figures 1 and 2 which are closely related to an important figure in the Mingos *et al.* paper [5], clarify this notation for distal atom positions.

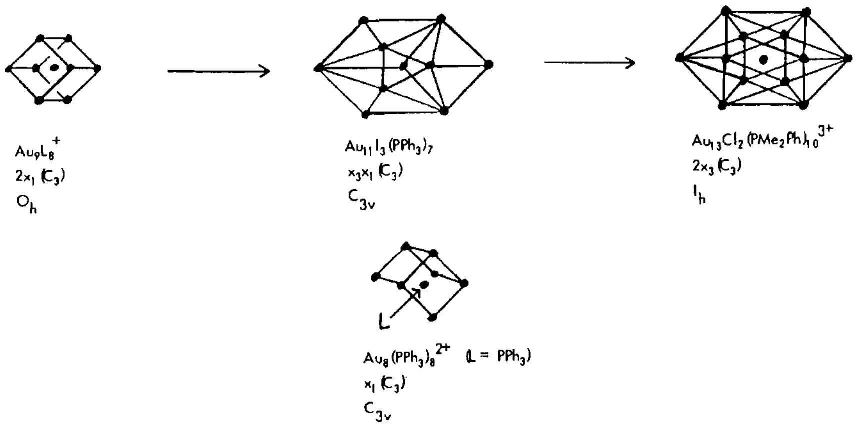


Fig. 2. Shapes of the spherical gold clusters with hexagonal belts listed in Table I. The indications below the structures are analogous to those in Fig. 1.

(3) The numbers of positive, zero, and negative eigenvalues in the spectrum of the graph corresponding to the polyhedron formed by the peripheral gold atoms. These graph spectra were determined at least to the level of eigenvalue signs using a symmetry factoring method [21] discussed in an earlier paper. An indication of the extent of possible symmetry factoring is also given in Table I in the form $3^c2^b1^a$ where c is the number of cubic factors, b is the number of quadratic factors, and a is the number of linear factors and entries with zero exponents of this type are suppressed.

All the toroidal gold clusters in Table I conform to the $Au_nL_yX_{n-1-y}^{(y-5)+}$ formula mentioned above. Thus the clusters $Au_7L_6^+$, $Au_8(PPh_3)_7^{2+}$, $Au_9(PPh_3)_8^{3+}$, $Au_9(SCN)_3(PCx_3)_5$, $Au_9[P(C_6H_4OMe\text{-}p)_3]_8^{3+}$, and $Au_{10}Cl_3(PCx_2Ph)_6^+$ correspond to this formula with $n = 7$, $y = 6$; $n = 8$, $y = 7$; $n = 9$, $y = 8$; $n = 9, y = 5$; $n = 9, y = 8$; and $n = 10, y = 6$, respectively. Note that three different configurations of the eight peripheral gold atoms are present in the three toroidal clusters $Au_9(PPh_3)_8^{3+}$, $Au_9(SCN)_3(PCx_3)_5$, and $Au_9[P(C_6H_4OMe\text{-}p)_3]_8^{3+}$. The cluster $Au_9[P(C_6H_4OMe\text{-}p)_3]_8^{3+}$ has a puckered octagonal belt of gold atoms whereas the clusters $Au_9(PPh_3)_8^{3+}$ and $Au_9(SCN)_3(PCx_3)_5$ have puckered hexagonal belts of gold atoms. The D_{2h} hexagonal belt cluster $Au_9(PPh_3)_8^{3+}$ and the C_{2v} hexagonal belt cluster $Au_9(SCN)_3(PCx_3)_5$ differ in the placement of the two distal gold atoms relative to the hexagonal belt as depicted in Fig. 1.

