

Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF $[\text{Au}_6(\text{PPh}_3)_6](\text{NO}_3)_2 \cdot 3\text{CH}_2\text{Cl}_2$; AN EDGE-SHARED BITETRAHEDRAL GOLD CLUSTER

CLIVE E. BRIANT, KEVIN P. HALL and D. MICHAEL P. MINGOS*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR (Great Britain)

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Summary

A single crystal X-ray crystallographic analysis of $[\text{Au}_6(\text{PPh}_3)_6](\text{NO}_3)_2 \cdot 3\text{CH}_2\text{Cl}_2$ has established that the gold atoms adopt the edge-shared bi-tetrahedral structure predicted on the basis of molecular orbital calculations.

The reaction of $[\text{AuCl}\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}]$ with NaBH_4 yielded on one occasion a sufficient quantity of yellow crystals of $[\text{Au}_6\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_6](\text{BPh}_4)_2$ for an X-ray structural analysis, which established that the cation had a distorted octahedral geometry with an average Au—Au bond length of 3.02 Å [1]. Numerous attempts to repeat the synthesis of this compound in our own and other laboratories have failed to yield sufficient quantities of the compound for a detailed examination of its spectroscopic and chemical properties [2]. Such studies are important in view of a suggestion [3] that for this compound the octahedral geometry might be associated with a paramagnetic ground state. A recent molecular orbital analysis of the bonding in low nuclearity gold cluster compounds [4] suggested that for an octahedral Au_6 cluster the gold—gold bonding is rather weak, because the AuPR_3 fragments form a six-centre two-electron bond. In addition it was demonstrated that more effective gold—gold bonding could be achieved if an edge bridged tetrahedral structure were adopted by the six gold atoms [4]. Such a structure is energetically favoured because it permits the formation of a pair of four-centre two-electron bonds (one for each tetrahedron) if the stoichiometry of the cluster is $[\text{Au}_6(\text{PR}_3)_6]^{2+}$. This paper reports the synthesis and characterisation of such a compound and a confirmation of the theoretical prediction.

When $\text{K}[\text{Ag}(\text{CN})_2]$ was added to a methanolic solution of $[\text{Au}_8(\text{PPh}_3)_8](\text{NO}_3)_2$ in a 1/1 molar ratio and the solution stirred for approximately 1 h, new spectral bands at 319, 331, 453 and 476 nm in the electronic spectrum indicated the for-

mation of a new cluster species. Precipitation of the compound using diethyl ether and its subsequent recrystallisation from CH_2Cl_2 /toluene resulted in the isolation of red-brown crystals which gave satisfactory analyses for $[\text{Au}_6(\text{PPh}_3)_6](\text{NO}_3)_2 \cdot \text{CH}_2\text{Cl}_2$ (I). The compound was obtained in 30% yield and the lack of incorporation of silver in the final cluster suggested that $\text{Ag}(\text{CN})_2^-$ might be initiating the reaction as a phosphine scavenger in a manner reported previously for $[\text{RhCl}(\text{COD})]_2$ [5].

Crystal data. $\text{C}_{111}\text{H}_{96}\text{Au}_6\text{O}_6\text{P}_6\text{N}_2\text{Cl}_6$ ($[\text{Au}_6(\text{PPh}_3)_6](\text{NO}_3)_2 \cdot 3\text{CH}_2\text{Cl}_2$) (I) $M = 3134.4$, monoclinic a 25.674(5), b 15.843(10), c 26.368(4) Å, β 91.76(2)°, U 10635.6 Å³, space group $P2_1/a$, $Z = 4$, D_c 1.96 g cm⁻³, $F(000)$ 5960 electrons, $\mu(\text{Mo-K}\alpha)$ 87.94 cm⁻¹. Intensity data were collected at ca. 291 K on an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo- $K\alpha$ (λ 0.71069 Å) radiation. Of 6144 unique reflections measured in the θ range 1.5 to 17.5°, 4430 with $I \geq 3\sigma(I)$ were used to solve (Patterson and Fourier methods) and refine (blocked matrix least-squares) the structure to a current R of 0.049 ($R_w = 0.066$).

