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Tetrahedral Gold Cluster $[Au_4]^{2+}$: Crystal Structure of $\{[(^tBu)_3PAu]_4\}^{2+}(BF_4^-)_2\cdot 2CHCl_3$

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Gold clusters continue to attract considerable interest.[1] The majority of the current studies are focusing on *very large* clusters ("super clusters"), however,[2] or even clusters of clusters,[3] and their transition to bulk metal. By contrast, work on the *very small* clusters has been neglected, and some of the most lucid predictions regarding stoichiometry and structure advanced in theoretical studies for this realm[4] have remained unconfirmed.

The smallest possible polyhedral gold cluster is a tetrahedral Au_4, for which a particularly stable electronic situation[4] is attained in the dication Au_4^{2+}. Within the framework of gold cluster taxonomy[5] a species $[(LAu)_4]^{2+}$, with L representing a 3-fold rotor ligand, is expected to adopt full tetrahedral symmetry (point group T_d or T), thus topologically resembling e.g. tetra-*tert*-butyltetrahedrane, $(^tBu)_4C_4$.[6] We now report the isolation and structural characterization of a stable salt $\{[(^tBu)_3PAu]_4\}^{2+}(BF_4^-)_2$ (**1**).

The reaction of tris(trimethylsilyl)phosphine[7] with {tris[(tri-*tert*-butylphosphino)aurio]oxonium} tetrafluoroborate[8] in tetrahydrofuran at −78 °C affords a number of products, two of which have been identified[9] and structurally characterized[10,11] recently as $\{[(^tBu)_3PAu]_4P\}^+BF_4^-$ and $\{[(^tBu)_3PAu]_5P\}^{2+}(BF_4^-)_2$. In an attempt to identify the remaining components of the reaction mixture, we have isolated the title compound through a series of chloroform/heptane crystallizations[12] in an overall yield of 5% (eq 1). It forms colorless, air- and water-stable crystals, soluble

$$\{[(^tBu)_3PAu]_3O\}^+BF_4^- \xrightarrow[-(Me_3Si)_2O]{+(Me_3Si)_3P} \{[(^tBu)_3PAu]_4\}^{2+}(BF_4^-)_2 \qquad (1)$$

in di- and trichloromethane. The ^{31}P NMR spectrum of $CDCl_3$ solutions shows only one signal at $\delta = 121.5$ ppm. The mass spectrum (FAB) of **1** exhibits the peak of the *di*cation at $m/z = 799.1$ (2%).

Colorless plates obtained from $CHCl_3/n\text{-}C_7H_{16}$ at 20 °C are monoclinic, space group $P2_1/c$, with four formula units in the unit cell and two molecules of crystal chloroform per formula unit ($\mathbf{1}\cdot 2CHCl_3$).[13] The lattice is built of $\{[(^tBu)_3P]_4Au_4\}^{2+}$ dications, BF_4^- anions, and $CHCl_3$ molecules with no unusual interionic or intermolecular contacts. The dications have no crystallographic symmetry, but their structure approaches tetrahedral symmetry quite closely. Thus the Au_4 core has six almost equidistant Au–Au edges in the narrow range from 2.7031(9) to 2.7302(7) Å (Figure 1). Accordingly, all twelve Au–Au–Au angles fall between 59.76(2) and 60.37(1)°. The four P–Au vectors [with distances Au–P very similar, between 2.304(4) and 2.306(4) Å] are roughly at tetrahedral angles and meet at the center of the Au_4 tetrahedron. Each of the four phosphorus atoms has a tetrahedral constitution with all angles C–P–Au and C–P–C close to 109°. The conformation of the $AuPC_3$ and Au_4 tetrahedra can be described as staggered, as shown by a typical Newman projection down a P–Au axis (Figure 2). Considering the small conrotatory "*tert*-butyl twist", typical for species with four *tert*-butyl groups at a given common central unit,[15] the overall structure is compatible with point group T. The structures of the tetrafluoroborate anions and chloroform molecules show no anomalies.

