

Design, Synthesis, and Structure of the Largest Trimetallic Cluster, [(Ph₃P)₁₀Au₁₂Ag₁₂PtCl₇]Cl: The First Example of a Trimetallic Biicosahedral Supracluster and Its Implication for the Vertex-Sharing Polyicosahedral Growth of the Au/Ag/Pt Ternary Cluster System

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Mixed-metal clusters^{1,2} often exhibit unusual structures and properties and cooperative (synergistic) effects which are important in the development of such critical technologies as catalysis³ and nanoelectronics.⁴ We report herein the synthesis and structure of the largest trimetallic (Au/Ag/Pt) cluster known to date.

Our recent work on bimetallic Au–Ag clusters has yielded a novel series of clusters whose metal frameworks are based on *vertex-sharing polyicosahedra*.^{5–10} We refer to these high-nuclearity mixed-metal clusters as “clusters of clusters”. This cluster of clusters series follows well-defined design rules, giving rise to a novel *growth sequence* by successive additions of icosahedral units via vertex-sharing, as exemplified by the biicosahedral⁸ [(*p*-tol₃P)₁₀Au₁₃Ag₁₂Br₈]⁺,^{8b} the triicosahedral⁹ [(*p*-tol₃P)₁₂Au₁₈Ag₂₀Cl₁₄]^{9a} and the tetraicosahedral¹⁰ [(Ph₃P)₁₂Au₂₂Ag₂₄Cl₁₀] clusters. The biicosahedral 25-metal-atom cluster (mac) series⁸ of general formulas [(R₃P)₁₀Au₁₃Ag₁₂X₈]⁺ and [(R₃P)₁₀Au₁₃Ag₁₂X₇]²⁺ (where R = phenyl or tolyl; X = Cl or Br) is particularly interesting in that these compounds exhibit various metal configurations and bridging ligand arrangements due to relative rotations of the two metal icosahedra (about the shared vertex) and the satellite ring of bridging ligands, respectively (represented by large circles and an ellipse, respectively, in Chart I, top figures). For example, the monocationic cluster [(Ph₃P)₁₀Au₁₃Ag₁₂Br₈]⁺ (1b), with a staggered-eclipsed-staggered (*ses*) arrangement of four adjacent metal pentagons, has a ring of six bromides bridging the two middle silver pentagons, while the dicationic clusters [(*p*-tol₃P)₁₀Au₁₃Ag₁₂Cl₇]²⁺ (2), with a nearly *ses* metal configuration, has five bridging halides.

(1) For reviews, see, for example: Shriver, D. F.; Kaesz, H. D.; Adams, R. D. Eds., *The Chemistry of Metal Cluster Complexes*; VCH Publishers: New York, 1990.

(2) See, for example: (a) Ceriotti, A.; Demartin, F.; Longoni, G.; Manassero, M.; Marchionna, M.; Piva, G.; Sansoni, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 697. (b) Woolery, A. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 6683.

(3) (a) Sachtler, W. M. H.; van Santen, R. A. *Adv. Catal.* **1977**, *26*, 69. (b) Sinfelt, J. H. *Bimetallic Catalysts: Discoveries, Concepts, and Applications*; J. Wiley & Sons: New York, 1983; and references cited therein.

(4) Stucky, G. D.; Herron, N.; Wang, Y.; Eddy, M.; Cox, D.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 530.

(5) Teo, B. K.; Zhang, H. *Proc. Natl. Acad. Sci. U.S.A.* **1991**, *88*, 5067.

(6) (a) Teo, B. K.; Zhang, H. *J. Cluster Sci.* **1990**, *1*, 223. (b) Teo, B. K.; Zhang, H. *J. Cluster Sci.* **1990**, *1*, 155. (c) Teo, B. K.; Zhang, H. *Polyhedron* **1990**, *9*, 1985. (d) Teo, B. K. *Polyhedron* **1988**, *7*, 2317.

