

Synthesis and Structural Characterization of $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_8](\text{BF}_4)_3$; A Cluster with a Centred Crown of Gold Atoms

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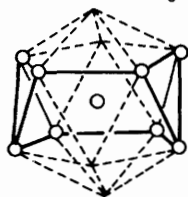
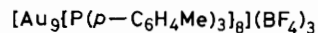
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The single crystal X-ray analysis of $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_8](\text{BF}_4)_3$ has provided the first example of a cluster compound with a metal atom incorporated into the centre of a puckered ring of like metal atoms.

Although the theoretical basis of transition metal cluster chemistry remains relatively primitive some progress has been made towards understanding the skeletal structures of these complex molecules through the development of electron counting rules based on cluster capping and fragmentation relationships derived largely from semi-empirical molecular orbital calculations.^{1,2} In gold cluster chemistry, for example,

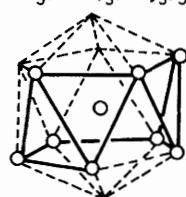
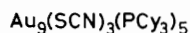
it has proved useful to describe the cluster geometries of the known Au_{11} , Au_9 , and Au_8 compounds³ in terms of a parent icosahedral structure.⁴ Thus the central core of gold atoms in $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_8](\text{BF}_4)_3$ (**1**)³ and $\text{Au}_9(\text{SCN})_3(\text{PCy}_3)_5$ (**3**)⁵ (Cy = cyclohexyl) may be derived from the centred icosahedron (**2**) either by the removal of a rectangle of four gold atoms, or a triangle of gold atoms in combination with a single



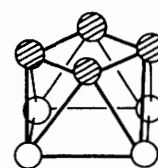
(1)



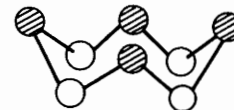
(2)



(3)



(5)



(6)

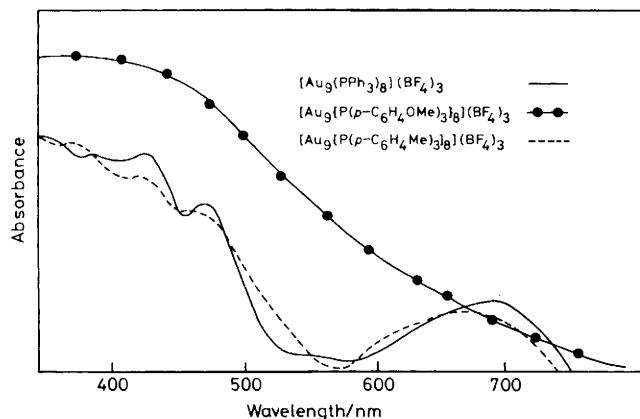


Figure 1. Comparison of the solid state reflectance spectra of the $[\text{Au}_9(\text{PR}_3)_8](\text{BF}_4)_3$ cluster compounds.

gold atom, although in the latter example it is necessary to break an additional gold-gold bond.

Although simple chemical considerations suggested that $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_8](\text{BF}_4)_3$ (**4**) should have a structure closely related to (**1**) its electronic spectral characteristics in the solid state (see Figure 1) and electrochemical properties were sufficiently different from those reported for (**1**) and $[\text{Au}_9(\text{PPh}_3)_8](\text{BF}_4)_3$ to warrant the determination of its molecular structure.[†]

Crystal Data: $\text{C}_{168}\text{H}_{168}\text{Au}_9\text{O}_{24}\text{P}_8 \cdot 3(\text{BF}_4)$, $M = 4852$, orthorhombic, space group *Pbcn* (No. 60), $a = 31.076(4)$, $b = 17.482(2)$, $c = 31.283(4)$ Å, $U = 16\,995$ Å³, $Z = 4$ formula units, $D_c = 1.896$ g cm⁻³, $F(000) = 9288$ electrons, $\mu(\text{Mo-K}\alpha) = 75.7$ cm⁻¹. Intensity data to $2\theta_{\text{max}} = 45^\circ$ (Mo-K α X-radiation, $\lambda = 0.71069$ Å) were collected at ca. 291 K on an Enraf-Nonius CAD4 diffractometer. Of 10 928 symmetry-independent reflections measured, 4656 having $F_o \geq 5\sigma(F_o)$ were used to solve (Patterson and Fourier methods) and refine (full-matrix least squares) the structure to a current R of 0.0701.

