Structural Characterisation of $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ (Cy = cyclohexyl) and the Development of a Structural Principle for High Nuclearity Gold Clusters

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$[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ which has been synthesised in low yield from $Au(NO_3)(PCy_2Ph)$ and $NaBH_4$ has a toroidal geometry based on a hexagonal ring of edge- and face-sharing tetrahedra which share a common central vertex.

The first examples of gold phosphine clusters were described as fragments of centred icosahedra;[1] however the single crystal *X*-ray crysallographic analysis of $[Au_9\{P(C_6H_4OMeH\text{-}p)_3\}_8](BF_4)_3$[2] required a re-evaluation of this generalisation since it revealed that the gold atoms were arranged in a centred crown geometry with approximately D_{4d} symmetry. This observation, together with the recognition that the potential energy surfaces connecting alternative polyhedral geometries were soft, necessitated a broad classification of gold clusters according to their gross topologies, with toroidal clusters characterised by a total of $12n + 16$ electrons (n is the number of peripheral gold atoms), *e.g.* $[Au_9(PPh_3)_8]^{3+}$, and spherical clusters with a total of $12n + 18$ electrons, *e.g.* $[Au_{11}I_3(PAr_3)_7]$.[3] A more detailed structural generalisation was not permitted by the lack of examples of toroidal clusters since only Au_8 and Au_9 derivatives had been structurally characterised. This paper reports the structure of $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ (Cy = cyclohexyl), the first example of an Au_{10} cluster, and which has suggested a new structural principle for rationalising the geometries of high nuclearity gold clusters in the solid state.

The reaction of $Au(NO_3)(PCy_2Ph)$ with $NaBH_4$ in ethanol

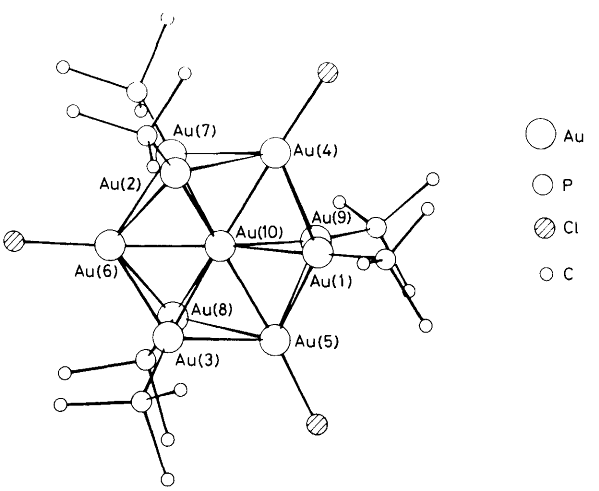
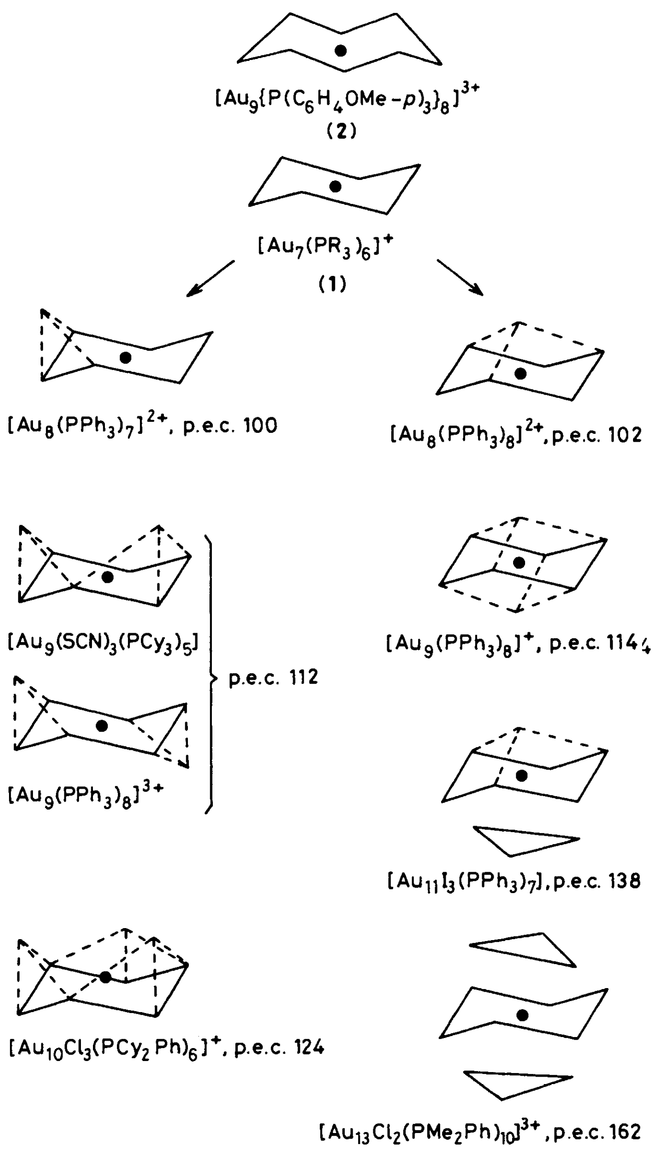


