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Supplementary Material Available: For complex $(Bu^n_4N)(2)$, tables of crystallographic data, complete atomic coordinates and anisotropic and isotropic thermal parameters, bond lengths, and bond angles (4 pages); a table of structure factors (9 pages). Ordering information is given on any current masthead page.

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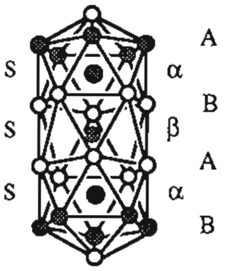
Cluster of Clusters. Structure of a New 25-Metal-Atom Cluster $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Cl_7](SbF_6)_2$ Containing a Nearly Staggered–Eclipsed–Staggered Metal Configuration and Five Doubly Bridging Ligands

Clusters of increasing nuclearity can often be obtained by fusing together smaller cluster units.[1-11] Recently we reported the synthesis and structural characterization of a 25-metal-atom cluster $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ (**1**),[6a] which can be described as two centered icosahedra sharing a common vertex. The metal framework is characterized by the staggered–staggered–staggered (sss) configuration of the four metal pentagons, giving rise to an idealized symmetry of D_{5d} for the metal core. We now wish to report the structure of a novel 25-metal-atom cluster $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Cl_7]^{2+}$ (**2**), which has a nearly staggered–eclipsed–staggered (ses) metal configuration with an idealized symmetry of D_5 for the metal core.



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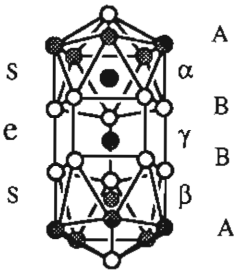

2

The title compound **2** was isolated as the SbF_6^- salt from the reduction of a mixture of $p\text{-}Tol_3P$, $HAuCl_4$, and $AgSbF_6$ with $NaBH_4$ in ethanol.[12] Other structurally characterized clusters of this series include the 37-metal-atom cluster $[(p\text{-}Tol_3P)_{12}Au_{18}Ag_{19}Br_{11}]^{2+}$ (**3**),[7] the 38-metal-atom cluster $[(p\text{-}Tol_3P)_{12}Au_{18}Ag_{20}Cl_{14}]$ (**4**),[8] and the 46-metal-atom cluster $[(Ph_3P)_{12}Au_{22}Ag_{24}Cl_{12}]$ (**5**).[9]

The title cluster **2** conforms to the crystallographic site symmetry C_2-2. Figure 1a depicts the metal core which can be described as two 13-atom-Au-centered icosahedra sharing a vertex (Au13). As shown in Figure 1b, there are 10 phosphine ligands, coordinated to the 10 peripheral Au atoms. Five doubly bridging chloride ligands connect the two Ag_5 pentagons and two terminal chloride ligands (Cl11 and Cl11′) coordinate to the two apical Ag atoms (Ag11 and Ag11′).

Several novel features of the structure of **2** are noteworthy. First, the most significant structural characteristic of **2** is the observed (nearly) staggered–eclipsed–staggered (ses) configuration for the metal core[13] (cf. Figure 1a,c), which is to be contrasted with the staggered–staggered–staggered (sss) metal configuration of **1**.[6a] Second, there are *five* bridging chloride ligands in **2** instead of *six* as in **1**. As shown in Figure 1c, all five bridging chloride ligands are symmetrical with an average Ag–Cl distance of 2.44 Å. Third, cluster **2** is a *dication* instead of a *monocation* (as in **1**). The last two observations are related in that removal of one halide ligand in **1** causes the increase of the overall charge of the cluster from +1 to +2 (as in **2**). As a result, the number of electrons remains the same (25 (metals) − 7 (Cl) − 2 (charges) = 16).

The intraicosahedral metal–metal distances (Au11-centered icosahedra) are significantly shorter than intericosahedral distances (Au13-centered bicapped pentagonal prism), suggesting that intraicosahedral bondings are substantially stronger than intericosahedral bonding (cf. Figure 1 caption). This observation is consistent with the *cluster of clusters* concept[10,11] wherein the individual icosahedra serve as the basic building blocks.

