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A New Structural Motif of Gold Clustering at Oxide Centers in the Dication $[Au_6O_2(PMe_3)_6]^{2+}$

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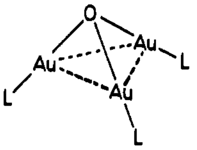
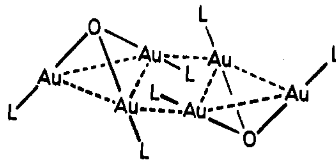
Aggregation of gold at small interstitial atoms is currently attracting considerable interest owing to the unusual facets of structure and bonding encountered for both the centroid element and the metal atoms in the resulting clusters.[1,2] Hypercoordinate carbon[3-12] and nitrogen[13-17] in octahedra and trigonal bipyramids of gold atoms have been detected in cationic complexes of the types $[(LAu)_6C]^{2+}$, $[(LAu)_5C]^+$, and $[(LAu)_5N]^{2+}$ with L representing mostly a tertiary phosphine like Ph_3P. Some of these results are finally confirming earlier theoretical predictions,[18] while others had not been foreseen: Intriguing nonclassical structures have even been found for complex cations with standard coordination numbers, as in the arsonium cation $[(LAu)_4As]^+$, where a square pyramidal geometry is present[19] instead of a tetrahedral array of four gold atoms.

For oxygen, the gold aggregation seemed to follow a more conventional pattern. The few trigold oxonium salts described to date[20-23] were found to contain cations $[(LAu)_3O]^+$ with a standard trigonal pyramidal structure. In the solid state, these were loosely associated through parallel edge–edge contacts with Au···Au distances of ca. 3.10 Å (**A**, **B**). In pertinent discussions of these structures it was overlooked, however, that the bulky ligands L employed in all of these cases render a more extended cluster formation in these oxide complexes impossible.



A



B

In an extension of the earlier studies, the smallest possible tertiary phosphine, Me_3P, has therefore been introduced as a ligand L, in order to detect intrinsic cluster geometries not codetermined by steric effects.

The reaction of chloro(trimethylphosphine)gold(I) with silver oxide and sodium tetrafluoroborate in tetrahydrofuran at 20 °C gives high yields (71%) of a colorless product (decomposition temperature 156 °C; from dichloromethane/pentane):

$$6Me_3PAuCl + 2Ag_2O + 2NaBF_4 \rightarrow 4AgCl + 2NaCl + [(Me_3PAu)_6O_2](BF_4)_2$$

The composition of the product is readily confirmed by its elemental analysis and by field desorption mass spectrometry

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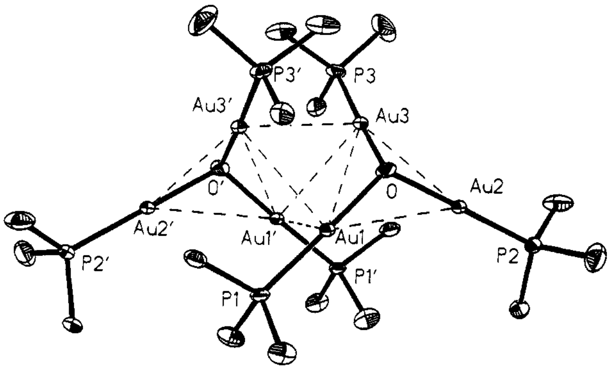
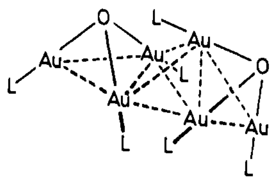


Figure 1. Molecular structure of the dication $[(Me_3PAu)_6O_2]^{2+}$ in crystals of its tetrafluoroborate salt (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Gold–gold contacts (Å): Au1–Au2, 3.333(1); Au1–Au3, 3.347(1); Au2-Au3, 3.247(1); Au1–Au1', 3.312(1); Au3–Au3', 3.220(1); Au1–Au3', 3.281(1).

