Synthesis and Structural Characterization of $[Au_9Ag_4Cl_4(PMePh_2)_8][C_2B_9H_{12}]\cdot H_2O\cdot 0.5CH_2Cl_2$: the First Example of an Icosahedral Silver–Gold Cluster

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The compound $[Au_9Ag_4Cl_4(PMePh_2)_8][C_2B_9H_{12}]\cdot H_2O\cdot 0.5CH_2Cl_2$ has been synthesised in high yield from $[Au_{11}(PMePh_2)_{10}]^{3+}$ and $[Ag(PMePh_2)Cl]$ in CH_2Cl_2 and its centred icosahedral geometry has been confirmed by single-crystal X-ray diffraction measurements.

Gold forms a wide range of cluster compounds where the metal has an intermediate oxidation state between 0 and +1 and is associated with tertiary phosphine ligands. By comparison, the cluster chemistry of silver is very poorly developed.[1] Nevertheless, an interesting series of high-nuclearity gold–silver cluster compounds[2–9] have been characterised. The geometries of these species are based on linear, trigonal and tetrahedral arrangements of vertex-linked icosahedra, an example of each being $[Au_{13}Ag_{12}Br_8\{P(C_6H_4Me\text{-}p)_3\}_{10}]^+$,[6] $[Au_{18}Ag_{20}Cl_{14}\{P(C_6H_4Me\text{-}p)_3\}_{12}]$[5] and $[Au_{22}Ag_{24}Cl_{10}(PPh_3)_{10}]$.[4] Teo and Zhang[10] have used these compounds to illustrate a theory of cluster growth based on the vertex sharing of icosahedral clusters. The closed-shell electronic requirements of such clusters have been defined theoretically by Kanters and coworkers.[11] To date, synthetic studies have not yielded any examples of silver–gold clusters with geometries based on a single icosahedron. In this communication we describe the first example of such a cluster.

When $[Au_{11}(PMePh_2)_{10}]^{3+}$ (ref. 12) is treated with 4 mol equivalents of $[Ag(PMePh_2)Cl]$ in CH_2Cl_2 an immediate darkening of the solution occurs. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the reaction mixture shows the complete disappearance of the original resonance and the appearance of four resonances in the ratio 4:2:2:6. The first three of these are due to $[Au_9Ag_4Cl_4(PMePh_2)_8]^+$ **1** and are discussed in more detail below. The fourth, to higher field, is assigned to a monomer according to the stoichiometry (1). This high yield 'Aufbau' synthesis

$$[Au_{11}(PMePh_2)_{10}]^{3+} + 4[Ag(PMePh_2)Cl] \longrightarrow [Au_9Ag_4Cl_4(PMePh_2)_8]^+ + 2[Au(PMePh_2)_3]^+ \quad (1)$$

contrasts with the lower-yield co-reduction routes previously used to synthesise high-nuclearity gold–silver clusters.[2–9]

The compound $[Au_9Ag_4Cl_4(PMePh_2)_8]^+$ was isolated in high yield as the $[C_2B_9H_{12}]^-$ salt. Its composition was confirmed by positive-ion fast atom bombardment (FAB) mass spectrometry. The parent ion was observed at m/z 3948, and the major peaks with m/z > 2000 could all be assigned to fragments of the cation after the loss of various combinations of the ligands and gold. Interestingly, in this higher-mass range, there was no evidence for the loss of silver atoms.

The crystal structure‡ shows that $[Au_9Ag_4Cl_4(PMePh_2)_8]^+$

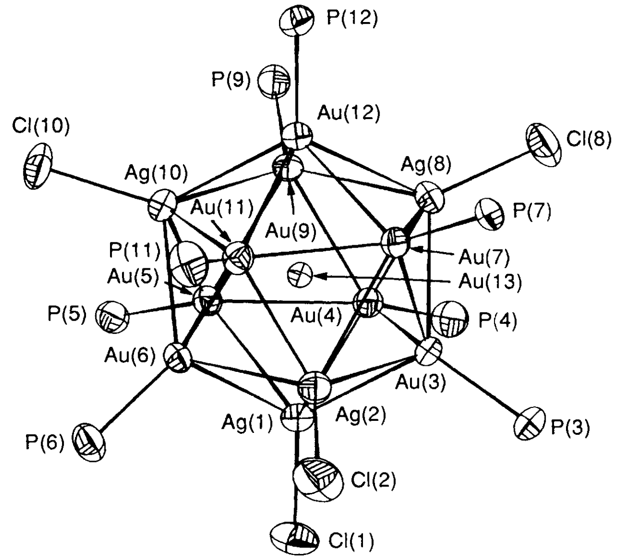

Fig. 1 Cation structure of compound **1** [carbon and hydrogen atoms omitted for clarity, along with bonds to Au(13)]. Selected bond length data (Å) (type, number, range, mean): radial Au(13)–Au(X), 8, 2.725(1)–2.767(1), 2.746; radial Au(13)–Ag(X), 4, 2.814(2)–2.853(2), 2.828; tangential Au(X)–Au(X), 11, 2.855(1)–2.951(1), 2.904; tangential Au(X)–Ag(X), 18, 2.814(2)–3.078(2), 2.924; tangential Ag(X)–Ag(X), 1, 2.946(2), 2.946