Figure 1. Molecular structure of the $[Au_{10}Cl_3(PCy_2Ph)_6]^+$ cation. For reasons of clarity the phenyl and cyclohexyl rings have been omitted. Important bond lengths include: Au(10)–Au(1) 2.712(2), Au(10)–Au(2) 2.740(2), Au(10)–Au(3) 2.733(2), Au(10)–Au(4) 2.674(1), Au(10)–Au(5) 2.669(1), Au(10)–Au(6) 2.666(1), Au(10)–Au(7) 2.703(2), Au(10)–Au(8) 2.728(2), Au(10)–Au(9) 2.729(2), Au(1)–Au(9) 2.738(2), Au(2)–Au(7) 2.748(2), Au(3)–Au(8) 2.744(2), Au(4)–Au(1) 2.941(2), Au(4)–Au(7) 2.890(2), Au(4)–Au(2) 2.814(2), Au(4)–Au(9) 2.849(2), Au(5)–Au(1) 2.868(2), Au(5)–Au(3) 2.866(2), Au(5)–Au(8) 2.925(2), Au(5)–Au(9) 2.840(2), Au(6)–Au(2) 2.897(2), Au(6)–Au(3) 2.869(2), Au(6)–Au(7) 2.910(2), and Au(6)–Au(8) 2.838(2) Å.

yielded a dark brown solid, which on recrystallisation from CH_2Cl_2–hexane led to a separation of $[Au_3O(PCy_2Ph)_3](NO_3)$ (yellow crystals, 25%) and $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ (red-brown crystals, 10%), both of which have been characterised by single crystal *X*-ray crystallographic determinations.†‡ Electronic spectral studies have indicated that $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ is formed in the recrystallisation process, but the initial cluster species has not been characterised.

$[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$ represents the first example of a ten-atom gold cluster and its skeletal geometry, which is illustrated in Figure 1, cannot be represented as a fragment of an icosahedron. It has a more open structure than those reported previously for ten-atom clusters, *viz.* bicapped square-antiprismatic, *e.g.* $[Rh_{10}S(CO)_{22}]^{2-}$,[5] tetra-capped octahedral, *e.g.* $[Os_{10}C(CO)_{24}]^{2-}$ [6] and $[Pd_{10}(CO)_{12}(PBu_3)_6]$,[7] and edge-shared bi-octahedral, *e.g.* $[Ru_{10}C_2(CO)_{24}]^{2-}$.[8] Although no crystallographic symmetry is imposed in the $[Au_{10}Cl_3(PCy_2Ph)_6]^+$ cation the central cluster core has approximately D_{3h} symmetry with 6 Au(PCy_2Ph) and 3 AuCl fragments arranged around the central gold atom in a circular fashion. The structure can be described as a hexagonal ring of six edge- and face-sharing $AuAu_3L_3$ tetrahedra which have a common central gold atom.[9] The observed toroidal topology for the Au_{10} cation is consistent with its polyhedral electron count of 124, *i.e.* $12n + 16$.[2,3]



Scheme 1. Left-hand side: toroidal clusters, polyhedral electron count (p.e.c.) $12n + 16$, edge-sharing AuL^+ fragments; right-hand side: spherical clusters, p.e.c. $12n + 18$, AuL^+ and Au_3L_3 fragments on 3-fold axis.

In $[Au_{10}Cl_3(PCy_2Ph)_6]^+$ the AuCl units occupy the higher-connectivity sites and the radial Au(10)–AuCl distances of 2.666(1)—2.674(1) Å are consistently shorter than the Au(10)–AuP distances of 2.712(1)—2.740(2) Å. Both effects can be attributed to the smaller steric requirements of the chloride ligands.[10] In common with other gold cluster compounds the radial Au–Au bond lengths are generally shorter than the peripheral Au–Au bond lengths which fall in the

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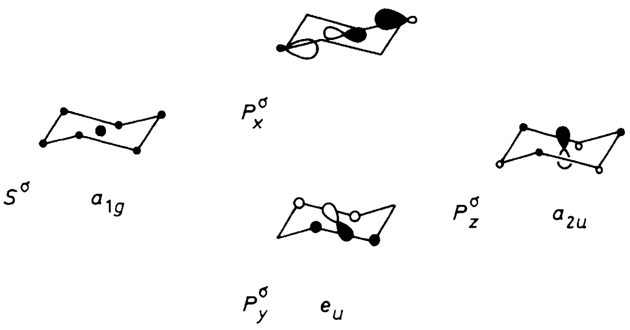
† Satisfactory chemical analyses were obtained for both compounds.

