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Clusters of Clusters. 25. Synthesis and Structure of a New 38-Metal-Atom Cluster $[(Ph_3P)_{14}Au_{18}Ag_{20}Cl_{12}]Cl_2$ and its Implications with Regard to Intracavity Chemistry on Metal Cluster Surfaces

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Our recent work on high-nuclearity mixed-metal clusters[1] gave rise to a novel series of Au-Ag clusters whose metal frameworks are based on *vertex-sharing polyicosahedra* which may be referred to as "clusters of clusters".[2-25] These metal clusters followed a well-defined growth sequence[22] and specific stereochemical rules.[26,27] We report herein the structure of a new 38-metal-atom cluster, $[(Ph_3P)_{14}Au_{18}Ag_{20}Cl_{12}]^{2+}$ (**1**), as the chloride salt, that violates one of the six empirical structural rules.[26,27]

Parts a and b of Figure 1 depict the $[Au_{18}Ag_{20}]$ metal core and the $[P_{14}Au_{18}Ag_{20}Cl_{12}]$ framework of **1**.[30] The structure conforms to an idealized D_{3h} symmetry with a (noncrystallographic) 3-fold axis passing through P7–Ag10 and Ag10′–P7′. Perpendicular to this axis is the crystallographic 2-fold axis, passing through Au7 and Au10. The structure consists of three Au-centered icosahedra (Au_7Ag_6) sharing three Au vertices in a cyclic manner that are capped by two apical Ag atoms (Ag10 and Ag10′). The title cluster **1** violates one of the six empirical structural rules[26] in that two (P7, P7′) of the 14 phosphines are bonded to the two apical Ag (instead of Au) atoms (cf. Figure 1b).

It is interesting to compare the cationic (title) cluster $[(Ph_3P)_{14}Au_{18}Ag_{20}Cl_{12}]^{2+}$ (**1**) with the closely related neutral cluster $(p\text{-}tol_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**2**).[9,16] These two clusters have the same vertex-sharing triicosahedral metal mainframe ($s_3(36)$)[31] and similar structural parameters. However, the replacement of the two terminal chlorides (bonded to the capping Ag atoms) in **2** by two phosphines in **1** increases the overall charge by +2 and causes a change of ligand polyhedra from 12P:14Cl to 14P:12Cl. Furthermore, the 12 phosphine ligands in **2** leave two "cavities" along the idealized 3-fold axis, which allow the approaches of two additional phosphine ligands in **1**.

It occurs to us that the stereochemistries of clusters **1** and **2** may lead to the concept of "intracavity" chemistry on the "surface" of a metal cluster parallel to intrazeolitic chemistry,[32] host–guest chemistry,[33] and inclusion complexes.[34] The distinctive feature of the cluster surface cavities in **1** and **2** is their *flexible* nature. Figure 1c depicts the size and shape of the cavities in **1** and **2** (after removal of the $[Ph_3PAgCl_3]$ and $[AgCl_4]$ moieties, respectively). It can be seen that the accessible "metal surface" of these clusters is the Ag_3 triangle, "picket-fenced"[35] by three aryl groups (shaded) from three separate phosphine ligands. The hydrophobic cavities measure roughly 6 Å (in diameter) at the base and 13 Å at the opening. Also shown is the cavity on the

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(26) The six empirical structural rules[27] that have been observed for this series of polyicosahedral Au–Ag clusters are as follows: (1) the centers of the icosahedra are gold atoms; (2) the "shared" vertices are often gold atoms; (3) phosphine ligands prefer coordination with surface gold atoms; (4) silver atoms prefer surface sites, especially those at the boundary of neighboring icosahedra; (5) the capping atoms are most likely to be silver atoms; (6) halide ligands prefer coordination with silver atoms.

(27) These structural rules can be rationalized in terms of the disparities in metal–metal and metal–ligand interactions, as well as in electronegativity of the constituents. The latter is related to relativistic effects.[28,29] In terms of metal–metal interactions, which are related to the energy of atomization (334 for Au vs 251 for Ag, in kJ/mol), gold atoms tend to prefer interstitial sites such as the centers of icosahedra (rule 1) or the shared vertices (rule 2). As far as the metal–ligand bonding is concerned, the more electron-donating phosphine ligands prefer to coordinate to the more electronegative Au atoms (rule 3), whereas the more electron-withdrawing halide ligands prefer to interact with the more electropositive Ag atoms (Rule 6). In terms of electronegativity (2.54 for Au vs 1.93 for Ag), the more electronegative gold atoms prefer sites of high electron densities (such as the centers of icosahedra or the shared vertices) whereas the more electropositive silver atoms tend to occupy surface sites (at the boundary of adjacent icosahedra) bridged by halide ligands (rule 4) or capping positions with high halide coordination (rule 5).

