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A New Class of Gold Cluster Compounds. Synthesis and X-Ray Structure of the Octakis(triphenylphosphinegold) Dializarinsulphonate, $[Au_8(PPh_3)_8](aliz)_2$

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Summary $[Au_9L_8]^{3+}$ (L = PPh_3) reacts with L to give the new dication $[Au_8L_8]^{2+}$; an X-ray analysis of $[Au_8(PPh_3)_8](aliz)_2$ (aliz = alizarinsulphonate) shows that the central gold atom, while still displaying the usual short interactions with all the peripheral metal atoms, is no longer confined in an entirely metallic cage, but is also directly bonded to a phosphine ligand.

GOLD cluster compounds, whose structures have been unequivocally elucidated by X-ray crystallography, can be divided in two distinct types: (a) compounds represented by the $Au_{11}L_7X_3$[1] and $[Au_9L_8]Y_3$[2] species (where L = PPh_3 or p-substituted triarylphosphines; X = I, CN, or SCN; and Y = NO_3, PF_6, ClO_4, *etc.*) which are characterized by the presence of a central gold atom encapsulated in an entirely metallic cage, with the phosphine ligands terminally bonded to the peripheral metal atoms, and (b) those represented so far by $[Au_6L_6](BPh_4)_2$,[3] in which the metal atoms of the six AuL species lie at the vertices of a distorted octahedron, and do not incorporate another gold atom, thus obtaining an overall ligand : metal ratio of 1 : 1. We now report (i) the synthesis of a series of new compounds, $[Au_8L_8]Y_2$ [L = PPh_3; Y = NO_3, picrate (pic), alizarinsulphonate (aliz), PF_6, ClO_4, or BPh_4], which are the first examples of a third type of gold clusters, characterized by structural features intermediate between those of the types (a) and (b) and (ii) the X-ray structure of one of them (Y = aliz).

Complex $[Au_8L_8]^{2+}$ (L = PPh_3) was obtained in solution by treating $[Au_9L_8](NO_3)_3$ with an excess of L in methanol, and precipitated as $[Au_8L_8](NO_3)_2{\cdot}8H_2O$ by addition of diethyl ether. The yield of the reaction is *ca.* 80% based on $[Au_9L_8](NO_3)_3$, and no other clusters have been detected in the mother liquor.† The complex is recrystallized from CH_2Cl_2 and diethyl ether, and the corresponding picrate, alizarinsulphonate, hexafluorophosphate, perchlorate, and tetraphenylborate were obtained by metathetical exchange. The compounds were formulated as $[Au_8L_8]Y_2$ on the basis of elemental analysis, conductivity measurements, crystallographic determination of the molecular weight (for Y = NO_3, pic, and aliz), and ^1H n.m.r. spectroscopy (Y = pic, in which the ratio of the signal areas of PPh_3 : pic is *ca.* 30 which is in accordance with the above formulation). At this stage, the proposed stoicheiometry of the cation could justify at least three different types of compounds: (i) an uncentred cluster (considered rather unlikely on the basis of previous M.O. calculations[4]), (ii) a metallic cluster stabilized by a central heteroatom,[4] and (iii) a gold-centred species displaying an unusual L : Au ratio. The last hypothesis has been proved correct by an X-ray structure analysis of $[Au_8L_8](aliz)_2$.

Crystal data: $C_{172}H_{134}Au_8O_{14}P_8S_2$, M 4312, deep red orthorhombic prisms, space group $Pbc2_1$ (non-standard setting of $Pca2_1$, no. 29) after refinement, a = 25·28(1), b = 17·90(1), c = 34·61(2) Å, U = 15660 Å^3, D_m = 1·84(2), D_c = 1·83 g cm^{-3} for Z = 4.

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† In particular, we have no evidence for the formation of $[Au_9L_{10}]^{3+}$, recently reported (F. A. Vollenbroek, J. J. Bour, J. M. Troosters, and J. W. A. van der Valden, *J.C.S. Chem Comm.*, 1978, 907) as the only product of the same reaction carried out in methylene chloride.