Note that the spectra of the graphs representing interactions of the peripheral gold atoms in all of the toroidal clusters have three positive eigenvalues in accord with the presence of three skeletal bonding orbitals corresponding to six skeletal electrons. Adding these six skeletal electrons to the 10 electrons required to fill the five d orbitals of the center gold atom gives the 16 electrons required to fill the 8-orbital toroidal sp^2d^5 manifold of the bonding orbitals of the center gold atom. In this connection the simple symmetry factoring procedure [21] finds two zero eigenvalues for the peripheral gold atom graphs of the toroidal clusters $Au_9[P(C_6H_4OMe\text{-}p)_3]_8^{3+}$ and $Au_{10}Cl_3(PCx_2Ph)_6^+$. Such zero eigenvalues correspond to non-bonding orbitals the electron occupancy of which does not affect the overall energy of the molecule. This ambiguity can be resolved by considering interactions of non-adjacent pairs of gold atoms joined to a common gold atom to be non zero but small compared with interactions of pairs of directly connected (*i.e.*, adjacent) gold atoms. In graph-theoretical terms [22] the interactions of pairs of vertices at distance 2 is considered to be non-zero but small compared with interactions of pairs of vertices at distance 1. Operationally the usual symmetry factoring procedure [21] is carried out with the interactions between adjacent vertices being given unit weight. When a zero eigenvalue is obtained, that particular branch of the symmetry factoring procedure is recalculated with added edges of weight δ where $0 < \delta \leqslant 1$ between pairs of vertices connected by a path two edges long. The eigenvalues which were zero when considering only 'nearest neighbor interactions now appear in the form $k\delta$ where the sign of k determines whether these eigenvalues are positive or negative thereby corresponding to bonding or antibonding orbitals, respectively. In this way the two zero eigenvalues in the peripheral gold atom graphs of $Au_{10}Cl_3(PCx_2Ph)_6^+$ and $Au_9[P(C_6H_4OMe\text{-}p)_3]_8^{3+}$ can be shown to become slightly negative when these additional interactions are considered. Thus these two clusters have three skeletal bonding orbitals like all of the other toroidal centered gold clusters.

The three spherical gold clusters $Au_{13}Cl_2(PMe_2Ph)_{10}^{3+}$, $Au_{11}I_3(PPh_3)_7$, and $Au_9(PPh_3)_8^+$ all conform to the $Au_nL_yX_{n-1-y}^{(y-7)+}$ formula noted above with $n = 13, y = 10$; $n = 11, y = 7$; and $n = 9, y = 8$, respectively. Their peripheral gold atom graphs all have four positive eigenvalues in accord with the presence of four skeletal bonding orbitals corresponding to eight skeletal electrons. Addition of these eight skeletal electrons to the 10 electrons required to fill the five d orbitals of the center gold atom gives the 18 electrons required to fill the 9-orbital spherical sp^3d^5 manifold of the bonding orbitals of the center gold atom. The peripheral 10-vertex gold polyhedron in $Au_{11}I_3(PPh_3)_7$ can be formed from the peripheral gold icosahedron in $Au_{13}Cl_2(PMe_2Ph)_{10}^{3+}$ by the following two-step process:

(1) Removal of a triangular face including its three vertices, its three edges, and the nine edges connecting this face with the remainder of the icosahedron.

(2) Addition of a new vertex in the location of the midpoint of the face that was removed followed by addition of three new edges to connect this new vertex to the degree 3 vertices of the 9-vertex icosahedral fragment produced in the first step.

These processes preserve a C_3 axis of the icosahedron. Also application of this two-step process twice to an icosahedron so as to preserve a C_3 axis throughout the whole sequence of steps leads to a cube such as that found in $Au_9(PPh_3)_8^+$ (ref. 19). In this sense the peripheral gold polyhedron of $Au_{11}I_3(PPh_3)_7$ can be considered to be halfway between an icosahedron and a cube.

The two clusters in Table I which do not conform to the $Au_nL_yX_{n-1-y}^{(y-5)+}$ rule for toroidal clusters or to the $Au_nL_yX_{n-1-y}^{(y-7)+}$ rule for spherical clusters are two clusters of the type $Au_n(PPh_3)_n^{(n-6)+}$ where $n = 7$ for $Au_7(PPh_3)_7^+$ and $n = 8$ for $Au_8(PPh_3)_8^{2+}$. The cluster $Au_8(PPh_3)_8^{2+}$ may be regarded as $(Ph_3PAu)_7AuPPh_3^{2+}$ in which the center gold atom is bonded to one triphenylphosphine ligand and the remaining seven gold atoms. The C_{3v} geometry of the seven peripheral gold atoms (see Fig. 2) derives from that of the $Au_{11}I_3(PPh_3)_7$ cluster by loss of the three gold atoms forming the triangular face through which the C_3 axis passes. In a sense these three gold atoms in $Au_{11}I_3(PPh_3)_7$ are replaced with a triphenylphosphine ligand in forming $Au_8(PPh_3)_8^{2+}$. The bipartite graph of the seven peripheral gold atoms in $Au_8(PPh_3)_8^{2+}$ has three positive eigenvalues (A_1 + E), one zero eigenvalue (A_1), and three negative eigenvalues (A_1 + E) which in isolation correspond to three bonding orbitals, one non-bonding orbital, and three antibonding orbitals as listed in Table I. However, interaction of this Au_7 system with the A_1 bonding orbital of the eighth gold atom leads to a system with four bonding and four antibonding orbitals. The four bonding orbitals receive eight electrons as follows:

7 Ph_3PAu vertices (peripheral gold atoms)	7 electrons
Center gold atom	1 electron
Ph_3P ligand on center gold atom	2 electrons
+2 charge of ion	−2 electrons
Net total of skeletal electrons	8 electrons