The cation and one BF_4 anion straddle positions (c) of the space group (No. 60) of four-fold multiplicity, site symmetry 2. The other anion lies in general space, but its central boron atom has not been located; in general, the crystallographic resolution falls off rapidly with increasing distance from the centre of the cluster, a projection of which is given in Figure 2.[‡]

The architecture of the Au_9 skeleton is that of a centred crown, i.e. a centred square-antiprism that has undergone distortion perpendicular to the S_8 axis such that the $\text{Au}(1)\text{-Au}(3)$, $\text{Au}(1)\text{-Au}(3')$, $\text{Au}(2)\text{-Au}(4)$, and $\text{Au}(2)\text{-Au}(4')$ connectivities (and their symmetry equivalents) are non-bonding since their lengths lie in the range 3.404–3.545 Å. Although only C_2 symmetry (perpendicular to the plane of Figure 2) is crystallographically required, the symmetry of the cluster core approximates very closely to D_{4d} , with peripheral gold-gold

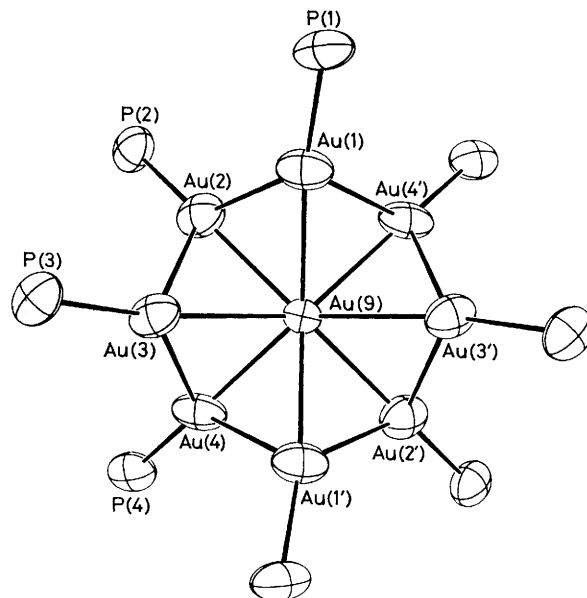


Figure 2. Molecular structure of the central portion of the cation of $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_8](\text{BF}_4)_3$ (**4**). Au-Au distances are: $\text{Au}(1)\text{-Au}(2)$ 2.815(3), $\text{Au}(2)\text{-Au}(3)$ 2.838(2), $\text{Au}(3)\text{-Au}(4)$ 2.799(3), $\text{Au}(4)\text{-Au}(1')$ 2.821(3), $\text{Au}(1)\text{-Au}(9)$ 2.651(2), $\text{Au}(2)\text{-Au}(9)$ 2.678(2), $\text{Au}(3)\text{-Au}(9)$ 2.667(2), and $\text{Au}(4)\text{-Au}(9)$ 2.661(2) Å.

distances of 2.799(3)–2.838(3) Å and the central-to-peripheral gold-gold bond lengths lying in the range 2.651(2)–2.678(2) Å. Comparable distances have been reported^{3,5} for other Au_9 and Au_8 cluster compounds, whilst somewhat longer gold-gold bond lengths have been observed for the centred icosahedral gold cluster compound.⁴ The Au-P bond lengths are internally consistent and quite normal. The phosphine ligands subtend angles at the peripheral gold atoms of 161.4(4)–165.3(4)° (to central gold atom) and 125.9(4)–136.9(4)° (to peripheral gold atoms).