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(30) Single-crystal X-ray diffraction data were collected using Enraf-Nonius CAD4 diffractometer (Mo Kα radiation) for $[(Ph_3P)_{14}Au_{18}Ag_{20}Cl_{12}]Cl_2 \cdot n EtOH$: monoclinic $C2/c$, $a = 30.049(12)$ Å, $b = 26.626(8)$ Å, $c = 37.807(19)$ Å, $\beta = 107.95(5)°$, $V = 28776.2$ Å^3, and $Z = 4$. The phenyl groups were refined as rigid bodies. Anisotropic (heavy atoms)–isotropic (carbon atoms) refinement gave $R_1 = 7.5\%$ for 6648 independent reflections ($2\theta \leq 44°$) with $I \geq 3\sigma$.

(31) As defined in refs 10 and 22, a supracluster with n vertex-sharing icosahedral units is represented by $s_n(N)$ where N is the nuclearity.

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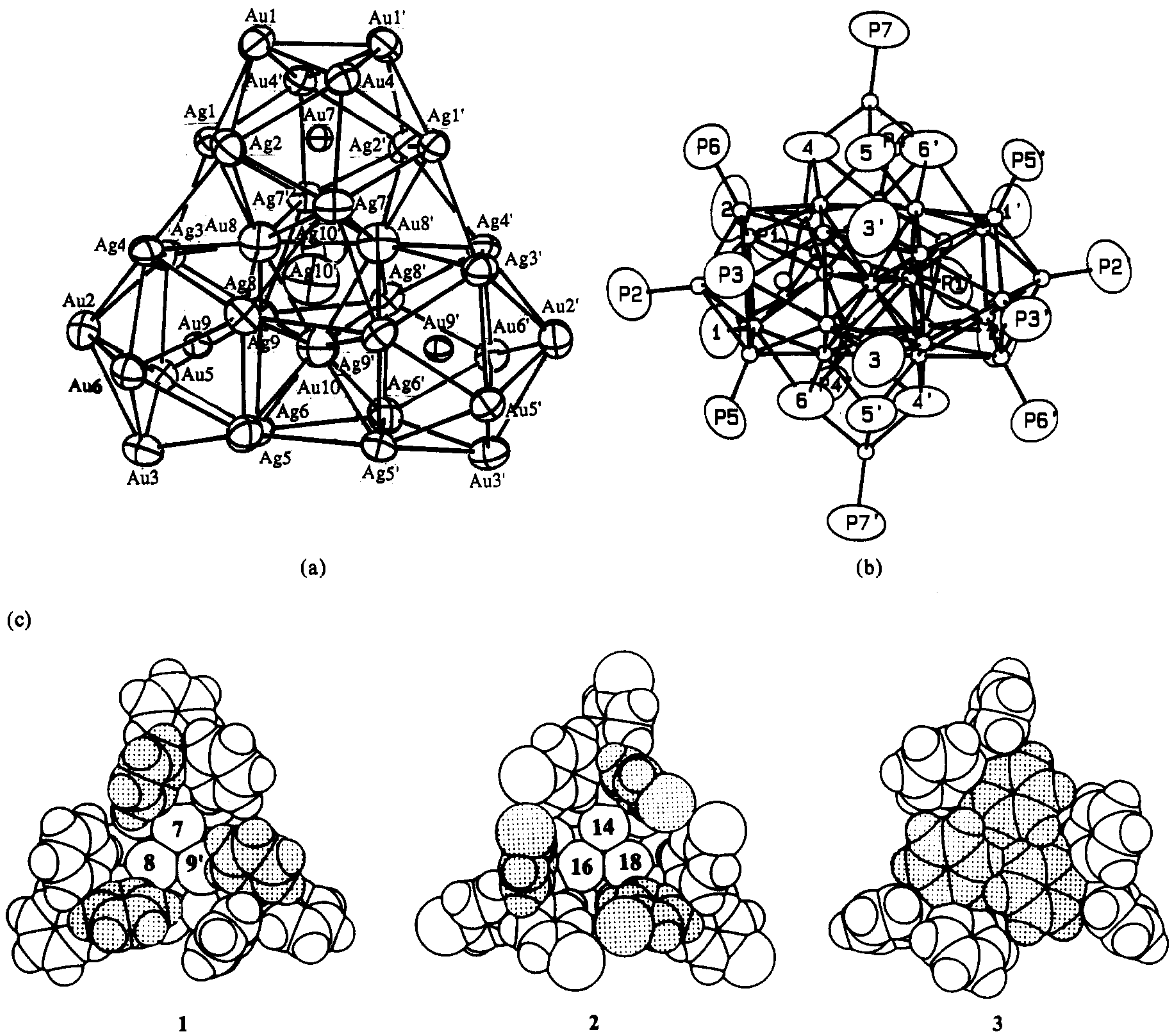

