Cluster of Clusters: Structure of a Novel 38-Atom Cluster $(p\text{-Tolyl}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$

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The *X*-ray crystal structure of a novel 38-atom cluster $(p\text{-tolyl}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$, the largest Au–Ag cluster known to date, is reported.

A basic understanding of the formation and properties of small metal aggregates, or clusters, is essential for progress in many industries, ranging from the materials problems in microelectronics[1] to catalysis.[2,3] Synthetic and structural studies of metal clusters will not only help to shed light on the important question of the development of metallic behaviour[4—7] as a function of particle size but also pave the way for the discovery of novel materials with unusual physical or chemical properties.

Recently we reported the synthesis and structural characterization of a 25-atom cluster containing gold and silver.[8] We now report the structure of a novel 38-atom cluster

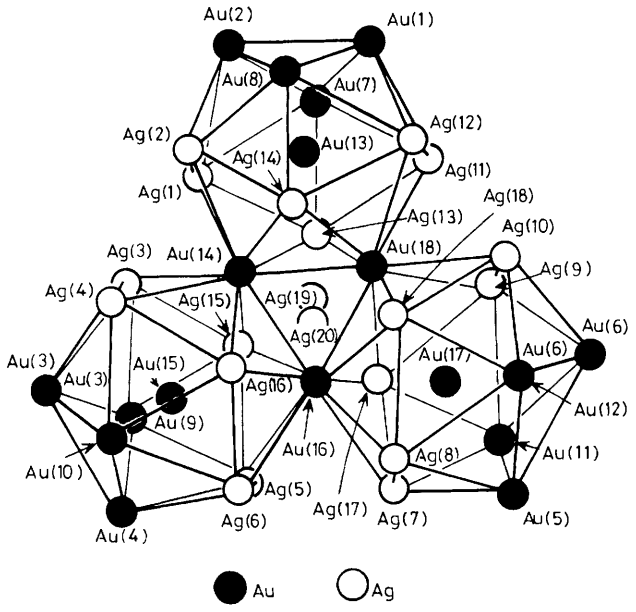

Figure 1. Metal framework of the 38-atom cluster $(p\text{-tol}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ depicting three centred icosahedra sharing three vertices. Note that not all metal–metal bonds are shown.

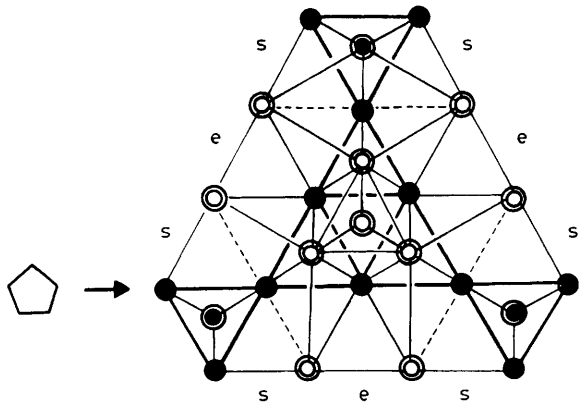

Figure 2. Metal framework of the 38-atom cluster $(p\text{-tol}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$: schematic representation of the close packing. Note that not all metal–metal bonds are shown.

$(p\text{-tol}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$† [$p$-tol$_3$P = tri-($p$-tolyl)phosphine] isolated from the reduction of a mixture of p-tol$_3$P, $HAuCl_4$, and $AgAsF_6$ with $NaBH_4$ in ethanol. It is the largest Au–Ag cluster known to date. Other examples of metal clusters with similar nuclearities are: $[Pt_6Ni_{38}(CO)_{48}H_{6-n}]^{n-}$ (n = 4,5);[9a] $[Ni_{38}(CO)_{42}C_6H]^{5-}$;[9b] $Ni_{34}Se_{22}(PPh_3)_{10}$;[9c] $Pd_{38}(CO)_{28}(PEt_3)_{12}$;[9d] $[Pt_{38}(CO)_{44}]^{2-}$;[9e] $[(p\text{-tol}_3P)_{12}Au_{18}Ag_{19}Br_{11}]^{2+}$.[9f]

