Preparation and Structure of the Hexakis(tris-*p*-tolylphosphinegold) Salt of Tetraphenylborate and Electronic Structure of Gold Cluster Compounds

By P. L. Bellon,* M. Manassero, L. Naldini, and M. Sansoni

(*Istituto di Chimica Generale ed Inorganica, Universita' degli Studi,* 21, *via G. Venezian,* 20133 *Milano, Italy*)

Summary The structure of the $[AuPAr_3]_6^{2+}$ cation is reported and an interpretation of the electronics of gold cluster compounds is proposed; the latter is parallel to current interpretations for boranes, carboranes and metal-carbonyl clusters.

When $NaBH_4$ is added to an ethanolic suspension of $Au(NO_3)P(tol)_3$ (where tol = *p*-tolyl) in a 1:4 molar ratio, the white solid slowly dissolves and a red solution results. Upon addition of sodium tetraphenylborate, red crystals separate whose chemical and crystallographic characterisation is presently being completed. The mother liquor produces, on standing, a few yellow crystals. This species, obtained in very low amount, has been characterised by an *X*-ray structural analysis. It consists of the tetraphenylborate of the hexakis(tris-*p*-tolylphosphinegold) dication, $[AuP(tol)_3]_6[B(Ph)_4]_2$. Crystal data are: $a = 17{\cdot}48(3)$, $b = 19{\cdot}02(3)$, $c = 13{\cdot}82(2)$ Å, $\alpha = 101{\cdot}1(1)°$, $\beta = 94{\cdot}2(1)°$, $\gamma = 116{\cdot}4(1)°$, $U = 3912$ Å^3, $Z = 1$; D_m 1·56(3), D_c 1·55 g cm^{-3}; space group $P\bar{1}$. The structure has been solved by conventional Patterson and Fourier methods and refined to $R = 0{\cdot}053$ from 3074 independent, counter measured reflections.

The dication contains the distorted centrosymmetric octahedron Au_6, shown in Figure 1. The distortion corresponds approximately to a squeezing of the octahedron along a C_3 axis.

Electron counting in the novel cluster gives a total of 76 outer shell electrons, that is, 5 pairs fewer than the total count in a typical octahedral carbonyl cluster such as, say, $Rh_6(CO)_{16}$.[1] The difference can, in part, be explained if account is taken of the fact that Group Ib elements very often do not reach, in their compounds, an inert gas configuration. Typically, in octakis- and tetrakis-copper(I) clusters[2,3] each copper atom possesses an effective atomic number of 34. It can thus be assumed that Au^0 and Au^I atoms, in gold clusters, will be filling only 8 orbitals.

A crude interpretation of the electronics in the present cation is now proposed. In $[Au_6L_6]^{2+}$ each metal atom contributes one orbital to the Au–P bonds and is left with five non-bonding orbitals (of which four only will be filled) if three orbitals are contributed to the cluster MOs;[4] 74 out of 76 electrons will then be distributed as follows: 12 in the Au–P bonds, 48 in the non-bonding orbitals and 14 in seven cluster bonding orbitals[4] having the same symmetry properties as in $[B_6H_6]^{2-}$ (ref. 5) and in $M_6(CO)_{16}$ cluster compounds.[6] This assignment would lead to a hypothetical species $[Au_6L_6]^{4+}$; this, probably, will not be stable because of the high charge density; stated in a different way, the positive charge makes possible the occupation of one MO more, possibly an antibonding one. The latter point is consistent with the following arguments: (i) the mean Au–Au distance in the present cation is longer than the corresponding mean interactions on the 'surfaces' of the Au_{11} and Au_9 clusters (2·98 and 2·81 Å, respectively);[7,8] (ii) a *nido* structure would actually be expected for a six-membered eight skeletal bond pair system.[4]

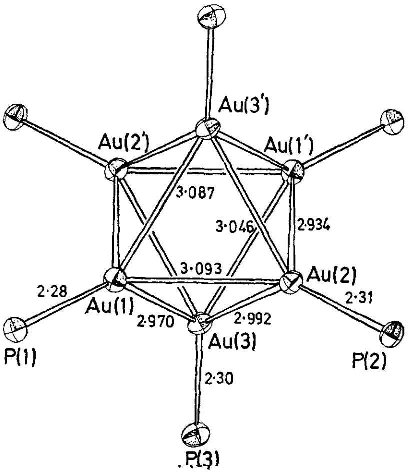

Figure 1. *View of the* Au_6P_6 *moiety. Mean e.s.d.'s are* 0·002 *and* 0·01 Å *for* Au—Au *and* Au—P *bonds, respectively.*

In an octahedral O_h cluster, if three appropriate orbitals per atom are combined, seven MO sets result which span, roughly in order of decreasing stability, the irreducible representations A_{1g}, T_{1u}, T_{2g}, T^*_{2u}, T^*_{1g}, T^*_{1u}, E^*_g; a diradical structure should therefore be expected for the present ion. We have not obtained enough salt to measure the magnetic susceptibility; however, the departure of the cluster from the ideal symmetry and the extent to which the degeneracy of T and E orbitals is removed is probably sufficient to allow a diamagnetic configuration to be reached.

