

## Communication

Molecular and crystal structure of an iodo-gold-silver-platinum cluster,  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\text{THF})_2$ , with a trimetallic icosahedral core capped with two planar  $[\text{AgI}_3]$  units

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Dedicated to Professor Sheldon Shore on his 70th birthday.

**Abstract**

The synthesis and crystal structure of the first trimetallic iodo-gold-silver-platinum cluster,  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\text{THF})_2$ , with a centered icosahedral metal core and two planar  $\text{AgI}_3$  capping units are described. The cluster core serves as the basic building block for a new series of trimetallic (Au–Ag–Pt) polyicosahedral clusters with iodo ligands. In the crystal, the clusters form a clathrate structural network capable of stabilizing weakly hydrogen-bonded  $(\text{THF})_2$  dimers. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Heteronuclear clusters; Mixed metal clusters; Icosahedron; Cluster clathrate

**1. Introduction**

The icosahedron has emerged as an important structural unit in metal cluster chemistry [1–8]. Structurally well-characterized gold-rich clusters with a centered icosahedral metal core, however, are limited to mono- [6] and bimetallic systems [7,8]. Furthermore, no icosahedral metal clusters with iodide ligands have been reported. With iodide ligands, gold-rich clusters have been restricted to incomplete icosahedra containing up to 11 metal atoms [9–11]. We report herein the first example of a complete icosahedral trimetallic cluster,  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\mathbf{1})(\text{THF})_2$ , which has six iodide ligands and two capping Ag atoms. The centered icosahedral core of **1** serves as the basic building block and thus opens the door to a new series of trimetallic (Au–Ag–Pt) vertex-sharing polyicosahedral clusters containing iodide ligands [12–15].

The title compound,  $(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{PtI}_6(\mathbf{1})$ , was synthesized by the reduction of a mixture of 100 mg of  $[(\text{Ph}_3\text{P})_8\text{Au}_7\text{Pt}(\text{H})(\text{NO}_3)_2]$  [16a] and 100 mg of  $[(\text{Ph}_3\text{P})_4\text{AgI}_4]$  [16b] (1:2 molar ratio) in 50 ml of absolute ethanol with an ethanolic solution of  $\text{NaBH}_4$  (100 mg in 50 ml) over a period of 30 h at ambient temperature. The dark brown precipitate formed was filtered and recrystallized with THF. A parallelepiped single crystal was used in the X-ray diffraction study<sup>1</sup>. The lantern-shaped bi-capped icosahedral metal core  $\text{Au}_6\text{Ag}_6\text{PtI}_6$  of **1**, shown

<sup>1</sup> X-ray diffraction data were collected using a Nonius CAD4 diffractometer (Mo– $\text{K}_\alpha$  radiation).  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\text{THF})_2$ : triclinic  $P\bar{1}$ ,  $a = 17.590$ ,  $b = 17.720$ ,  $c = 23.917$  Å,  $\alpha = 71.05$ ,  $\beta = 72.03$ ,  $\gamma = 60.52^\circ$ ;  $V = 6036.95$  Å<sup>3</sup>, and  $Z = 2$ . Anisotropic (heavy atoms) — isotropic (carbon and oxygen atoms) refinements gave  $R_1 = 6.4\%$  for 3251 independent reflections ( $2\theta < 44^\circ$ ) with  $I > 3\sigma$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (see Section 2). Anal. Found: C, 28.98; H, 2.20. Calc for  $\text{C}_{108}\text{H}_{90}\text{P}_6\text{Au}_6\text{Ag}_6\text{PtI}_6$  ( $M_w$  4574.9): C, 28.35; H, 1.98%. Energy dispersive X-ray analysis (using SEM) on single crystals gave the average Au:Ag:Pt ratio of 5.7:8.3:1 (calibrated with standards), in accord with the expected ratio of 6:8:1.

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in Fig. 1(a) has the idealized  $D_{3d} (-3m)$  symmetry. When the triphenylphosphine ligands are included (Fig. 1(b)), the idealized symmetry of the cluster is lowered to  $S_6 (-3)$  which is a subgroup of  $D_{3d} (-3m)$ . Under P-1 space group, however, no crystallographic site symmetry is imposed on the cluster.