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(12) The cluster $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Cl_7](SbF_6)_2\cdot n\text{EtOH}$ forms dark red prismatic crystals. It crystallizes in the tetragonal space group $P4_32_12$, with $a = 20.510$ (6) Å, $c = 61.78$ (1) Å, $V = 25988.1$ Å^3, and $Z = 4$. Single-crystal X-ray diffraction data were collected by using an Enraf-Nonius diffractometer (Mo Kα radiation). The tolyl groups and the SbF_6^- anion were refined as rigid bodies with C(methyl)–C(ring), C(ring)–C(ring), and Sb–F distances of 1.47, 1.395, and 1.86 Å, respectively (see ref 8a for details). Anisotropic refinement gave $R_1 = 9.6\%$ for 5811 independent reflections ($2\theta \leq 46°$) with $I > 3\sigma$. Crystallographic (Tables I–VI and VIII) and preparative (Table VII) details can be found in the supplementary material.

(13) One can envision the successive buildup of a one-dimensional structure of nuclearities 1, 7, 13, 19, 25, 31, 37, ... by adding one atom and one pentagon at a time. The infinite chain analogue is observed in the solid-state compounds Ta_2S (Franzen, H. F.; Smeggil, J. G. *Acta Crystallogr.* **1969**, *B25*, 1736) and Ta_6S (Franzen, H. F.; Smeggil, J. G. *Acta Crystallogr.* **1970**, *B26*, 125). The structural relationship of the high nuclearity clusters and the solid-state compounds therefore provides a link between clusters and the bulk.[11c]

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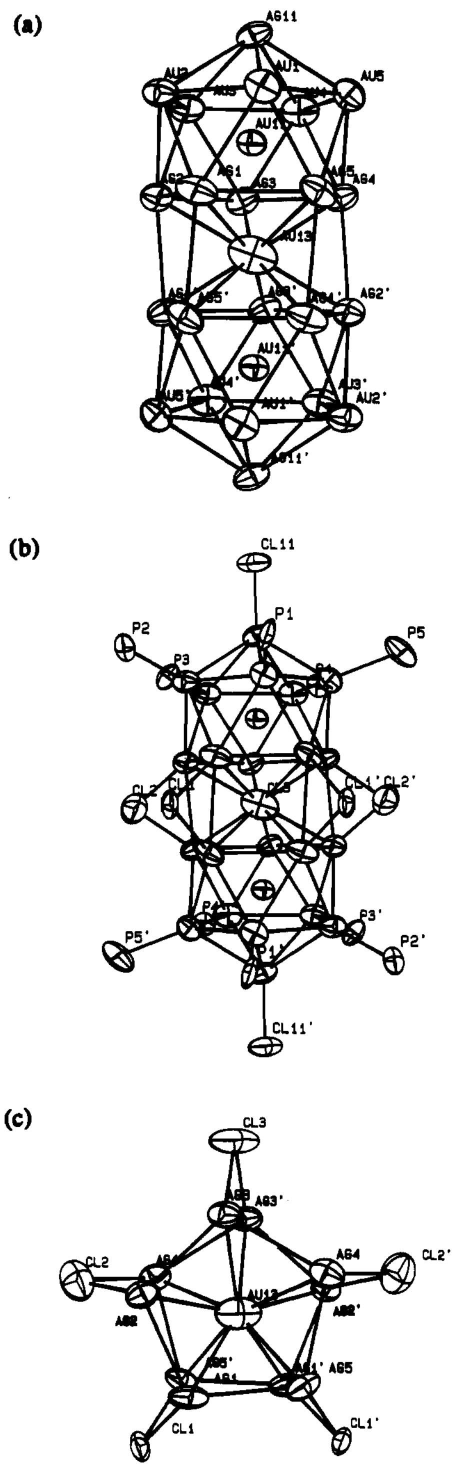