The idea that a gold cluster is to be regarded as an electron deficient structure similar to boranes, carboranes, and carbonyl clusters suggests that the relation between electronics and topology recently proposed by Wade[4] should be applicable in this class of compounds, too. A rationalisation of the structure of a species such as $Au_{11}X_3(PAr_3)_7$ ($X = SCN^-$, I^- *etc.*)[7] is in fact rather straightforward once that the assumption is made that each gold atom has one empty non-bonding orbital. An Au_{11} cluster consists of a central Au^0 atom (the oxidation number is however immaterial) surrounded by a *closo* Au_{10} cage; according to Wade the cage is expected to be stabilized by 11 filled MOs. Actually the cage possesses 127 valence electrons and, if 20 electrons are used in the metal–ligand bonds and 80 more to fill all but 10 non-bonding orbitals, there remain 27 electrons to reach the total count, that is 5 electrons in excess of the 11 cluster bonding pairs. The role of the central atom is therefore to accept these extra electrons; in so doing, this atom, too, fills all but one of its orbitals. The situation is the reverse of that existing in carbido-carbonyl clusters [*e.g.* $Ru_6(CO)_{17}C$] in which a central carbon donates 4 electrons to the cluster.[9]

A *closo* Au_{10} cage should possess the same topology as $[B_{10}H_{10}]^{2-}$ and $B_8C_2H_{10}$, which is that of a dicapped archimedean antiprism. The actual structure of the cage is an incomplete icosahedron, but it can be derived from the dicapped anti-cube by simply stretching three edges, as shown in Figure 2. The rearrangement takes place in order to make the central cavity large enough to lodge the acceptor atom. It would seem appropriate to mention that simultaneous stretching of edges has been proposed to account for the rearrangements of mono- and di-substituted derivatives of $[B_{10}H_{10}]^{2-}$ (ref. 10). This fact suggests that the actual structure of the Au_{10} cage is to be regarded as an excited state of the dicapped anticube.

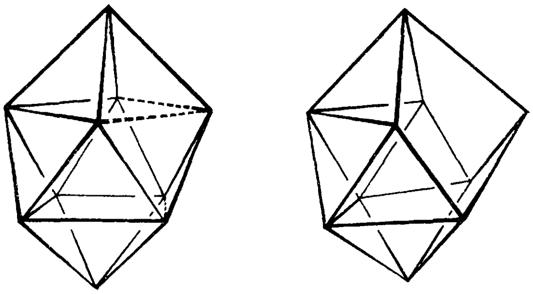

FIGURE 2. *Transformation of a dicapped archimedean antiprism* (*a*) (*left hand structure*) *into the incomplete icosahedral cage of* Au_{11} *clusters* (*b*) (*right hand structure*).

The electronics of the next class of gold clusters, the cations $[Au_8(PAr_3)_9]^{3+}$, is not simply rationalized in terms of Wade's scheme. Here again an incomplete icosahedron is centred by a gold atom;[8] however, the Au_8 cage is neither a *closo*, a *nido*, nor an *arachno* structure and this is probably an effect of ligand overcrowding. The central atom certainly plays the same role as in the Au_{11} species but its effective atomic number cannot be unambiguously assigned as in the previous example. If again this atom accepts 5 electrons, then an electron count allows 8 pairs to be allocated into cluster bonding MOs.

We thank Drs. V. Albano, F. Cariati, and D.M.P. Mingos for helpful discussions, and the National Research Council of Italy for financial support.

(*Received*, 9*th June* 1972, *Com.* 989.)

---

[1] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[2] L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, 1968, **90**, 7357.

[3] J. M. Guss, R. Mason, I. Sofolte, G. van Koten, and J. G. Noltes, *Chem. Comm.*, 1972, 447.

[4] K. Wade, *Chem. Comm.*, 1971, 792.

[5] W. N. Lipscomb, 'Boron Hydrides,' Benjamin, New York, 1963.

[6] P. Chini, *Inorg. Chim. Acta Rev.*, 1968, 31.

[7] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Chem. Comm.*, 1965, 212; F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 1971, **5**, 172; M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 1969, 334; V. G. Albano, P. L. Bellon, M. Manassero, and M. Sansoni, *ibid.*, 1970, 1210; P. L. Bellon, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1972, 1481.

[8] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc.* (*A*), 1968, 2865.

[9] A. Kaczmarczyc, R. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U.S.A.*, 1962, **48**, 729.

[8] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *Chem. Comm.*, 1971, 1423.