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‡ *Crystal data.* $C_{106}H_{116}Ag_4Au_9B_9Cl_4P_8\cdot H_2O\cdot 0.5CH_2Cl_2$, M = 4141.6, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), a = 33.584(5), b = 15.161(4), c = 26.115(4) Å, β = 112.195(12)°, U = 12 312 Å^3, Z = 4, D_c = 2.23 g cm^{-3}, μ(Mo-Kα) = 115 cm^{-1}, 15 997 reflections measured, 15 047 unique [merging R = 0.0230 after azimuthal absorption correction (minimum, maximum correction 1.34, 6.11)], giving 7656 with $I > 3\sigma(I)$. Stable intensity controls. Direct methods (Au and Ag atoms). Chebyschev weighting scheme (coefficients 3.35, −0.07, 2.16) giving R = 0.041, R' = 0.047.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

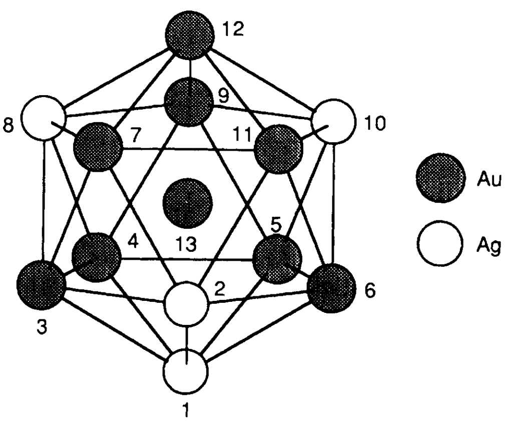

Fig. 2 Metal framework of compound **1**

and $[C_2B_9H_{12}]^-$ crytallise as well separated ions and that the former has a geometry based on a centred icosahedron, as shown in Fig. 1. The geometry closely resembles that reported previously for $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$, which is isoelectronic and isostructural.[12] The gold and silver atoms are not disordered and a gold atom occupies the interstitial site as predicted from site-preference considerations derived theoretically.[13] Although no crystallographic symmetry is imposed on the cation, it has effectively C_{2v} symmetry, with the silver atoms occupying the 1, 2, 8 and 10 positions, shown in Fig. 2

The bond length data show similarities to those found in the other silver–gold clusters with extended geometries, although the latter sometimes have different bridging ligands. As an example, in each of the vertex-linked icosahedra of $[Au_{13}Ag_{12}Cl_7\{P(C_6H_4Me\text{-}p)_3\}_{10}]^{2+}$ [8] the equivalent mean distances to those shown in the legend to Fig. 1 are 2.760, 2.804, 2.914, 2.912 and 2.885 Å respectively.

The radial metal–metal bond lengths are shorter than the tangential bonds and have a smaller spread. This is consistent with similar trends for other metal-centred clusters. The Au–Au bond lengths are very similar to those found in $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ [radial, 2.716(2)–2.789(2); peripheral, 2.852(3)–2.949(3) Å]. The Au–Ag radial bonds are longer than the Au–Au radial bonds. A comparison of the bond lengths in $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ and $[Au_9Ag_4Cl_4(PMePh_2)_8]^+$ suggests that this arises from a difference in the metal–metal bonding rather than from ligand effects.

There are large variations in the peripheral metal–metal bond lengths and they are less amenable to interpretation. The fact that there is no obvious difference, as there was in the radial case, could suggest that the tangential bonding interactions are less perturbed by the inclusion of Ag atoms. More clearly there must be a subtle interplay of electronic and steric effects.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of compound **1** is consistent with the structure shown in Fig. 1: δ [121.497 MHz, solvent CD_2Cl_2, standard $PO(OMe)_3$], 52.5 (4 P, s), 46.3 [2 P, dd, ^3J(Ag–P) 68 and 17] and 41.3 [2 P, d, ^3J(Ag–P) 70 Hz]. The cluster is stereochemically rigid on the NMR time-scale and there is no evidence for the fluxionality generally associated with non-icosahedral gold cluster compounds.[1] The ^{31}P nuclei observed as a singlet are connected to gold atoms 4, 5, 7 and 11. The ^{31}P nuclei associated with gold atoms 3 and 6 give rise to a multiplet which is upfield of a second multiplet due to the ^{31}P nuclei on gold atoms 9 and 12. The former is essentially a doublet, with the latter resembling a doublet of doublets. The multiplets observed in the NMR spectrum are due to ^3J(Ag–P) coupling. Unfortunately, the resolution is not sufficiently good to resolve the ^{107}Ag–P and ^{109}Ag–P coupling constants: the peak widths at half height are approximately 25 Hz. The spectrum has therefore been simulated on the basis of average coupling constants. The magnitude of the coupling depends on the angle subtended at Au(13) by the Ag and the Au bearing the P. If the Au and Ag atoms have a *para* relationship, ^3J(Ag–P) is in the region of 70 Hz but this drops to 17 Hz when Au and Ag have a *meta* relationship.

The electronic spectra of gold cluster compounds depend on nuclearity and are relatively insensitive to the ligands surrounding the cage.[1] Interestingly, the UV/VIS spectrum of compound **1** [$\lambda_{max}(CH_2Cl_2)$ 303 (sh), 323 (log ε 5.11), 364 (sh) and 420 (4.59) nm] has the same band-shape pattern as that of $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ but with the major feature at 323 nm blue shifted by approximately 15 nm. Teo *et al.*[14] have noted that the effect of increasing the proportion of Ag in mixed gold–silver colloids is to cause a similar blue shift in the electronic spectrum.

The availability of this cluster compound in high yield provides the opportunity for synthesising other high-nuclearity clusters based on vertex-linked icosahedra *via* cluster condensation reactions.

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