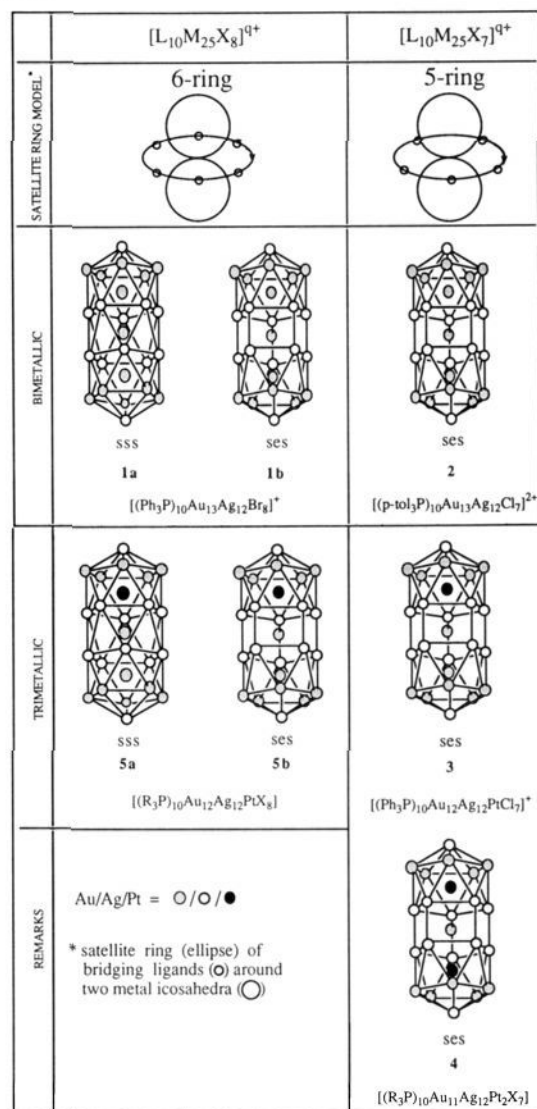
(7) (a) Teo, B. K.; Zhang, H. *Inorg. Chem.* **1988**, *27*, 414. (b) Teo, B. K.; Zhang, H. *Inorg. Chim. Acta* **1988**, *144*, 173.

(8) (a) Teo, B. K.; Keating, K. *J. Am. Chem. Soc.* **1984**, *106*, 2224. (b) Teo, B. K.; Zhang, H.; Shi, X. *Inorg. Chem.* **1990**, *29*, 2083. (c) Teo, B. K.; Shi, X.; Zhang, H. *J. Am. Chem. Soc.* **1991**, *113*, 4329. (d) Teo, B. K.; Zhang, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 445. (e) Teo, B. K.; Zhang, H. *Inorg. Chem.* **1991**, *30*, 3115.

(9) (a) Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1990**, *112*, 8552. (b) Teo, B. K.; Hong, M.; Zhang, H.; Huang, D.; Shi, X. *J. Chem. Soc., Chem. Commun.* **1988**, 204. (c) Teo, B. K.; Hong, M.; Zhang, H.; Huang, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 897.

(10) Teo, B. K.; Shi, X.; Zhang, H. cited in *Chem. Eng. News*, **1989**, 67, 6.

Chart I



The title cluster, [(Ph₃P)₁₀Au₁₂Ag₁₂PtCl₇]Cl (3), which represents the first example of a trimetallic polyicosahedral supracluster, was synthesized by reducing a mixture of [(Ph₃P)₈Au₈Pt](NO₃)₂¹¹ (0.07 mmol) and (Ph₃P)₄Ag₄Cl₄¹² (0.1 mmol) with NaBH₄ (0.3 mmol) in ethanol. The resulting dark red precipitate was filtered and recrystallized from CH₂Cl₂/CH₃CN. Preparative and spectroscopic details are given in the supplementary material. Figures 1a and b depict the [Au₁₂Ag₁₂Pt] core and [P₁₀Au₁₂Ag₁₂PtCl₇] framework of 3, respectively.¹³ Under space group *P2₁/m*, the cluster resides on the crystallographic C₂ site symmetry (passing through Au13 and Cl1–Cl5). The metal core can be described as two Au₆Ag₆ icosahedra, one Pt-centered and one Au-centered (designated as AP11 and AP11' due to the mirror-related disorder), sharing a common gold (Au13) atom.¹⁴ The four metal pentagons adopts the *ses* configuration. The 10

(11) Bour, J. J.; Kanters, R. P. F.; Schlebos, P. P. J.; Bosman, W. P.; Behm, H.; Beurskens, P. T.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 157.

(12) Teo, B. K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.

(13) Single crystal X-ray diffraction data were collected using an Enraf-Nonius diffractometer (Mo radiation). [(Ph₃P)₁₀Au₁₂Ag₁₂PtCl₇](Cl): monoclinic *P2₁/m*, *a* = 16.534(4) Å, *b* = 24.360(5) Å, *c* = 29.819(5) Å, β = 103.25(3)°; *V* = 11690.3 Å³, and *Z* = 2. Anisotropic (heavy atoms)–isotropic (rigid-body phenyl rings) refinement gave *R*₁ = 7.0% for 3014 independent reflections (2θ ≤ 45°) with *I* > 3σ.