Figure 1. (a) Top view of the $[Au_{18}Ag_{20}]$ core (50% thermal ellipsoids) of cluster **1** depicting three Au-centered icosahedra sharing three Au vertices (Au8, Au8′, and Au10) in a cyclic manner that are capped by two apical Ag atoms (Ag10 and Ag10′). All radical bonds from the centers of the icosahedra (Au7, Au9, and Au9′) are omitted for clarity. (b) Side view (perpendicular to view a) of the $[P_{14}Au_{18}Ag_{20}Cl_{12}]$ framework of cluster **1**. The labeling of the chloride ligands is represented by the corresponding numbers. The 2-fold symmetry related atoms are designated by primes. The thermal ellipsoids are 100% for P and Cl atoms except the metal atoms which are represented by small circles for the sake of clarity. (c) Space-filling models of the cluster surface cavities in **1** (same view as in a), **2**, and **3**, after removal of the fragments $[Ph_3PAgCl_3]$, $[AgCl_4]$, and μ_3-Cl, respectively. In part c, the numbers 7, 8, 9′ and 14, 16, 18 designate the Ag_3 triangle at the bottom of the picket-fenced surface cavities in clusters **1** and **2**, respectively. See text for other details.

μ_3-Cl side of the 37-metal-atom cluster $[(Ph_3P)_{12}Au_{18}Ag_{19}Cl_{11}]^{2+}$ (**3**),[7,36] which is completely sealed off by three phenyl rings (shaded). (Note that **3** is related to **2** in that one of the two $[AgCl_4]^{3-}$ units is replaced by a $[\mu_3\text{-Cl}]^-$ ligand.) Specifically, the three *p*-tolyl rings (shaded) in **2** are oriented nearly parallel to the idealized 3-fold axis, making it a triangular-cylinder-shaped cavity. In **1**, these phenyl rings (shaded) are twisted and tilted away, causing an enlargement of the opening of the cavity, thereby allowing the coordination of the Ph_3P to the capping Ag atom(s). It is apparent that this "breeding" mode will allow approaches of a variety of small molecules or ions. The interactions (and the driving force) may range from strong covalent or ionic bonding to weak van der Waals or hydrogen bonding. In addition to $[Ph_3PAgX_3]$ (as in **1**), $[AgX_4]$ (as in **2**), or μ_3-X (as in **3**)[7,36] moieties (X = halides), other functional groups or solvent molecules can also be incorporated in the cavities (via coordination to the capping Ag atoms).[36] The ability of the cavities in **1** and **2** to expand and contract is to a large extent due to the fact that the shared vertices resemble *flexible connectors*, which allow individual icosahedral units to twist around, thereby causing conformational changes of the phosphine ligands.

The existence of the *accessible*, "picket-fenced" metal surfaces as well as the *flexible* (structurally nonrigid) cavities on the surface of a large metal cluster—both of which can easily be tailored to incorporate a variety of guest molecules—may have further implications in the studies of inclusion complexes,[32-34] metal surfaces,[37] and catalysis.[38]

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Supplementary Material Available: Full listings of complete structural data (Table A), positional parameters (Table B), interatomic distances (Table C), interatomic angles (Table D), and anisotropic thermal parameters (Table E), and text giving preparation and crystallization procedures for the title compound (20 pages). Ordering information is given on any current masthead page.

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