Data were collected on a BASIC diffractometer[5] with graphite-monochromatized Mo-K_α radiation up to $2\theta = 48°$. The structure was solved by conventional Patterson and Fourier methods on the basis of 3120 independent reflections having $\sigma(I)/I \leqslant 0{\cdot}25$. A block-matrix least-squares refinement, in which the anions are not included, the phenyl rings are constrained in D_{6h} symmetry, and the anisotropic thermal vibration of gold atoms is taken into account, gave a current R value of 0·081.‡

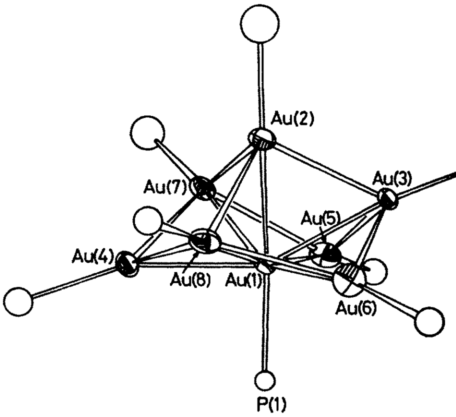

FIGURE 1. Perspective view of the Au_8P_8 fragment in $[Au_8(PPh_3)_8]^{2+}$. Principal bond parameters are (e.s.d.s not stated for mean values): Au(1)–Au(2), 2·587(5); Au(1)–Au(3), 2·723(5); Au(1)–Au(4), 2·718(5); Au(1)–Au(5), 2·771(5); Au(1)–Au(6), 2·672(5); Au(1)–Au(7), 2·746(5); Au(1)–Au(8), 2·726(5); Au(periph.)–Au(periph.), 2·878; Au(1)–P(1), 2·38(2); and Au-(periph.)–P, 2·30 Å; ∠Au(2)–Au(1)–P(1), 175·8(6) and ∠Au(1)–Au(periph.)–P, 171·3°.

The structure of the dication (Figure 1) shows that (i) $[Au_8L_8]^{2+}$ is still a gold-centred cluster, (ii) the overall 1 : 1 ligand : metal ratio observed is achieved through the bonding of one phosphine group to each gold atom, including the central one, and (iii) the central gold atom is also linearly bonded to the gold atoms of seven AuL species, thus reaching the co-ordination number of eight. The resulting co-ordination polyhedron around the central atom may be described as a deformed cube whose largest distortion is due to the different lengths of the Au–Au and Au · · · P edges (mean values 2·88 and 3·59 Å, respectively). Alternatively, the overall metal atom arrangement can easily be related to those found in the already known Au_9 and Au_{11} clusters as shown in Figure 2, which also shows the chair-like hexagon, of icosahedral derivation,[1,2] which remains nearly unaltered in the three species.

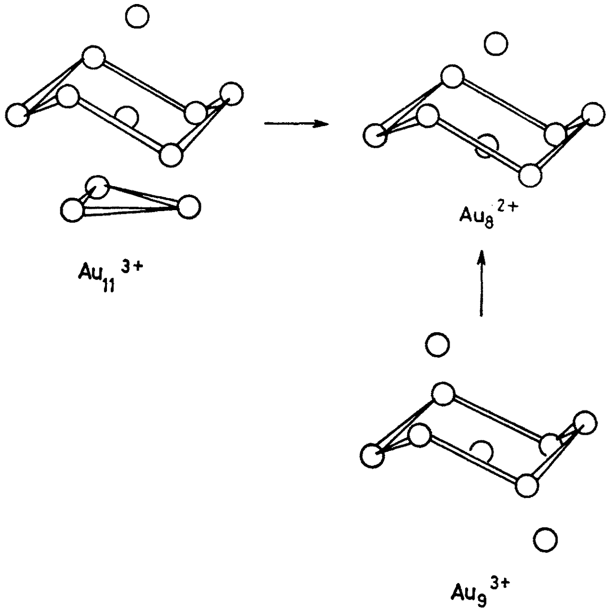

FIGURE 2

The $[Au_8L_8]Y_2$ salts belong, therefore, to a novel class of gold cluster compounds, whose peculiar feature is the presence of a central gold atom directly bonded not only to all the other metal atoms, but also to a phosphine ligand. The metal–metal bond distances display the usual pattern, the centre-to-periphery ones being distinctly shorter than those in the periphery (mean values 2·706 and 2·878 Å, respectively). It is of interest to compare the Au(1)–P(1) bond length [2·38(2) Å] with the mean Au–P distance in the periphery (2·30 Å). The lengthening observed reflects both the lower availability of the Au(1) orbitals for this interaction, and the probable presence on Au(1) of a higher positive charge, a common feature of the central gold atom in both the Au_{11} and Au_9 clusters.[4,6] Finally, the Au(1)–Au(periph.)–P interactions are essentially linear, with minor deviations which can be attributed to the bulky nature of the ligands.

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‡ The atomic co-ordinates for this work 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.

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