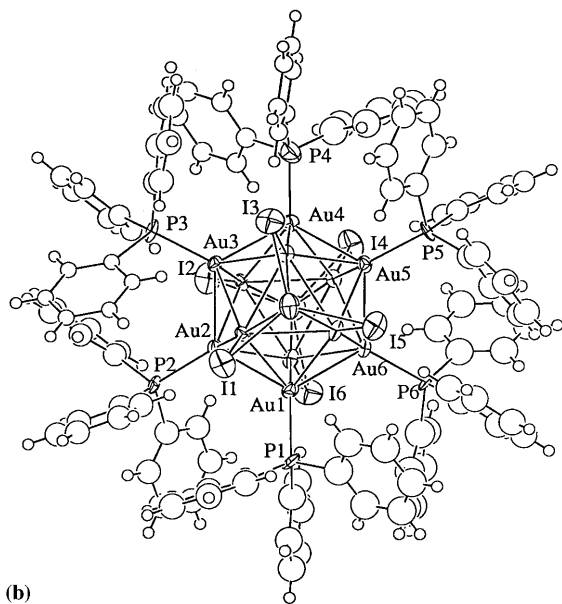
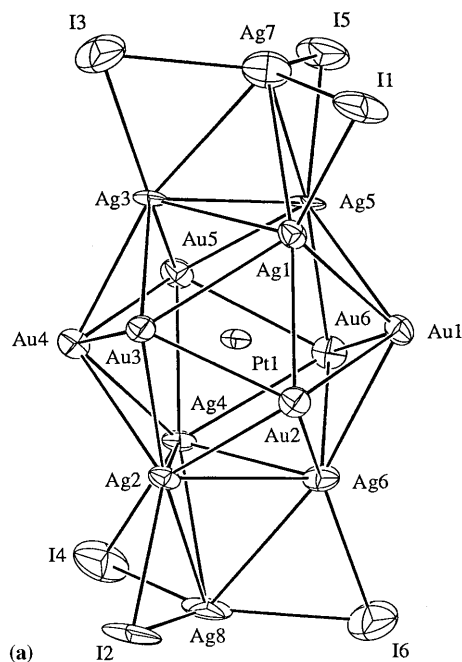


Fig. 1. (a) The  $[\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2]$  core of  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2]$  (1) depicting the bi-Ag-capped Pt-centered  $\text{Au}_6\text{Ag}_6\text{Pt}$  icosahedral structure; (b) Cluster 1 as viewed along the idealized  $S_6 (-3)$  axis. All thermal ellipsoids are 50%. Some important bond lengths and angles are: Pt–Au, 2.728, Pt–Ag, 2.774, Au–Au, 2.855, Au–Ag, 2.908, Ag–Ag, 2.890, Ag–Ag (capping), 2.996, Au–P, 2.31, Ag–I, 2.704, and Ag (capping)–I, 2.765 Å; and Pt–Au–P, 177.3, Pt–Ag–I, 162.1, and Ag–I–Ag (capping), 66.4°. The twelve radial bonds from the center (Pt1) of the icosahedron have been omitted for clarity.

The metal core of the title compound can be described as a complete, Pt-centered,  $\text{Au}_6\text{Ag}_6$  icosahedral cluster capped with two Ag atoms (Ag7 and Ag8). The six surface gold atoms form a cyclohexane-like ‘chair’ configuration capped on top and below by two silver triangles. The six triphenylphosphine ligands coordinate (one each) to the six gold atoms in a radial fashion; or, in terms of the cyclohexane-like ‘chair’ form analogy, occupying the ‘equatorial’ positions (Fig. 1(b)). All six iodide ligands are doubly-bridging, connecting the two capping silver atoms to the two surface silver triangles (on opposite sides of the cluster). Alternatively, the cluster core can be described as a Pt-centered  $\text{Au}_6\text{Ag}_6$  icosahedral cluster with six phosphine and six iodide ligands coordinating to the six gold and six silver atoms, respectively. The six iodide ligands ‘capture’ two additional Ag atoms, forming two virtually planar  $\text{AgI}_3$  moieties, one on each side of the cluster. The latter description is supported by the average Pt–Au–P angle of 177.3° and the average Pt–Ag–I angle of 162.1°. Yet a third description of the cluster structure is a Pt-centered  $\text{Au}_6\text{Ag}_6$  icosahedron,  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}]^{4+}$  capped with two trigonal planar  $[\text{AgI}_3]^{2-}$  moieties. In this context, the planar  $[\text{AgI}_3]$  groups are similar to the planar  $[\text{CuI}_3]$  group observed in  $[(\text{Ph}_3\text{P})_7\text{Au}_6\text{PtCu}_3(\text{CuI}_3)]^+$  except that the latter cluster has an *incomplete* Pt-centered icosahedral  $\text{Au}_6\text{PtCu}_3$  structure capped with only one  $[\text{CuI}_3]$  group [11].