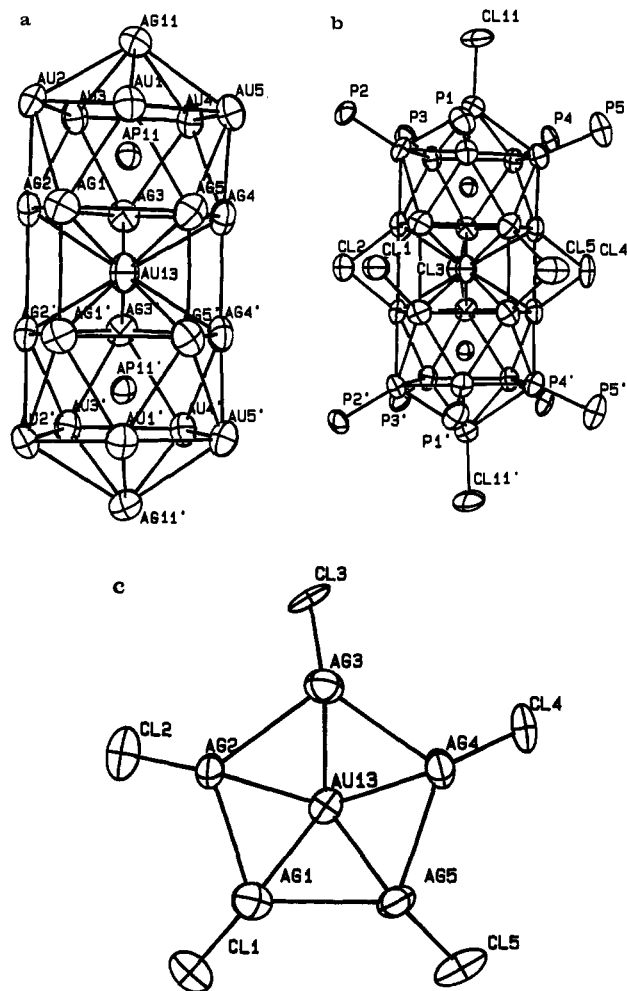


Figure 1. Molecular architecture of the 25-metal-atom cluster $[(\text{Ph}_3\text{P})_{10}\text{Au}_{12}\text{Ag}_{12}\text{PtCl}_7]^+$ (**3**), as the Cl^- salt: (a) the metal core, $\text{Au}_{12}\text{Ag}_{12}\text{Pt}$; (b) the metal-ligand framework, $\text{P}_{10}\text{Au}_{12}\text{Ag}_{12}\text{PtCl}_7$; (c) projection of the two silver pentagons onto the crystallographic mirror which passes through Au_{13} and the five doubly bridging chloride ligands Cl_1 – Cl_5 . Atoms AP_{11} and AP_{11}' (centers of icosahedra) represent an equal admixture of Au and Pt due to the crystallographically imposed mirror (C_s -m) symmetry. Atoms related by the mirror symmetry are designated as primes. All radial bonds (12 each) from AP_{11} and AP_{11}' have been omitted for clarity. Some important distances are (Å): AP_{11} – $\text{Au}(n)$, 2.687(av); AP_{11} – $\text{Ag}(n)$, 2.810(av); AP_{11} – Ag_{11} , 2.767(2); AP_{11} – Au_{13} , 2.824(7); Au_{13} – $\text{Ag}(n)$, 2.873(av). Intrapentagonal: $\text{Au}(n)$ – $\text{Au}(n+1)$, 2.888(av); $\text{Ag}(n)$ – $\text{Ag}(n+1)$, 2.898(av). Interpentagonal: $\text{Ag}(n)$ – $\text{Ag}(n')$, 2.949(av) where $n = 1$ –5; Au – P , 2.30(av); Ag_{11} – Cl_{11} , 2.389(5); $\text{Ag}(n)$ – $\text{Cl}(n)$, 2.50(av) where $n = 1$ –5. The five doubly bridging chloride ligands form a slightly distorted pentagon with nonbonding distances (Å) of: Cl_1 – Cl_2 , 4.87, Cl_2 – Cl_3 , 5.15, Cl_3 – Cl_4 , 5.31, Cl_4 – Cl_5 , 5.28, and Cl_1 – Cl_5 , 5.69.

Ph_3P groups coordinate to 10 surface Au atoms in a radial fashion. As shown in Figure 1c, there are five doubly-bridging chloride ligands (Cl_1 – Cl_5) connecting the two inner Ag_5 pentagons. Two more chloride ligands (Cl_{11} and Cl_{11}') coordinate terminally to the two apical Ag atoms (Ag_{11} and Ag_{11}').

