

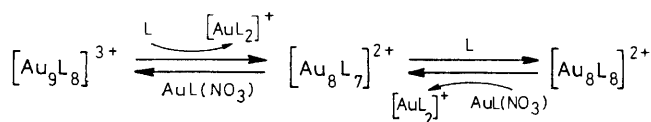
Synthesis and X-Ray Crystal Structure Determination of the Cationic Gold Cluster Compound $[\text{Au}_8(\text{PPh}_3)_7](\text{NO}_3)_2$

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Summary The reaction of $[\text{Au}_8\text{L}_8](\text{NO}_3)_2$ ($\text{L} = \text{PPh}_3$) with the phosphine scavenger $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ yields $[\text{Au}_8\text{L}_7](\text{NO}_3)_2$, X-ray analysis of which reveals the Au skeleton to be a fragment of the centred icosahedron; the cluster is an intermediate in the reactions of $[\text{Au}_9\text{L}_8]^{3+}$, and its ^{197}Au Mössbauer spectrum lacks, like that of $[\text{Au}_9\text{L}_8]^{3+}$, a separate resonance for the central Au atom.

RECENTLY the reactivity of $[\text{Au}_9\text{L}_8]^{3+}$ towards Lewis bases L or X ($\text{L} = \text{PPh}_3$; $\text{X} = \text{Cl}^-$, SCN^-) has been reported.¹ From $^{31}\text{P}\{^1\text{H}\}$ n.m.r. experiments an intermediate in the formation of $[\text{Au}_8\text{L}_8]^{2+}$ (refs. 2 and 3) from $[\text{Au}_9\text{L}_8]^{3+}$ was postulated, according to the Scheme. While the forward



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reaction proceeds in the presence of free phosphine, the reaction can be reversed with $\text{AuL}(\text{NO}_3)$. The complex $[\text{Au}_8\text{L}_7](\text{NO}_3)_2$ can be prepared by the reaction of $[\text{Au}_8\text{L}_8]$ -

$(\text{NO}_3)_2$ with the phosphine scavenger $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2^4$ in a 4:1 molar ratio in CH_2Cl_2 . After 10 min a light brown product may be precipitated with toluene. Dark red-brown crystals suitable for X-ray analysis can be obtained by slow diffusion of diethyl ether into a methylene dichloride solution of the precipitate. After drying *in vacuo* the analytical data for these crystals are consistent with the formula $[\text{Au}_8(\text{PPh}_3)_7](\text{NO}_3)_2$; conductivity measurements in methanol indicate a 1:2 electrolyte. The molecular structure was determined by X-ray analysis.

Crystal data: $\text{C}_{126}\text{H}_{105}\text{Au}_8\text{N}_2\text{O}_6\text{P}_7 \cdot 2\text{CH}_2\text{Cl}_2$, monoclinic, space group $P2_1/n$, $a = 25.444(6)$, $b = 17.332(6)$, $c = 28.795(6)$ Å, $\beta = 97.66(3)^\circ$, $U = 12584.9$ Å³, $D_m = 2.053$ g/cm³, $Z = 4$. During the measurement, the crystal, with mother liquor, was kept in a sealed capillary to prevent loss of solvent. The X-ray data were measured on a Nonius CAD-4 diffractometer, (ω - 2θ) scan, with monochromated Cu-K α radiation. A total of 2829 symmetry-independent reflections were measured, of which 2180 had $I > 3\sigma(I)$ [$\sigma(I)$ based on counting statistics]. The positions of the gold atoms were obtained from a Patterson map; the DIRDIF⁵ procedure and difference Fourier maps revealed the positions of the remaining non-hydrogen atoms, including two nitrate ions and two methylene dichloride molecules. The final R -value was 0.056.†

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

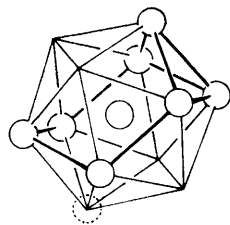


FIGURE 1. The Au skeleton of the $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ cluster in relation to the regular icosahedron. The dotted circle represents the extra Au atom in $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$.

The Au skeleton can be described as being derived from the regular icosahedral Au_{13} -cluster^{6,7} by removing two and three gold atoms, respectively, above and below the centred hexagon, a common feature of all gold clusters containing 8, 9, 11, or 13 Au atoms (Figure 1). Every peripheral gold atom has one bonded triphenylphosphine ligand, in contrast with the rather exposed atom Au(1) in the centre of the hexagon (Figure 2). The Au(1)-Au_{per.} (2.63–2.72 Å), Au_{per.}-Au_{per.} (2.80–2.94 Å), and Au-P (2.24–2.36 Å) distances are normal for gold-phosphine clusters, the short Au(3)-Au(5) distance [2.706(5) Å] being an exception. The Au-P vectors point approximately towards the central gold atom [$\angle \text{P-Au}_{\text{per.}}\text{-Au}(1)$ 160–172°], with the exception of $\angle \text{P}(3)\text{-Au}(3)\text{-Au}(1)$ 133.0(6)° and $\angle \text{P}(5)\text{-Au}(5)\text{-Au}(1)$ 145.6(6)°. It can be concluded that the phosphine ligand abstracted from $[\text{Au}_8\text{L}_8]^{2+}$ was originally bonded to the central gold atom, as was already predicted from the rather long Au_{centr.}-P distance [2.42(3) Å]. However, the overall Au-P skeleton shows a strong similarity to that of the $[\text{Au}_9\text{L}_8]^{3+}$ cluster, from which it can be obtained by abstraction of an $[\text{AuL}]^+$ ion originally bonded to the central gold atom. Another intriguing resemblance to the $[\text{Au}_9\text{L}_8]^{3+}$ cluster can be found in the ¹⁹⁷Au Mössbauer spectrum of the title compound, which also shows only one quadrupole doublet, with isomer shift (2.42 mm s⁻¹ relative to the ¹⁹⁷Pt source) and quadrupole splitting (6.88 mm s⁻¹) in the range normally found for peripheral Au atoms bonded to ligands

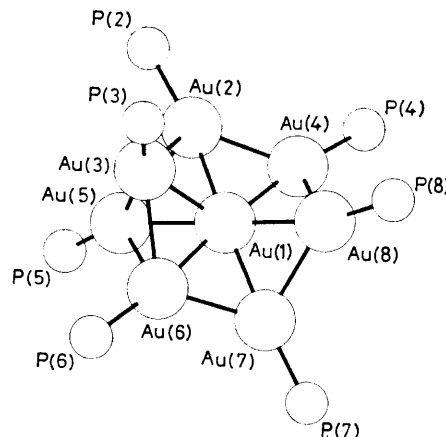


FIGURE 2. The Au-P skeleton of the $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ cluster.

L. In contrast with all other centred gold clusters, where a single resonance line could be assigned to the central gold atom, no separate resonance line could be observed for the central atom in either of these compounds, indicating that the Mössbauer parameters of Au_{centr.} are almost the same as those of the peripheral gold atoms.⁸

The reported reactivity¹ of $[\text{Au}_6\text{L}_8]^{3+}$ towards Lewis bases is puzzling in view of the screening by co-ordinated phosphines; we therefore assume that the active species in these reactions is the $[\text{Au}_6\text{L}_7]^{2+}$ cluster, formed by a dissociation of $[\text{AuL}]^+$. The crystal-structure determination clearly shows an exposed central gold atom which should be sensitive to nucleophilic attack. Therefore the reactions of the $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ cluster are now being explored.⁹

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