The structure of the $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_8]^{3+}$ cation illustrated in Figure 2 violates the generally accepted principle³ that high nuclearity cluster compounds of gold may be regarded as fragments derived from a centred icosahedron. In addition it represents the first example of a cluster compound generated by the incorporation of a metal atom into the centre of a puckered ring of bonded metal atoms. The observed structure throws some light on the long-standing controversy^{3,6,7} concerning the relative importance of radial and peripheral gold-gold bonding interactions in centred gold cluster compounds. The structure illustrated in Figure 2 has the same number of radial gold-gold bonds as the cluster compounds (**1**) and (**3**), but four fewer peripheral gold-gold bonds clearly suggesting that the peripheral gold-gold interactions are not of great significance energetically.

Extended Hückel molecular orbital calculations which we have completed on a wide range of high nuclearity gold cluster compounds of the type $\text{Au}_x\text{L}_{x-1}^{m+}$ (where L is a neutral two-electron ligand) have demonstrated that the stoichiometries of these cations are decided primarily by the topology of the polyhedron defined by the peripheral atoms. This relationship arises because the metal-metal bonding occurs primarily through the overlap of the gold 6s orbitals⁸ and therefore the resultant molecular orbitals may be simply expressed in terms of spherical harmonics.⁹

i, If the peripheral gold atoms define a closed spherical polyhedron then the cluster molecular orbitals can be represented, in order of decreasing stability, as S, P, D functions etc. When $x = 7\text{--}13$ only the S and P functions are bonding

[†] (**4**) was synthesised in ca. 70% yield from $[\text{AuCl}\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}]$ and $\text{Ti}(\text{toluene})_2$ according to the method described in reference 4 and recrystallised from CH_2Cl_2 , propan-2-ol, and hexane as golden brown crystals, m.p. 248–252 °C; ³¹P {¹H} n.m.r. (Me_2CO) δ 54.2 p.p.m. (s) with respect to trimethylphosphate.

[‡] Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

and therefore in such complexes there are only four bonding skeletal molecular orbitals (corresponding to S , P_x , P_y , and P_z), $(x-1)$ Au-L bonding molecular orbitals, and a d-band with $5x$ molecular orbitals, resulting in a filled closed shell electronic configuration when $12x + 6$ valence electrons are present. Interactions between the S and P functions with the $6s$ and $6p$ orbitals of the central gold atom reinforce this bonding pattern. The structural characterisation of $Au_{13}Cl_2(PR_3)_{10}^{3+}$ (162 valence electrons), $Au_{11}I_3(PR_3)_7$ (138 valence electrons), and $Au_8(PR_3)_8^{2+}$ (102 valence electrons) confirm the reliability of this generalisation.

ii, If the peripheral gold atoms have a topology related to a ring or torus [*e.g.* in (1), (3), and (4)] then only the spherical harmonic solutions corresponding to S , P_x , and P_y functions are bonding and the P_z function is antibonding. This topological distinction can be illustrated by comparing the P_z functions for the square antiprism (spherical topology) and crown (torus topology) shown in (5) and (6). It follows that $Au_xL_{x-1}^{m+}$ cations of this topology are characterised by $12x + 4$ valence electrons, *e.g.* $Au_9(PR_3)_8^{3+}$ (112 valence electrons) and $Au_8(PR_3)_7^{2+}$ (100 valence electrons).

iii, The potential energy surface for the interconversion of the alternative polyhedral forms which conform to the topological requirements outlined in i and ii is soft because the radial Au-Au interactions are energetically more significant than the peripheral Au-Au interactions. For example, for (1), (3), and (4) the following total energies have been computed: (1), -1314.8 , (3), -1314.6 , and (4), -1314.7 eV. The energy differences separating these alternative polyhedral forms are within the errors associated with this type of calculation and are sufficiently small to enable crystal packing and ligand packing effects to exert a dominant influence on the observed structure in the solid state. Variable temperature n.m.r. studies¹⁰ also suggest that these cations are highly fluxional in solution. For polyhedra with spherical topologies the computed energy differences between alternative polyhedra are slightly larger and the preferred polyhedron is that which

maximises the number of next nearest neighbours, *e.g.* the icosahedron when $x = 13$.

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