‡ *Crystal data:* $C_{108}H_{162}Au_{10}Cl_3NO_3P_6$, $M = 3784.3$, monoclinic, $P2_1/n$, $a = 16.118(2)$, $b = 28.807(8)$, $c = 26.902(8)$ Å, $\beta = 90.68(2)°$, $U = 12\,490$ Å^3, $D_c = 2.01$ g cm^{-3}, $Z = 4$, $F(000) = 7088$, μ(Mo-K_α) = 122.4 cm^{-1}. 13 770 reflections were measured on an Enraf-Nonius CAD4F diffractometer in the range $3.0 \leq 2\theta \leq 40°$. The structure was solved by a combination of direct methods, Patterson, and Fourier methods, and refined by blocked least-squares (Au, P, Cl anisotropic; C, N, O isotropic) to $R = 0.050$ for 6 824 unique observed reflections $[F \geq 3\sigma(F)]$.

The atomic co-ordinates for this structure 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.

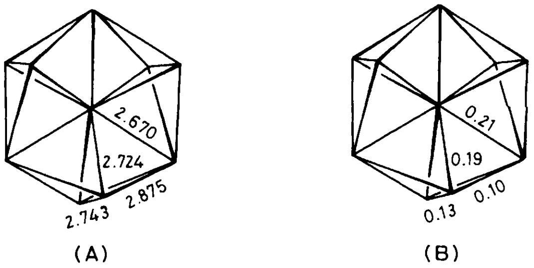
The single crystal *X*-ray analysis of $[Au_3O(PCy_2Ph)_3](NO_3)$ revealed that the cation had essentially the same molecular structure as those reported for $[Au_3X(PPh_3)_3]^+$ (X = O, S, or Se).[4]



Scheme 2.

range 2.738(2)—2.941(2) Å, and emphasise the greater importance of the radial Au–Au bonding interactions.[11]

The structural determination of $[Au_{10}Cl_3(PCy_2Ph)_6]^+$ and semi-empirical molecular orbital calculations[12] have highlighted a structural generalisation which rationalises the observed solid-state structures of centred gold clusters. With the exception of $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8]^{3+}$ (**2**) which has a centred crown arrangement the observed structures of the gold clusters can be derived by adding AuL fragments to the hypothetical centred chair cluster $[Au_7(PR_3)_6]^+$ (**1**) (see Scheme 1). The toroidal clusters $[Au(AuPR_3)_n]^{x+}$ shown on the left-hand side side of this scheme are characterised by a total of $12n + 16$ electrons and are derived from (**1**) by adding AuL fragments to three-atom gold sequences along the periphery of the cluster. In contrast the spherical clusters on the right-hand side of Scheme 1 are characterised by $12n + 18$ electrons and are derived from (**1**) by the addition of either AuL or Au_3L_3 triangular fragments along the three-fold axis. This electronic and structural difference can be understood in terms of the molecular orbital calculations which have been performed on the clusters in Scheme 1 and by reference to the skeletal molecular orbitals of (**1**) and (**2**). The calculations[12] have demonstrated that (**1**) and (**2**) have a total of three bonding skeletal molecular orbitals; $S^\sigma(a_{1g})$, P_x^σ, P_y^σ (e_{1u}); and one antibonding skeletal molecular orbital; P^σ (a_{2u}) (in Stone's notation[13]) (Scheme 2). The edge-bridging $AuPR_3^+$ fragments are characterised by a single empty hybrid orbital of a_1 symmetry.[12] The location of this fragment (or an Au_3P_3 fragment which has an a_1 combination of hybrid orbitals) along the three fold axis of (**1**) stabilises the antibonding P_z^σ (a_{2u}) molecular orbital and results in a total of four skeletal molecular orbitals and a total electron count of $12n + 18$. The maintenance of three skeletal molecular orbitals can only be achieved if the $AuPR_3^+$ fragments minimise their interactions with P_z^σ (a_{2u}) and interact strongly with S^σ (a_{1g}), P_x^σ and P_y^σ (e_u). This is most effectively achieved by adopting the edge-bridging configurations illustrated on the left-hand side of Scheme 1. An analogous series of clusters based on the Au_9 centred crown cluster are clearly also possible on this basis of the orbital topologies although they are electronically less favoured because of the fewer number of gold–gold interactions.



(A) (B)

(A) average bond lengths/Å; (B), overlap populations.

Besides providing a rationalisation of the gross polyhedral geometries the M.O. calculations have provided a more detailed understanding of the trends in the Au–Au bond lengths in these clusters as the comparison of (B) computed overlap populations and (A) observed bond lengths indicates.

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