Several novel features of the structure of **3** are noteworthy. First, the most significant structural characteristic of **3** is that

(14) This disorder model is based on the structure of the Ni analog of the title cluster (work in progress). In $[(\text{Ph}_3\text{P})_{10}\text{Au}_{12}\text{Ag}_{12}\text{NiCl}_7](\text{SbF}_6)$, the site preference for Au, Ag, and Ni can be discerned unequivocally due to their differences in X-ray scattering power.

one of the two centers of icosahedra is occupied by the unique Pt atom.¹⁴ Second, the shared vertex is Au, as in the majority of the bimetallic biicosahedral (Au/Ag) supraclusters.⁸ Third, the observed metal configuration is exactly *ses* instead of nearly *ses* as in **2**. Fourth, there are five symmetrical-bridging chloride ligands in **3** instead of six as in **1b**. Fifth, while **1b** is a *monocation* and **2** is a *dication*, **3**, with a Pt atom replacing one of the Au atoms, is a *monocation* (vide infra).

The intermetallic bonding distances follow the trends (presumably bond strength in reversed order) of: (1) $\text{Pt-Au} < \text{Pt-Ag} < \text{Au-Au} \leq \text{Au-Ag} < \text{Ag-Ag}$;^{8–11} (2) $M_c-M_s < M_c-M_v < M_v-M_s < M_s-M_s$ (where c, v, and s denote centers of icosahedra, shared vertex, and "surface" metal atoms, respectively); and (3) intraicosahedral $<$ intericosahedral. These structural trends can be rationalized in terms of the disparities in cohesive energy and in electronegativity. The latter is related to the relativistic effects.¹⁵ These structural trends and their electronic origins provide strong evidence for the cluster of clusters^{5–10} concept, in which the individual icosahedral units serve as basic building blocks.

Finally, the observation of **3** suggests the existence of a parallel sequence of trimetallic (Au/Ag/Pt) vertex-sharing polyicosahedral supraclusters, from a single icosahedron of 13 metal atoms to an icosahedron of icosahedra of 127 metal atoms, in analogy to the bimetallic (Au/Ag) vertex-sharing polyicosahedral clusters.^{5–10} Within the biicosahedral series, preliminary studies¹⁶ suggest the existence of a series of 25-metal-atom trimetallic (Au/Ag/Pt) clusters of general formulas $[(\text{R}_3\text{P})_{10}\text{Au}_{11}\text{Ag}_{12}\text{Pt}_2\text{X}_7]$ (**4**) and $[(\text{R}_3\text{P})_{10}\text{Au}_{12}\text{Ag}_{12}\text{PtX}_8]$ (**5**), as depicted in Chart I. In fact, **2**, **3**, and **4** are members of the 5-ring (Chart I, top) series $[(\text{R}_3\text{P})_{10}\text{Au}_{13-n-m}\text{Ag}_{12+n}\text{M}_m\text{X}_7]^{(2-m)+}$ ($m = 0$ –2), whereas **1** and **5** are members of the 6-ring series $[(\text{R}_3\text{P})_{10}\text{Au}_{13-n-m}\text{Ag}_{12+n}\text{M}_m\text{X}_8]^{(1-m)+}$ ($m = 0, 1$), where $n = 0, 1$; R = aryl, alkyl; M = Pt, Pd, Ni; and X = Cl, Br. All of these *biicosahedral* clusters satisfy the $M-X-Q = 8n = 16$ electrons^{7a,17} rule where M, X, Q refer to the numbers of Au or Ag atoms, halide ligands, and the overall charge, respectively. (Note that each group 11 or 10 metal atom contributes *one* or *zero* electron for cluster bonding, respectively.) The new synthetic strategy (reductive addition of a third metal to a preformed bimetallic cluster) reported here, in combination with those developed for the bimetallic (Au/Ag) system^{5–10} (cluster of clusters approach), should allow a systematic design and synthesis of a new high-nuclearity trimetallic (Au/Ag/Pt) vertex-sharing polyicosahedral cluster sequence (work in progress).

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Supplementary Material Available: Tables listing complete structural data, positional parameters, positional and orientational parameters of 15 phenyl groups, interatomic distances and angles, and anisotropic thermal parameters, and details of the preparation and crystallization of the title compound (17 pages); full listing of observed and calculated structure factors for the title compound (37 pages). Ordering information is given on any current masthead page.

(15) (a) Gorling, A.; Rosch, N.; Ellis, D. E.; Schmidbaur, H. *Inorg. Chem.* **1991**, *30*, 3986. (b) Pyykko, P.; Desclaux, J. *Acc. Chem. Res.* **1979**, *12*, 276. (c) Pitzer, K. S. *Ibid.* **1979**, *12*, 271.

(16) Teo, B. K.; Zhang, H.; Shi, X., to be published.

(17) Teo, B. K.; Zhang, H.; Shi, X. Clusters of Clusters: Coining Coinage Metal Clusters. In *The Chemistry of the Copper and Zinc Triads*; Welch, A. J., Chapman, S. K., Eds.; Royal Society of Chemistry; Cambridge, 1993, pp 211–234.