The metal framework of the 38-atom cluster, which conforms to idealized D_{3h} symmetry, is portrayed in Figure 1. The most obvious description of the structure is as three 13-atom (Au_7Ag_6) Au-centred icosahedra sharing three Au vertices plus two capping Ag atoms located on the idealized threefold axis. As such, the 18 Au atoms (solid circles) can be divided into two categories: 12 on the surface and 6 in the interior. The 20 Ag atoms (open circles) can be classified into three types (with decreasing distance from the centroid of the cluster): 12 on the peripherals (type A), 6 in the centre (type B), and 2 on the idealized threefold axis (type C). There are 12 phosphine ligands co-ordinated to the 12 peripheral Au atoms and 14 chloride ligands co-ordinated to the 20 Ag atoms in the following manner: six doubly bridging (connecting type A Ag atoms of adjacent icosahedra); six triply bridging (connecting type B and type C Ag atoms); and two terminal (co-ordinated to type C Ag atoms).

† The cluster $(p\text{-tol}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ forms dark red prismatic crystals. It crystallizes in the triclinic space group $P\bar{1}$, a = 23.240(8), b = 31.93(2), c = 33.98(2) Å; α = 112.15(5), β = 90.38(5), γ = 98.38(5)°, U = 23050.8 Å^3, and Z = 2. The single crystal X-ray diffraction data were collected using an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation. The structure determination (*via* direct methods) is based upon 10509 independent reflections ($2\theta \leq 44°$) with $I > 2\sigma(I)$. Anisotropic refinement (metal atoms only) gives R = 8.8%. Though tentatively formulated here as a neutral cluster, the overall charge of the cluster cannot be determined at this point. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

A second description of the structure is based on close-packing of metal atoms (Figure 2). In this description, imagine a two-dimensional 'close-packing' of 12 Au atoms to form a v_2 triangle and three v_1 triangles sharing corners.[10] Above and below the three small triangles are six Au atoms conceptually changing the smaller triangles into trigonal bipyramids. Above and below the central (large) triangle are eight Ag atoms arranged in two tetrahedral arrays, giving rise to a v_2 trigonal bipyramid. On the three edges are 12 Ag atoms (not closest-packed), 6 above and 6 below the plane of the 12 Au atoms.

Yet a third description of the structure is that it can be considered as three interpenetrating 25-atom clusters.[8] Thus, if one views along the pseudo-5-fold axes marked by an arrow in Figure 2, the same 1:5:1:5:1:5:1:5:1 structural arrangement of metal atoms can be seen. (Note, however, that the four pentagons are arranged in a s–e–s configuration instead of the s–s–s configuration in the 25-atom cluster, where s and e denote staggered and eclipsed, respectively.) The structure is completed by two 'apical' Ag atoms located on the idealized three-fold axis.

The metal–metal distances follow the approximate trend of Au–Au (2.68—3.20 Å) ~ Au–Ag (2.70—3.14 Å) < Ag–Ag (2.81—3.29 Å) which can be considered as more or less bonding. There are four groups of Ag–Ag distances: 2.81—2.97 Å for unbridged, 3.08—3.29 Å for doubly bridged, and 3.12—3.28 Å for triply bridged Ag–Ag distances. The Ag · · · Ag contacts of 3.69—3.85 Å involving the two apical Ag atoms (*cf.* Figure 2) are best considered as nonbonding. The terminal, doubly, and triply bridging Ag–Cl distances fall in the ranges of 2.21—2.37, 2.32—2.70, and 2.53—2.86 Å, with an average of 2.29, 2.48, and 2.66 Å, respectively. The 12 Au–P distances fall in the range of 2.04—2.34 Å, with an average of 2.21 Å.

The most interesting structural characteristic of the 25- (ref. 8) and 38-atom (this work) clusters is that they can both be considered as being built from 13-atom *centred* icosahedral cluster units. Thus, the 25-atom cluster can be considered as *two* icosahedra sharing a vertex ($2 \times 13 - 1 = 25$); the 38-atom cluster as *three* icosahedra sharing three vertices in a cyclic manner ($3 \times 13 - 3 = 36$) plus two capping atoms.

It is hoped that the molecular architectures of the 25- and 38-atom clusters will open new doors to novel high nuclearity metal clusters based on smaller cluster units as building blocks *via* either vertex-, edge-, face-sharing, or simple close packing arrangements.

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