Synthesis and *X*-Ray Characterization of an Iodine-bridged Tetranuclear Gold Cluster, Di-μ-iodo-tetrakis(triphenylphosphine)-*tetrahedro*-tetragold

By FRANCESCO DEMARTIN, MARIO MANASSERO,* LUCIANA NALDINI,* RUGGERO RUGGERI, and MIRELLA SANSONI
(*Istituto di Chimica Generale ed Inorganica, Università degli Studi, Via G. Venezian* 21, 20133 *Milano, Italy*)

Summary The reaction of $[Au_9(PPh_3)_8][NO_3]_3$ with KI in acetone yields $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$, which has been shown by *X*-ray crystallography to contain a tetrahedral gold cluster connected to four terminal triphenylphosphine groups and two edge-bridging iodine ligands; the latter bonding mode is novel for gold clusters.

RECENT developments in the chemistry of gold cluster compounds have led to the synthesis and *X*-ray characterization of $[Au_8(PPh_3)_8]X_2$ (X = alizarinsulphonate,[1] or PF_6[2]), $[Au_5(dppmH)_3(dppm)][NO_3]_2$ [dppmH = bis(diphenylphosphino)methane],[3] and $[Au_9(PCy_3)_5(SCN)_3]$ (Cy = cyclohexyl).[4] We describe here the synthesis and *X*-ray structure determination of $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$, (**1**), the first tetranuclear gold cluster to be reported, and compare its stereochemistry and electronic structure with those of the pentanuclear cation $[Au_5(dppmH)_3(dppm)]^{2+}$ (**2**).[3]

Compound (**1**) was prepared by reaction of $[Au_9(PPh_3)_8][NO_3]_3$[5] and KI in acetone in a molar ratio of 1 : 4. After *ca.* 30 min, a pale yellow precipitate was obtained, which was recrystallized from $CHCl_3$–acetone. The reaction is reproducible and the overall yield is *ca.* 15% with respect to gold. Both the elemental analysis and the diamagnetism of the novel compound are in accordance with the formulation of $Au_4I_2(PPh_3)_4$, which was established by a single-crystal *X*-ray diffraction study.

Crystal data: $C_{72}H_{60}Au_4I_2P_4$, $M = 2090{\cdot}3$, pale yellow air-stable monoclinic prisms, space group $C2/c$ (after refinement), $a = 12{\cdot}989(4)$, $b = 26{\cdot}042(11)$, $c = 20{\cdot}543(5)$ Å, $\beta = 107{\cdot}25(2)°$, $U = 6636$ Å^3, $Z = 4$, $D_m = 2{\cdot}11$, $D_c = 2{\cdot}09$ g cm^{-3}, μ(Mo-K_α) = 101·7 cm^{-1}. Intensity data were collected on our BASIC diffractometer with graphite-monochromated Mo-K_α radiation in the 2θ range 6—50°. The structure was solved by conventional Patterson and Fourier methods on the basis of 3289 independent, absorption-corrected reflections having $I \geqslant 4\sigma(I)$. Block-matrix least-squares refinement, with anisotropic thermal parameters for Au, I, and P atoms, and with the phenyl rings constrained to D_{6h} geometry, led to a current *R* value of 0·033.†

The molecular structure of $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$, of crystallographic C_2-2 symmetry, is shown in Figure 1. It is based on an $Au_4(\mu\text{-}I)_2P_4$ core of D_{2d}–$\bar{4}m2$ idealized symmetry, with the iodine ligands doubly bridging opposite edges of the metal tetrahedron, and the terminal phosphine groups connected to the same edges in an essentially linear manner. The latter feature is probably responsible for these two edges being significantly shorter than the other four[6] [2·649 and (mean) 2·793 Å, respectively]. Other important bond parameters are: Au(1)–I 2·968(1), Au(2)–I 2·922(1), Au(1)–P(1) 2·289(3), Au(2)–P(2) 2·292(3), P–C(average) 1·826 Å, ∠Au(1)–Au(2)–P(2) 176·3(1), Au(2)–Au(1)–P(1) 174·0(1)°

† 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.

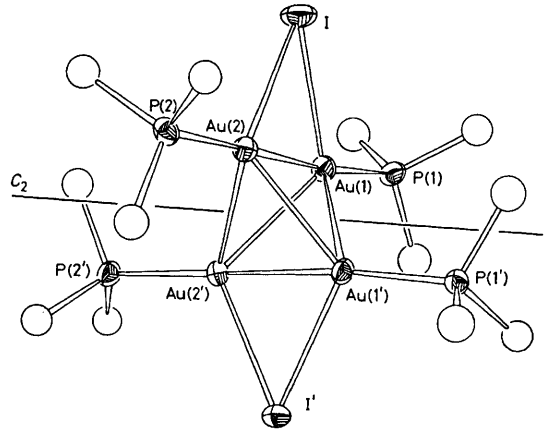
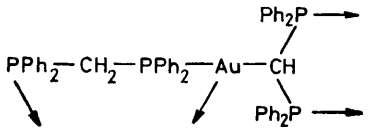


FIGURE 1. ORTEP view of the structure of $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$. Metal–metal bond lengths are: Au(1)–Au(2) 2·649(1), Au(1)–Au(1′) 2·744(1), Au(2)–Au(2′) 2·771(1), Au(1)–Au(2′) [=Au(1′)–Au(2)] 2·828(1) Å.

