Novel Cluster Complexes of Gold(0)–Gold(I)

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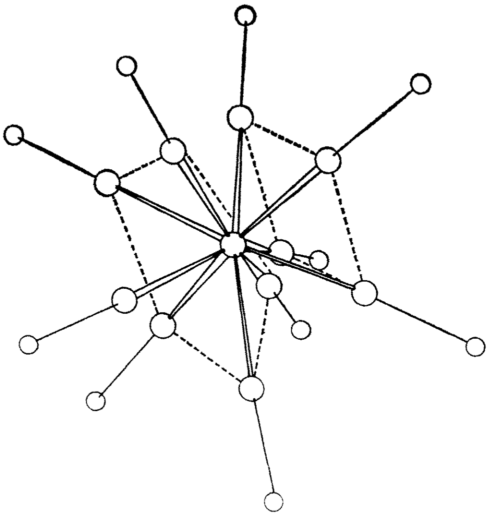
THE synthesis of a number of gold(0)–gold(I) polynuclear complexes of unusual stoicheiometry has been reported.[1,2] The stoicheiometries suggested that the structures of these complexes might be based on clusters of three, five,[1] and six[2] gold atoms although *X*-ray studies now indicate that a number of the compounds may be much more complex.

A triphenylphosphine (L) complex which, on the basis of analytical data, was believed to be $Au_6L_4(CNS)_2$, crystallises *in the* space group $P2_1/c$ with $a = 18{\cdot}00$, $b = 26{\cdot}50$, $c = 31{\cdot}59$ Å, $\beta = 122{\cdot}2°$. All $\{hkl\}$ reflexions for $l = 2n + 1$ are very weak and a structure analysis has therefore been based on the simple cell which has $c = 15{\cdot}80$ Å and the space group $P2_1/m$. Weakly diffracting crystals provided integrated intensities of 1562 independent reflexions (Pailred automatic diffractometer; $F_0^2/\sigma(F_0^2) \geqslant 2{\cdot}0$). In $P2_1/m$ the complex is required to have C_s symmetry (this corresponds to an 'averaging' of the positions of a number of ligand light-atoms). Vector and difference Fourier methods showed the position of eleven gold atoms and ten ligands; least-squares refinement of these parameters give a reliability index of 0·15 and the carbon and nitrogen atoms of the ligands have not yet been located. However the location of all heavy atoms (Au, P, and S) is sufficient to establish the existence of an entirely novel cluster (Figure).

A central gold atom is surrounded, at an average distance of 2·67 Å (σ 0·02 Å), by ten remaining gold atoms each of which has one ligand attached to it. There is a striking resemblance between the symmetry of the co-ordination sphere of the central gold atom and the deca-co-ordination established for several lanthanum(III) complexes.[3] The co-ordination polyhedron can be described approximately as a combination, by apex sharing, of a pentagonal bipyramid and square pyramid with gold atoms at all vertices (the shared apex is the ten-co-ordinate central gold atom). The symmetry plane is defined by the two axial atoms of the bipyramid and one of the diagonals of the square pyramid.



FIGURE

The analytical data together with the recognition of eleven gold atoms and only ten ligands provides the formula of the cluster as $Au_{11}(PPh_3)_7(SCN)_3$ (D_m 2·20 ± 0·02, D_c 2·17 g. cm.$^{-3}$). The structure of the complex can be understood in a simple and perhaps naïve way; metal–metal bonds are postulated only between the central gold atom and its ten neighbours (the minimum peripheral gold–gold distance is 2·83 Å); the central, formally Au^0, atom then achieves a rare-gas configuration by one-electron donation from each of the seven peripheral Au^0 atoms. The reason for the structural similarities with La^{III} follows from the identical valence-shell configurations. Each of the peripheral gold atoms has a linear stereochemistry (again ignoring the possibility of metal–metal bonds on the periphery of the cluster), as would be expected for ions which all formally have a d^{10} configuration. It has been pointed out previously that $d^{10}s^1$ atoms such as Au^0 have unusually high electronegativities and readily form metal–metal bonds; there are a number of examples in which triphenylphosphinegold(0) may be thought of as a one-electron donor to the central metal.[4]

Our results suggest that other clusters having the formulae $[Au_nL_{n-1}]^{(n-8)+}$ should exist. A complex, formulated on the basis of analytical data as $Au_9L_8,3PF_6$, crystallises in the space group *Pbcn* with $a = 81{\cdot}56$, $b = 18{\cdot}84$, $c = 26{\cdot}98$ Å. D_m is 2·04 g. cm.$^{-3}$ and, in view of the above structural comments, the probable molecular unit is $Au_{13}L_{12}(PF_6)_5$ occupying a general position in the space group (D_c 2·06 g. cm.$^{-3}$). The detailed stereochemistry of this cluster is under investigation, but we can anticipate the results by analogy with the established icosahedral symmetry of dodeca-co-ordination.[5] The existence of other clusters such as $Au_{10}L_7X_2$ and $Au_{12}L_7X_4$ is predicted.

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[1] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Co-ord. Chem. Rev.*, 1966, 1255.
[2] L. Naldini, F. Cariati, G. Simonetta, and L. Malatesta, *Chem. Comm.*, 1966, 647.
[3] M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 1611; D. B. Shinn and H. A. Eick, *Inorg. Chem.*, 1968, **7**, 1340; A. L. Al-Karaghouli and J. S. Wood, *J. Amer. Chem. Soc.*, 1968, **90**, 6548; N. L. Norrow and L. Katz, *Acta Cryst.*, 1968, **24** *B*, 1466.
[4] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741; J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 5035; B. T. Kilbourn, R. L. Blundell, and H. M. Powell, *Chem. Comm.*, 1965, 444.
[5] E. L. Muertterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 173.