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LETTER

A Novel Au–Ag Supracluster: Preparation and Structure of $[Au_{13}Ag_{12}(\mu_2\text{-}Cl)_6(Ph_3P)_{10}Cl_2]\cdot n$EtOH

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The increasing effort for a better understanding of the facts in heterogenous catalysis and of the formation of small metal aggregates had led to considerable interest in transition metal clusters with high nuclearity [1–10]. These clusters are in a class of compounds the skeletal atoms of which are arranged in close-packed lattices and stabilized by a ligand shell. Synthetic and structural studies of these metal clusters will not only shed light on the important question of the dependence of metallic behavior on particle size but also pave the way for the discovery of novel materials with unusual physical or chemical properties. Since Teo and coworkers reported the first 25-atom cluster, $[Au_{13}Ag_{12}(Ph_3P)_{12}Cl_6]^{m+}$ [5], the Au–Ag supraclusters have been of great interest. In recent years, the syntheses and structures of several Au–Ag clusters have been reported [6, 7]. In this paper, we report the synthesis and structure of a novel 25-atom Au–Ag cluster cation, $[Au_{13}Ag_{12}(\mu\text{-}Cl)_6(Ph_3P)_{10}Cl_2]^+$.

Experimental

Synthesis

A mixture of $HAuCl_4\cdot 4H_2O$ (82 mg, 0.2 mmol), Ph_3P (105 mg, 0.4 mmol) and $[Ph_3PAgCl]_4$ (81 mg, 0.05 mmol) in absolute EtOH (40 ml) was stirred in a Schlenk flask for 30 min; the solution changed from yellow to colorless with a small amount of white precipitate. To this solution was slowly added a solution of $NaBH_4$ (16 mg, 0.42 mmol) in absolute EtOH (15 ml). The reaction mixture was stirred for 24 h at room temperature. After addition of 50 ml of hexane and filtration, the resultant brown solid was treated with 50 ml of CH_2Cl_2/EtOH (vol./vol., 1:1). The resulting solution was allowed to stand for 2 weeks in a brown desiccator with octane at room temperature to give dark red crystals of the title compound suitable for X-ray diffraction study.

Crystal Data

A single crystal of dimensions $0.2 \times 0.35 \times 0.4$ mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a Mo Kα radiation source and graphite monochromator. The crystal is monoclinic, space group $C2$ with $a = 36.618(19)$, $b = 16.788(7)$, $c = 19.629(5)$ Å; $\beta = 99.24(3)°$, $V = 11\,910.5$ Å^3, $Z = 2$. A total of 7748 independent reflections were collected in the range of $2° \leqslant 2\theta \leqslant 44°$, of which 4504 reflections with $I \geqslant 3\sigma(I_0)$ were used in structure determination and refinement after Lp and empirical absorption corrections. The coordinates of seven gold and six silver atoms were determined by direct methods and the remaining non-hydrogen atoms were located from difference Fourier maps. The structure was refined by a full-matrix least-squares technique with anisotropic temperature factors for gold, silver, phosphorus and chlorine atoms, and isotropic factors for all carbon atoms. The final R and R_w were 0.089 and 0.098, respectively.

Discussion

The important atomic distances of the cluster cation are listed in Table 1, and a perspective view of the cation with phenyl rings omitted is shown in Fig. 1. This structure possesses a crystallographic 2-fold axis passing through atom Au(1) and the midpoint of Ag(4) and Ag(4'), and a pseudo-5-fold axis through the atoms of Ag(1), Au(2), Au(1), Au(2') and Ag(1'). These two axes mentioned above are perpendicular to each other. Along the pseudo-5-fold axis the metal atoms are arranged in nine layers: 1(Ag), 5(Au), 1(Au), 5(Ag), 1(Au), 5(Ag), 1(Au), 5(Au) and 1(Ag). The five atoms in the 2nd, 4th, 6th, or 8th layers are linked together in a pentagon. So, if one views the structure from the pseudo-5-fold axis, four metal-atom pentagons, which are parallel to each other, can be seen. Two silver-atom pentagons are nearly eclipsed, (E) and are linked by six chlorines (Fig. 2). So the four pentagons are arranged in an S–E–S configuration instead of the S–S–S one reported by Teo *et al.* [5] (S = staggered). In this cluster, the metal atoms can be divided into two kinds: polyhedron center atoms and