Figure 1. Molecular architecture of the 25-metal-atom cluster $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Cl_7]^{2+}$ (**2**) as the $(SbF_6)^-$ salt: (a) the metal core, $Au_{13}Ag_{12}$; (b) the metal-ligand framework, $P_{10}Au_{13}Ag_{12}Cl_7$; (c) projection of the two silver pentagons and the five doubly bridging chloride ligands along the idealized 5-fold axis (which passes through Ag11, Au11, Au13, Au11′, and Ag11′). Atoms related by the crystallographic 2-fold (C_2-2) symmetry are designated as primes. All radial bonds (12 each) from Au11 and Au11′ have been omitted for clarity. All molecular parameters are normal. The importance distances are as follows (n = 1-5): Au11-Au(n) = 2.749 (av) Å, Au11-Ag(n) = 2.816 (av) Å, Au11-Ag11 = 2.743 (9) Å, Au11-Au13 = 2.813 (5) Å, Au13-Ag(n) = 2.881 (av) Å; intrapentagonal, Au(n)-Au(n + 1) = 2.914 (av) Å, Ag(n)-Ag(n + 1) = 2.912 (av) Å; interpentagonal, Au(n)-Ag(n or n − 1) = 2.885 (av) Å, Ag1-Ag5′ = 3.04 (1) Å, Ag2-Ag4′ = 2.94 (1) Å, Ag3-Ag3′ = 2.92 (1) Å, Au-P = 2.35 (av) Å, Ag11-Cl11 = 2.43(3) Å, Ag(n)-Cl(n) = 2.44 (av) Å. The five doubly bridging chloride ligands form a distorted pentagon with nonbonding (crystallographically independent) distances of Cl1···Cl1′ = 5.34 Å, Cl1···Cl2 = 4.69 Å, and Cl2···Cl3 = 5.53 Å.

The relative orientation of the four metal pentagons can be described as ABAB (sss) for **1** and ABBA (ses) for **2**, respectively. The corresponding orientation of the *two* icosahedra may be described as $\alpha(\beta)\alpha$ and $\alpha(\gamma)\beta$, respectively. The former has an "additional" icosahedron (whose orientation is in parentheses) in the middle due to the staggered arrangement of the two middle rings in the sss configuration. The latter produces a bicapped pentagonal prism whose orientation is designated as γ (in parentheses). The *propagation* of icosahedra via vertex, edge, or face sharing through space is critically dependent upon the relative orientation of the icosahedral units (the building blocks) and is of current interest in terms of the structures of quasicrystals[14] and amorphous materials.[15]

Finally, we note that the ses metal configuration (as observed for **2**) allows stereochemically a "polyicosahedral" growth pathway via vertex sharing to give bi-, tri-, and tetraicosahedral supraclusters as exemplified by the structurally characterized 25- (**2**), 37- (**3**)[7] or 38- (**4**),[8] and 46- (**5**)[9] metal-atom Au-Ag clusters, respectively. In all these structures, the icosahedral units are linked by (interpenetrating) bicapped pentagonal prisms (γ), instead of the (interpenetrating) icosahedra (β) as observed in the 25-metal-atom cluster **1**[6a] with an sss metal configuration.

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Supplementary Material Available: Full listings of complete structural data (Table I), positional parameters (Table II), anisotropic thermal parameters (Table III), positional and orientational parameters of 15 tolyl groups (Table IV), interatomic distances (Table V), interatomic angles (Table VI), and details of the preparation and crystallization (Table VII) for the title compound (20 pages); a listing of observed and calculated structure factors (Table VIII) (61 pages). Ordering information is given on any current masthead page.

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Short Spin-Lattice Relaxation Times of Hydride Ligands. Proton-Metal Dipole-Dipole Interactions

T_1 measurements have recently been used for obtaining structural information about metal hydride complexes.[1-3] Crabtree and Luo[4] have recently tested the basis of the T_1 method, assuming that only proton-proton dipole-dipole interactions (HHDDI) dominates the relaxation. They have found that, for a series of mononuclear polyhydrides for which both structural and relaxation data are available, there was good agreement between the calculated and observed $T_{1\,\min}$ values.

This agreement is rather surprising in the case of rhenium hydrides, where significant metal-H dipole-dipole interactions (MHDDI) can be expected. Indeed, with r_{Re-H} = 1.7 Å and τ_c = $0.62/2\pi\nu^5$ at 250 MHz, the well-known[6] eq 1 (where C =

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