All metal–metal distances, including the capping silver atoms, are within bonding distances and follow the expected trend [13] of Pt–Au < Pt–Ag < Au–Au < Au–Ag ~ Ag–Ag < Ag–Ag (capping). Here Ag (capping) refers to Ag7 and Ag8. Selected average bond lengths and angles are given in the caption of Fig. 1. The center of the icosahedron is occupied by the unique platinum atom since platinum has the highest cohesive energy among the three metals present. Furthermore, the disposition of the six silver atoms within the cluster core can be described as 1,2,3,9,10,12 (adopting the IUPAC numbering system for an icosahedron) which is one of the second most stable stereoisomers of an icosahedral  $\text{A}_6\text{B}_6$  cluster system. These two observations are in accord with the site preference rules (the Strong-Bond rule and the Hetero-Bond rule, respectively) established by us via theoretical calculations [20–22]. The bridging modes of the iodo ligands are slightly asymmetric (Ag–I of 2.704 Å versus Ag (capping)–I of 2.765 Å) with highly acute Ag–I–Ag (capping) angles (average value of 66.4°).

The capping silver atoms in 1 differ from those observed so far in the vertex-sharing triicosahedral clusters [17–19] such as  $(\text{Ph}_3\text{P})_{12}\text{Au}_{18}\text{Ag}_{20}\text{Cl}_{14}$  (2) [18] in a number of ways. First, each of the two capping silver atoms in 2 caps three Ag atoms from three different icosahedra whereas each capping Ag atom in 1 caps three Ag atoms from a triangular face of the same

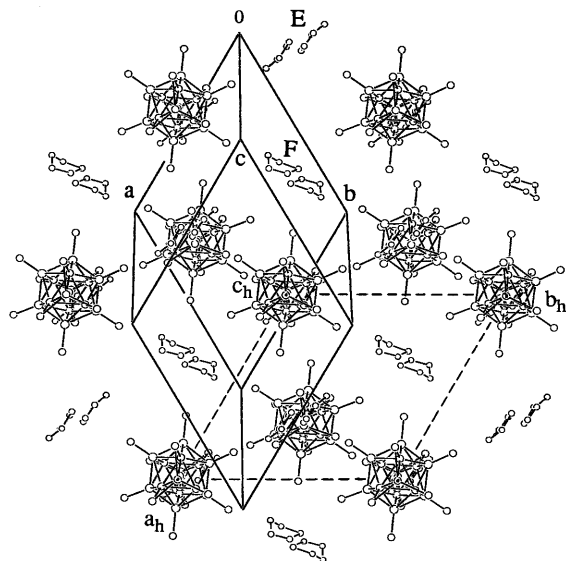


Fig. 2. Packing diagram of the crystal structure of  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\mathbf{1})\cdot(\text{THF})_2$ , as viewed along the idealized  $S_6$  ( $-3$ ) symmetry axis of cluster  $\mathbf{1}$ , showing the crystallographic triclinic ( $P\bar{1}$ ) unit cell (solid lines) and the noncrystallographic rhombohedral ( $R-3$ ) unit cell (dashed lines, in hexagonal setting). Only two layers of the ABCABC pattern of the clusters in the noncrystallographic rhombohedral cell are shown. The  $(\text{THF})_2$  dimers of types E and F occupy edge  $(1/2, 0, 0)$  and face  $(0, 1/2, 1/2)$  centers, respectively, of the crystallographic triclinic unit cell. In the noncrystallographic rhombohedral unit cell, they occupy octahedral holes created by the clusters in adjacent layers. Some cluster and/or  $(\text{THF})_2$  dimers have been omitted for clarity.