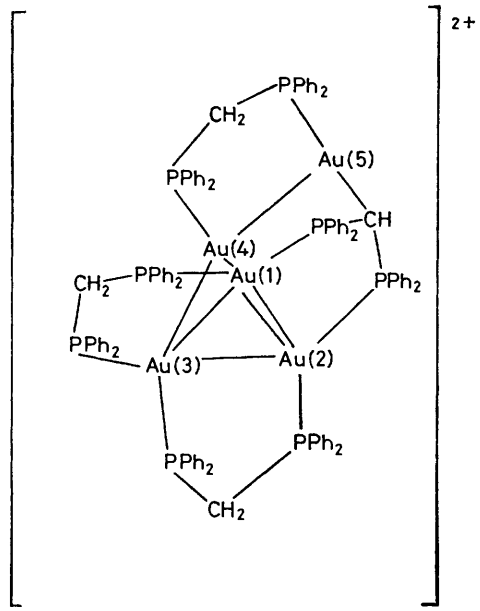
The Au–Au and Au–P contacts are in the range usually found in gold–phosphine cluster compounds (see ref. 1 and references therein), while the Au–I distances (mean 2·945 Å) are much longer than in $Au_{11}I_3[P(p\text{-}FC_6H_4)_3]_7$ [Au–I 2·600(5) Å][7] in which, however, the iodine ligands are terminal. Comparably long metal–iodine bridges can be found in both the chair-like and cubane-like forms of $[Ag_4I_4(PPh_3)_4]$ [Ag–I in the range 2·724(1)—3·037(2) Å].[8]

$[Au_4(\mu\text{-}I)_2(PPh_3)_4]$ is the first example of a gold cluster bearing monodentate bridging ligands. This feature is of interest when considering that a tetrahedral metal core of gold atoms has also been found in the recently reported cation (**2**),[3] where two (bridging) bidentate dppmH ligands and one (bridging and chelating) tetradentate group (X)



(X)

are present (see Figure 2). Although the steric bulk and the electron-donor ability of some of the ligands are widely different in the two species, the overall bonding arrangements in the two tetrahedra are very similar, two ligand atoms being co-ordinated to each gold atom of the tetrahedral clusters (see Figure 2). Thus, the two tetrahedra may be considered to be isoelectronic and each to contain 58 valence electrons, provided that an Au(5)→Au(4) dative bond is assumed in cation (**2**)[9] [in both compounds 42 e⁻ would be contributed by the tetrahedral cluster (formally Au_4^{2+}) and 16 e⁻ by the ligands; substantially different electron countings, while being possible in both cases, seem less probable].



(2)

FIGURE 2. Line drawing of $[Au_5(dppmH)_3(dppm)]^{2+}$ (ref. 3).

Finally, it is to be noted that the structure of $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$ provides further evidence that the chemistry of gold cluster compounds is not limited to those species in which the linear co-ordination of gold is largely dominant.

We thank the Italian C.N.R. for financial support.

(*Received*, 24*th November* 1980; *Com.* 1249.)

[1] M. Manassero, L. Naldini, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1979, 385.
[2] F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik, and P. T. Beurskens, *J. Chem. Soc., Chem. Commun.*, 1979, 387.
[3] J. W. A. Van der Velden, J. J. Bour, F. A. Vollenbroek, P. T. Beurskens, and J. M. M. Smits, *J. Chem. Soc., Chem. Commun.*, 1979, 1162.
[4] M. K. Cooper, G. R. Dennis, K. Henrick, and M. McPartlin, *Inorg. Chim. Acta*, 1980, **45**, L151.
[5] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *Chem. Commun.*, 1971, **1423**; F. Cariati and L. Naldini, *J. Chem. Soc., Dalton Trans.*, 1972, 2286.
[6] The role played by the phosphine ligands in determining strong linear gold–gold and gold–phosphine bonding has been discussed in detail by D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1976, 1163.
[7] P. L. Bellon, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1972, 1481.
[8] B. K. Teo and J. C. Calabrese, *Inorg. Chem.*, 1976, **15**, 2474.
[9] A Pt→Pt dative bond between dppmH-bridged platinum atoms has recently been reported in the structure of $[Pt_2Me_3(\mu\text{-dppmH})_2][PF_6]$: A. A. Frew, L. Manojloviç-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1980, 624.