The structure illustrated in Fig. 1 for the $[\text{Au}_6(\text{PPh}_3)_6]^{2+}$ cation confirms the edge-shared bi-tetrahedral geometry predicted [4]. The structure resembles that reported for the mixed metal cluster $[\text{Au}_6(\text{PPh}_3)_4\{\text{Co}(\text{CO})_4\}_2]$ (II) which has the same number of electrons involved in skeletal bonding [6]. Furthermore the compounds show a similar pattern in Au—Au bond lengths. In I and II the edge sharing Au—Au bond is significantly shorter than the bonds radiating from the gold atoms which define this bond, i.e. 2.651(2) Å vs. 2.762(2)—2.839(2) Å for I and 2.66 Å vs. 2.77—2.81 Å for II [5]. The asymmetry in Au—Au bond lengths in I and II has been satisfactorily accounted for in terms of the nodal characteristics of the highest occupied skeletal MO [4]. The outer Au—Au bonds perpendicular to the edge shared bond (Au(5)—Au(6) and Au(1)—Au(4) in Fig. 1) have an average of 2.666(3) Å for I which is longer than the average reported for

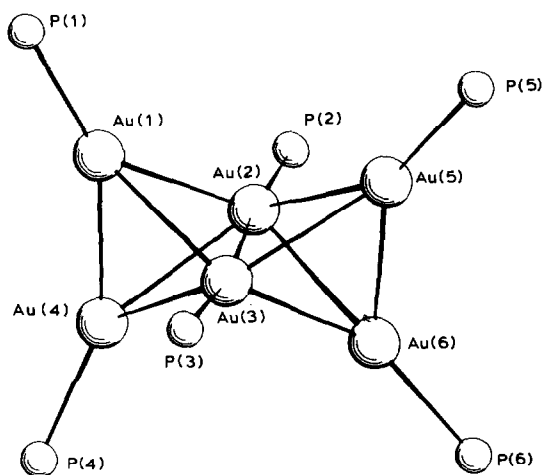


Fig. 1. Molecular structure of the cation in $[\text{Au}_6\{\text{P}(\text{Ph})_3\}_6](\text{NO}_3)_2$; for reasons of clarity the phenyl rings have been omitted. Au—Au distances are: Au(1)—Au(2) 2.820(2), Au(1)—Au(3) 2.776(2), Au(1)—Au(4) 2.669(2), Au(2)—Au(3) 2.651(2), Au(2)—Au(4) 2.797(2), Au(2)—Au(5) 2.775(2), Au(2)—Au(6) 2.808(2), Au(3)—Au(4) 2.790(2), Au(3)—Au(5) 2.839(2), Au(3)—Au(6) 2.762(2), Au(5)—Au(6) 2.663(2) Å.

II (2.62 Å). This can be attributed to the greater steric strain imposed by the additional pair of triphenylphosphine ligands in I. The observation that the Au—P vectors of the peripheral gold atoms in I no longer point towards the centres of the tetrahedra may also be attributed to the steric effects.

It is noteworthy that the Au—Au bond lengths in I are all significantly shorter than the Au—Au bond lengths reported for the octahedral $[\text{Au}_6\{\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\}_6]$ cation (average 3.02 Å), since it is consistent with the greater degree of bond localisation proposed for I [4]. The observation that a pair of such closely related clusters should have such different skeletal geometries and Au—Au bond lengths, prompted us to synthesise $[\text{Au}_6\{\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\}_6](\text{NO}_3)_2$ (Ia) from $[\text{Au}_8\{\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\}_8](\text{NO}_3)_2$ and $\text{K}[\text{Ag}(\text{CN})_2]$. Ia was obtained as a red-brown microcrystalline solid with electronic spectral characteristics almost identical to those observed for I. Since the structurally characterised octahedral $[\text{Au}_6\{\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\}_6](\text{BPh}_4)_2$ complex has been described as yellow [1] we are forced to conclude that the $[\text{Au}_6\{\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\}_6]^{2+}$ can crystallise in alternative skeletal geometries depending on the nature of the counter anion [7]. Unfortunately, the complex Ia is significantly less stable in solution than I and this has limited a detailed investigation of its properties.

The soft nature of the potential energy surface separating the alternative skeletal geometries of the $[\text{Au}_6(\text{PR}_3)_6]^{2+}$ cations has been confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR studies on I in CH_2Cl_2 solutions. At 203 K two resonances at 49.6 and 60.7 ppm with respect to trimethylphosphate with relative integration ratios of 4/2 are observed, and this is consistent with the edge sharing bi-tetrahedral structure observed in the solid state. However, at room temperature only a weighted average single sharp resonance at 53.3 ppm is observed.

We conclude from these observations that the steric and electronic factors affecting the relative stabilities of the bi-tetrahedral and octahedral geometries work in opposing directions and lead to comparable energies for the alternative structures. This suggests that in favourable circumstances it should be possible to isolate in the solid state isomeric forms of gold cluster compounds with different skeletal geometries.

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- 7 K.P. Hall, B.R.C. Theobald, D.I. Gilmour, A.J. Welch, and D.M.P. Mingos, *J. Chem. Soc., Chem. Commun.*, (1982) 582, illustrates another example of closely related $[\text{Au}_9(\text{PR}_3)_9]^{3+}$ clusters having different solid state structures.