The spherical sp^3d^5 bonding orbital manifold of the center gold atom receives the required 18 electrons as follows:

Neutral center gold atom	11 electrons
7 Ph_3PAu 'ligands' 7 × 1 =	7 electrons
Ph_3P bonded directed to the center gold atom	2 electrons
+2 charge of ion	−2 electrons
Net outer electronic configuration of center gold atom	18 electrons

In a sense the spherical gold cluster $Au_8(PPh_3)_8^{2+}$ or $(Ph_3PAu)_7AuPPh_3^{2+}$ is formed from the toroidal cluster $Au_8(PPh_3)_7^{2+}$ by coordination of a triphenylphosphine ligand. In this process the antibonding p orbital excluded from the 8-orbital sp^2d^5 toroidal manifold becomes bonding to form the 9-orbital sp^3d^5 spherical manifold. The extra two electrons required for the 9-orbital spherical manifold relative to the 8-orbital toroidal manifold comes from the eighth triphenylphosphine ligand. In a sense such an addition of two electrons to a toroidal gold cluster to give a spherical gold cluster is analogous to the addition of two electrons to a closed deltahedral 'closo' borane cluster to give a more open 'nido' polyhedral cluster having one non-triangular face [6–8]. However, the topologies of these two processes are totally different.

The other $Au_n(PPh_3)_n^{(n-6)+}$ cluster is the uncentered $Au_7(PPh_3)_7^+$ which has the shape of a pentagonal bipyramid which is squashed so that the two axial gold atoms on opposite sides of the belt of five equatorial gold atoms are pushed to within bonding distance [20]. An appropriate graph to use to represent the bonding topology of this system is the 1-skeleton [23] of a pentagonal bipyramid with an added edge connecting the two axial vertices. Symmetry factoring [21] of the characteristic polynomial of this graph with 7 vertices and 16 edges indicates three positive eigenvalues and four negative eigenvalues. This indicates that the $Au_7(PPh_3)_7^+$ skeleton has three bonding orbitals which can obtain the required six skeletal electrons from the following source:

7 Ph_3PAu vertices	7 electrons
+1 charge of ion	−1 electron
Net skeletal electrons	6 electrons

This uncentered gold cluster thus conforms to the same bonding model as that used for the centered gold clusters discussed above.

5. Summary

This paper shows that previously discussed topological bonding models [6–8] can be applied to gold clusters even though superficially their shapes and stoichiometries appear to be quite different from the clusters discussed earlier. The following special points arise when considering gold clusters:

(1) One or two of the three outer p orbitals of gold atoms are often not involved in the primary bonding apparently because of relativistic increase of p orbital energies [9]. The 14-electron 7-orbital spd^5 manifold with cylindrical geometry and the 16-electron 8-orbital sp^2d^5 manifold with toroidal geometry are particularly important in gold chemistry.

(2) The topology of the core bonding in gold clusters is generally not that of the K_n complete graph found in other clusters [6–8] but instead mimics the topology of the polyhedron formed by the surface or peripheral gold atoms. This apparently is a consequence of poor lateral overlap of the cylindrical spd^5 manifolds of the peripheral gold atoms.

(3) The high energy of the outer p orbitals not used in the spd^5 manifold of the peripheral gold atoms eliminates the possibility of surface bonding similar to that found in other clusters [6–8]. However, these empty p orbitals can receive electron density through $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ backbonding from filled d orbitals of adjacent peripheral gold atoms thereby placing adjacent peripheral gold atoms within bonding distances of each other.

(4) Centered gold clusters are frequently found. The volume of the polyhedron formed by the peripheral gold atoms must be large enough to contain the center gold atom. This excludes most of the polyhedra found in other types of metal clusters including deltahedra with ten or less vertices. However, the volume of an icosahedron is large enough to contain a center gold atom. Centered gold clusters having fewer than 12 peripheral gold atoms are generally based on icosahedral fragments for the polyhedra formed by the peripheral gold atoms. Alternatively, such centered gold clusters may be regarded as consisting of a center gold atom, a puckered hexagonal belt of six peripheral gold atoms, and the remaining gold atoms located in distal positions above and/or below the belt.

(5) Centered gold clusters may be classified into spherical or toroidal clusters depending upon whether the center gold atom has a 9-orbital sp^3d^5 spherical bonding orbital manifold or an 8-orbital sp^2d^5 toroidal bonding orbital manifold. Spherical gold clusters have 8 skeletal electrons and toroidal gold clusters have 6 skeletal electrons not counting the 10 electrons required to fill the five d orbitals of the center gold atom.

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