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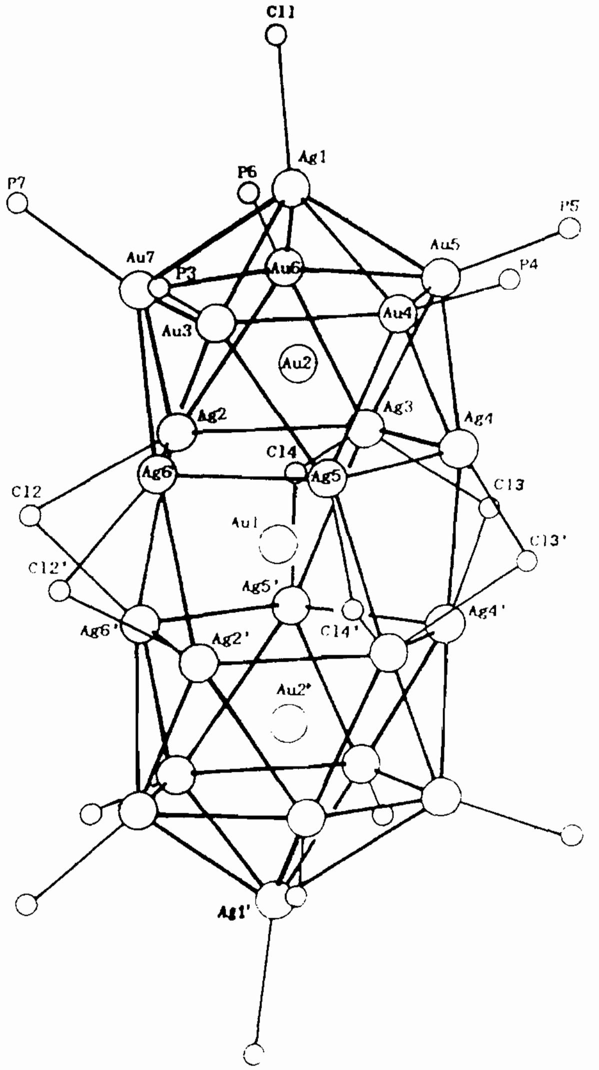

Fig. 1. Molecular structure of $[Au_{13}Ag_{12}(\mu_2\text{-}Cl)_6(Ph_3P)_{10}Cl_2]^-$ with phenyl rings omitted.

polyhedron vertex atoms. The polyhedron center atoms, which are analogous to the metal atoms in closed-packed lattices, are each surrounded by other twelve atoms. However, besides bonding to other metal atoms, each polyhedron vertex atom is coordinated by one ligand, phosphine for gold atoms and chlorine for silver atoms. It is reasonable to assume this small metal aggregate is stabilized by these ligands.

The most interesting structural characteristic of this 25-atom cluster is that it can be considered as two icosahedral cluster units (Au_7Ag_6) sharing one vertex ($2 \times 13 - 1 = 25$). The Au–Au, Au–Ag and Ag–Ag distances in the icosahedral cluster units fall in the ranges 2.69–2.96, 2.72–3.00 and 2.82–2.95 Å, respectively, which indicate that metal–metal bonds indeed exist. The atomic distances between the two silver-atom pentagons can be classified into two types: one in the range 3.03–3.07 Å, which can be considered as partially bonding, and the other in the range 3.36–3.46 Å, which can be considered as non-bonding. The terminal Ag–Cl distance is 2.464 Å. The distances between Ag and the bridged Cl are somewhat longer and