[m/z = 835.3 (100%) for the cation]. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of solutions in chloroform-d_1 show the expected doublet and singlet resonances at $\delta = 1.70$ [$J(P,H) = 11.0$ Hz], 16.1 [$J(P,C) = 41.3$ Hz], and −17.9 ppm, respectively. Cooling of the sample to −60 °C does not induce major changes in the spectra. The standard infrared absorptions and ^{11}B and ^{19}F resonances of the anion are also detected in the spectra of chloroform-d_1 solutions.

Single crystals of the compound are obtained from solutions of the new gold oxide complex in CH_2Cl_2.[24] The lattice is composed of independent cations and anions with no unusual sub-van der Waals contacts. Accordingly, the anions have largely undistorted tetrahedral geometries.

The structure of the dication is shown in Figure 1. The core of the structure is an almost regular tetrahedron of gold atoms (Au1, Au1', Au3, Au3') (**C**). A 2-fold rotational axis passes through the centers of two opposite edges (top and bottom) of this polyhedron. Two of the side edges are bridged by the two remaining gold atoms to form almost equilateral triangles (Au1, Au2, Au3 and the symmetry-related unit Au1', Au2', Au3') capped by the two oxygen atoms (O, O'). These two oxygen-capped triangles represent the OAu_3 pyramids of the two individual monocation components $[(Me_3PAu)_3O]^+$. Each gold atom bears one of the phosphine ligands to generate the expected quasi-linear O–Au–P coordination geometry at each metal center.



C

The overall geometry is a new structural motif for chalcogen-centered gold clusters in that the monomeric units are aggregated through crossed edges (to give a tetrahedron, **C**) instead of parallel edges (to give a square, **B**). This mode leads to an unprecedented, much more intimate clustering in which the gold atoms Au1 and Au3 are in contact with as many as four other gold atoms at approximately equal distances. (The gold atoms Au2 retain their initial coordination pattern already present in the monomers.) Even if only small energy contributions (of ca. 6–8 kcal/bond)[25–27] are ascribed to each of these Au···Au contacts of an average length of 3.25 Å, the energy level of the aggregate is clearly lowered more than in the alternative structure with parallel edges. The low-temperature NMR results are indicative, however, of low-energy barriers for skeletal rearrangements in solution.

The new structure is not only an interesting case of a well-characterized gold oxide complex but also an important corroboration of the validity of the aurophilicity concept,[1,2] i.e. the affinity of gold atoms for their congeners in virtually any structural environment, which is only limited by steric effects originating from the auxiliary ligands.

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Supplementary Material Available: Listings of crystallographic data and data collection and refinement details, atomic positional parameters, anisotropic thermal parameters, bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

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(24) Crystal and structure solution data: $C_{18}H_{54}Au_6O_2P_6B_2F_8$ (M_r 1843.90), monoclinic; $a = 21.792(2)$ Å, $b = 17.280(2)$ Å, $c = 15.680(2)$ Å, $\beta = 133.95(2)°$, space group $P2/c$ (No. 15, *International Tables for X-ray Crystallography*), $V = 4250.9$ Å^3, $Z = 8$, $D_{calc} = 2.88$ g cm^{-3}; $T = -70$ °C; λ(Mo Kα) = 0.710 69 Å; CAD4 diffractometer; 9432 reflections measured, 4481 unique, and 3885 observed [$F_o \geq 4\sigma(F_o)$]; empirical absorption correction applied ($T_{max} = 52.09\%$, $T_{min} = 99.68\%$); structure solution by direct methods, with all hydrogen atoms located by difference Fourier syntheses; refinement of 191 parameters converged at $R = 0.0538$ (unit weights), including hydrogen atoms in idealized, fixed positions; maximum and minimum residual electron density 5.77 and −5.35 e Å^{-3}. Supplementary material has been deposited.

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