icosahedron. Second, the distances between the capping silver atoms and the silver atoms within the triicosahedral framework in  $\mathbf{2}$  are more or less nonbonding (average  $3.73 \text{ \AA}$ ) whereas the corresponding distances in  $\mathbf{1}$  are bonding (average  $2.996 \text{ \AA}$ ). Third, while the bridging chloride ligands associated with the capping Ag atoms in  $\mathbf{2}$  are triply (or nearly quadruply) bridging, the iodide ligands in  $\mathbf{1}$  are doubly bridging. And finally, while all previously known bimetallic (Au–Ag) or trimetallic (Au–Ag–M, M = Group 10 metals) icosahedral or polyicosahedral clusters contain either Cl or Br ligands, the title cluster represents the first example of a complete trimetallic icosahedral cluster with iodide ligands. As such, it opens the door to a new series of polyicosahedral Au–Ag–Pt cluster with iodo ligands [12–15,17–23].

In the triclinic unit cell of space group  $P\bar{1}$ , the crystal structure consists of two formula units of  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\mathbf{1})\cdot(\text{THF})_2$  ( $Z = 2$ ). The asymmetric unit comprises one cluster ( $\mathbf{1}$ ), centered at the general position  $(0.283, 0.701, 0.750)$ , and two  $(\text{THF})_2$  dimers at special positions, one (designated as E) centered at the midpoint of the  $a$  axis  $(1/2, 0, 0)$  and the other (designated as F) at the  $bc$  face center  $(0, 1/2, 1/2)$ , as depicted in Fig. 2. The two slightly puckered and ‘twisted’ THF molecules within each dimer are

related by the crystallographic inversion centers ( $-1$ ). The closest hydrogen bonding  $\text{C}(\text{H})\cdots\text{O}$  contacts between the THF molecules within each dimer are  $2.42$  and  $2.83 \text{ \AA}$  for types E and F dimers, respectively. The  $(\text{THF})_2$  dimers also make weak but extensive hydrogen bonding and/or van der Waals contacts with the clusters ( $\mathbf{1}$ ). To the best of our knowledge, this is the first time a  $(\text{THF})_2$  dimer is observed in a crystal structure. We believe that the observation of a  $(\text{THF})_2$  dimer in the present structure is facilitated by the crystal packing of the clusters. Indeed, as shown in Fig. 2, the clusters form an approximate, two-dimensional, hexagonal net in the  $ab$  plane of the triclinic cell. The hexagonal nets are stacked in an ABCABC pattern, giving rise to an approximate face-centered-cubic (fcc) structure, ‘compressed’ along one of the fcc body diagonals. The idealized space group symmetry of the resulting noncrystallographic unit cell is  $R-3$ . The unique,  $c_h$ , axis of this noncrystallographic rhombohedral unit cell, in the hexagonal setting, coincides with the idealized threefold axis of the cluster. The  $(\text{THF})_2$  dimers occupy all the ‘octahedral holes’ of the approximate face-centered-cubic (fcc) cluster network, giving rise to the overall formulation of  $\mathbf{1}\cdot(\text{THF})_2$ . In this context, the crystal structure of the title compound may be considered as a ‘cluster clathrate’ capable of stabilizing highly unusual forms or aggregates of smaller molecules (such as the weakly hydrogen-bonded  $(\text{THF})_2$  dimers).

## 2. Supplementary material

Crystallographic data for  $[(\text{Ph}_3\text{P})_6\text{Au}_6\text{Ag}_6\text{Pt}(\text{AgI}_3)_2](\mathbf{1})\cdot(\text{THF})_2$  have been deposited with the Cambridge Crystallographic Centre, CCDC no. 149516. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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