TABLE 1. Selected bond lengths (Å) for $[Au_{13}Ag_{12}(Ph_3P)_{10}Cl_8]^+$

Au(1)–Au(2)	2.8051(9)	Au(6)–Ag(1)	2.976(3)
Au(1)–Ag(2)	2.840(4)	Au(6)–Ag(2)	2.956(4)
Au(1)–Ag(3)	2.901(3)	Au(6)–Ag(3)	2.831(4)
Au(1)–Ag(4)	2.957(4)	Au(7)–Ag(1)	2.898(3)
Au(1)–Ag(5)	2.851(3)	Au(7)–Ag(2)	2.899(4)
Au(1)–Ag(6)	2.719(4)	Au(7)–Ag(6)	3.001(3)
Au(2)–Au(3)	2.711(2)	Ag(2)–Ag(3)	2.951(4)
Au(2)–Au(4)	2.698(2)	Ag(3)–Ag(4)	2.822(5)
Au(2)–Au(6)	2.687(2)	Ag(4)–Ag(5)	2.895(6)
Au(2)–Au(7)	2.764(3)	Ag(5)–Ag(6)	2.852(5)
Au(2)–Ag(1)	2.732(2)	Ag(2)–Ag(6')	3.003(5)
Au(2)–Ag(2)	2.869(2)	Ag(3)–Ag(5')	3.007(4)
Au(2)–Ag(3)	2.850(3)	Ag(4)–Ag(4')	3.065(4)
Au(2)–Ag(4)	2.855(5)	Ag(2)–Ag(5')	3.463(3)
Au(2)–Ag(5)	2.807(3)	Ag(3)–Ag(4')	3.417(4)
Au(2)–Au(6)	2.760(2)	Ag(6)–Ag(6')	3.361(3)
Au(3)–Au(4)	2.901(2)	Au(3)–P(3)	2.273(9)
Au(3)–Au(7)	2.964(2)	Au(4)–P(4)	2.380(7)
Au(3)–Ag(1)	2.985(3)	Au(5)–P(5)	2.330(8)
Au(3)–Ag(5)	2.904(2)	Au(6)–P(6)	2.349(9)
Au(3)–Ag(6)	2.852(2)	Au(7)–P(7)	2.347(8)
Au(4)–Au(5)	2.888(3)	Ag(1)–Cl(1)	2.464(9)
Au(4)–Ag(1)	3.003(2)	Ag(2)–Cl(2)	2.635(10)
Au(4)–Ag(4)	2.922(3)	Ag(3)–Cl(3)	2.504(8)
Au(4)–Au(5)	2.764(3)	Ag(3)–Cl(4)	2.712(9)
Au(5)–Au(6)	2.838(2)	Ag(4')–Cl(3)	2.634(7)
Au(5)–Ag(1)	2.951(2)	Ag(5')–Cl(4)	2.491(7)
Au(5)–Ag(3)	2.964(2)	Ag(6')–Cl(2)	2.531(9)

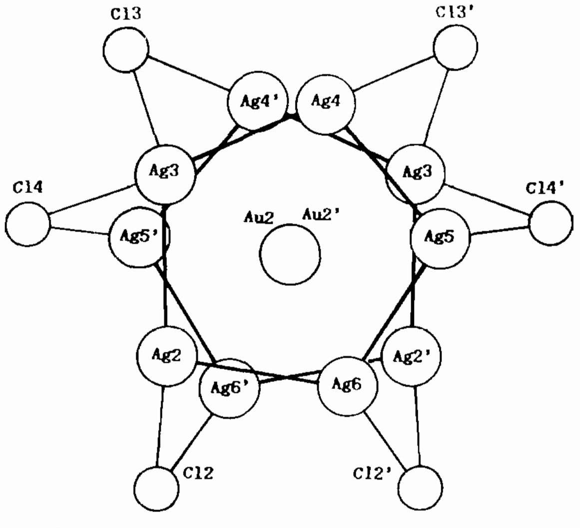

Fig. 2. Two silver-atom pentagons linked by six μ_2-Cl and viewed along the pseudo-5-fold axis.

vary from 2.50 to 2.71 Å. The ten Au–P distances fall in the range 2.27–2.35 Å.

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