Novel Gold Clusters. Preparation, Properties, and X-Ray Structure Determination of Salts of Octakis(triarylphosphine)enneagold, [Au9L8]X3

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Summary A series of uni–ter-valent electrolytes of general formula [Au9L8]X3 has been prepared and characterized; preliminary X-ray structural results are reported for the salt [Au9{P(C6H4-*p*-Me)3}8][PF6]3.

THE synthesis and properties of a number of gold cluster compounds of general formula $Au_{11}X_3L_7$ (X = CN, SCN, I; L = tris-*para*-substituted-phenylphosphine) have been reported.[1] We now report preliminary results for a novel series of gold cluster compounds: the salts [Au9L8]X3 (L as above, X = NO3, PF6, or picrate).

The nitrate derivatives are obtained by reaction of ethanolic solutions of LAuNO3 with NaBH4 (mol. ratio 1 : 0·25). Green crystals separate when the mixture is set aside, which give analytical data consistent with the formulation [Au9L8][NO3]3. The hexafluophosphates and picrates are obtained by metathesis from the corresponding nitrates and give analytical data in accord with the general formula above. The stoicheiometry of the picrate derivatives has also been determined by comparison of the areas of the n.m.r. peaks due to the phosphine and the anion protons.

All the compounds of this family are diamagnetic. Conductivity measurements in solution for the picrates and hexafluophosphates are consistent with the behaviour expected for uni–ter-valent electrolytes. The salt–like nature of solid nitrates and hexafluophosphates is shown by the presence of characteristic i.r. bands of the anions.

Crystal data: [Au9{P(C6H4-*p*-Me)3}8][PF6]3 forms deep green tetragonal crystals: $a = 20\cdot31(1)$, $c = 20\cdot34(1)$ Å, $U = 8390(12)$ Å³; $D_m = 1\cdot84(2)$, $D_c = 1\cdot836$ g cm⁻³ for $Z = 2$. The observed extinctions (0*kl* for $k + l \neq 2n$) are consistent with either of the space groups $P4_2nm$ (No. 102), $P\bar{4}n2$ (No. 118) or $P4_2/mnm$ (No. 136). The structure determination is based upon 1292 symmetry independent reflections measured by counter methods, $\sigma(I)/I < 0\cdot25$.

The vector map was interpreted in terms of an Au9 cluster with essentially *mmm* symmetry, which could lie around the special positions a (*mm*), d (222), or a (*mmm*) of space groups No. 102, 118, or 136, respectively. This report is based upon the assumption that space group No. 118 is correct and that the Au9P8 fragment possesses 222 symmetry.†

Electron density maps gave the positions of most of the remaining atoms; the phosphine ligands and the anions appear to be rather disordered. A full interpretation of this disorder is not available at present.

The result of the preliminary least-squares refinement (*R* 0·07) is shown in the Figure (a). The metal atom cluster does not significantly depart from *mmm* symmetry; the central atom is bonded only to peripheral gold atoms and has a co-ordination number 8. There are two crystallographically independent centre-to-periphery distances,
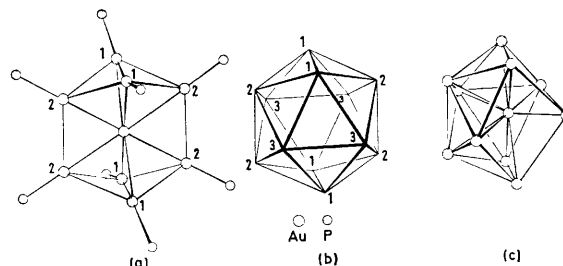

FIGURE. (a) *Structure of the* Au9P8 *fragment in* [Au9{P(C6H4-*p*-Me)3}8][PF6]3. (b) *Apices of the ideal icosahedron labelled to show three equatorial rectangles.* (c) *Structure of* Au11 *clusters.*

2·689(3) and 2·729(3) Å. Each peripheral metal atom is bonded to the central atom, to a phosphine ligand [Au–P mean distance 2·30(1) Å] and to three more peripheral atoms; the Au–Au distances in the periphery are in the range 2·752(3)—2·868(3) Å, with a mean value (2·805 Å) which is shorter than that (2·884 Å) found in the metal.[2]

The geometry of this cluster is that of a centred icosahedron from which one equatorial rectangle has been removed. [In the Figure (b) an ideal icosahedron is orientated as in the Au9P8 moiety; the missing equatorial rectangle is defined by the four apices with label 3].

A qualitative examination of the molecular transform of some of the picrate and nitrate derivatives of this class shows that essentially the same metal atom cluster as in [Au9{P(C6H4-*p*-Me)3}8][PF6]3 is present in all of them. [Au9L8]³⁺ cations represent, therefore, the second well established class of gold cluster compounds. The structure of the first class, *viz.* the molecular compounds $Au_{11}X_3L_7$, has been characterized.[3,4] Au11 clusters may also be derived from a centred icosahedron in which three apices, defining one face, are replaced by a single gold atom [see Figure (c)].

The interpretation of the electronic structure of Au11† clusters has been based upon the assignment of the rare-gas configuration to the central gold atom.‡ The stoicheiometry and the structure of the novel cations, however, do not establish a simple, general rule for the stability of gold clusters in terms of the effective atomic number of the

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† The assumption of either of the space groups 102 or 136 would require *m* symmetry for all the phosphine ligands.

‡ In Mason's interpretation, the central gold atom (Au⁰) achieves the radon configuration by one-electron donation from each of seven peripheral Au⁰ atoms (see ref. 3). We interpreted the smaller atomic radius of the central atom, as compared to the peripheral ones, by assigning to that atom the total oxidation state of the metal cluster (+3); the central Au^III then needs ten Au⁰ neighbours to reach the radon configuration (see ref. 4).

central atom. In discussing the structure of Au_{11} clusters[4] we have pointed out that the centred icosahedral pattern, which is commonly found in intermetallic compounds, arises from (i) the existence, in the cluster, of two kinds of metal atoms, with different atomic radii§ and (ii) the essentially bonding character of the peripheral interactions. Both conditions, and especially the latter, are met in the novel cations; one might describe their geometry as derived from the centred cube through a deformation such that the shortest peripheral interactions are obtained.

§ In the ideal icosahedron, the central cavity has a radius 0·9 times smaller than that of the twelve peripheral contacting spheres.

[1] F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 1971, 172.
[2] W. B. Pearson, 'Lattice Spacings and Structures of Metals and Alloys,' Pergamon, London, 1951.
[3] M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 1969, 334.
[4] V. G. Albano, P. L. Bellon, M. Manassero, and M. Sansoni, *Chem. Comm.*, 1970, 1210.