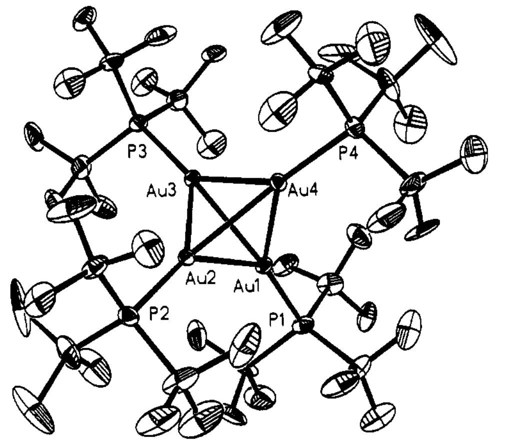

Figure 1. Structure of the dication $\{[(^tBu)_3PAu]_4\}^{2+}$ in the crystals of $\mathbf{1}\cdot 2CHCl_3$ with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). For dimensions, see text.

A simplified molecular orbital description of cluster bonding in the dication $[Au_4]^{2+}$ and its tetraphosphine complexes $[(LAu)_4]^{2+}$ has already been included in the early treatises on gold clusters: If only four gold sp hybrid orbitals oriented toward the center of the cluster are considered, a filled single orbital of a_1 symmetry and a set of empty triply degenerate orbitals of t_1

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[12] Treatment of the reaction mixture obtained from $(Me_3Si)_3P$ (0.29 g, 1.15 mmol) and $\{[(^tBu)_3PAu]_3O\}^+BF_4^-$ (2.0 g, 1.54 mmol) in tetrahydrofuran (20 mL) with pentane leads to the separation of a red oil.[9–11] This oil is redissolved in chloroform and the solution is treated with *n*-heptane to precipitate **1**, which is recrystallized twice from $CHCl_3/n\text{-}C_7H_{16}$ to give colorless crystals, 102 mg (5%) yield.

[13] Crystal and structure solution data for compound $\mathbf{1}\cdot 2CHCl_3$ ($C_{50}H_{110}Au_4B_2Cl_6F_8P_4$, M_r = 2009.50): monoclinic, space group $P2_1/c$, a = 14.032(1) Å, b = 12.138(2) Å, c = 42.037(1) Å, β = 91.19(1)°, V = 7158.2 Å^3, Z = 4, ρ_{calcd} = 1.846 g cm^{-3}, μ(Mo Kα) = 85.24 cm^{-1}, $F(000)$ = 3880 e; CAD4 diffractometer, λ(Mo Kα) = 0.710 69 Å, T = −80 °C, graphite monochromator, 15 747 reflections measured, 15 509 unique, 6927 observed ($F_o \geq 4.0\sigma(F_o)$); Lp, intensity, and absorption corrections applied (DIFABS, 0.741/1.162). Final refinement of all non-hydrogen atoms was with anisotropic temperature factors by block matrix approximation (600 parameters in 4 blocks); H atoms were in idealized geometry with fixed U_{iso} = 0.075. R/R_w = 0.047/0.053 (using the weighting scheme of Prince[14]); residual electron density max/min = 2.37/−3.89 (e/Å^3).

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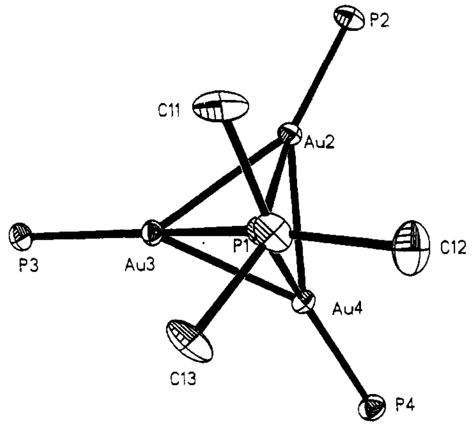

Figure 2. Projection down the axis P1–Au1 in the dication of **1**·2CHCl$_3$, showing the staggered conformation and the "*tert*-butyl twist" leading to *T* symmetry for the cluster.

symmetry represent the wide-gap HOMO–LUMO region, in good agreement with the observed diamagnetism (NMR) and the absence of optical absorption in the visible region for the title compound. With the remaining Au 6p orbitals and the Au 5d block taken into account, this picture reaches a much higher level of complexity, and no full treatment including relativistic effects[16] has yet been carried out.

Tetrahedral gold clusters have previously been detected in a diiodide complex (Ph$_3$P)$_4$Au$_4$I$_2$, with the two iodine atoms in bridging positions at two opposite edges of a tetrahedron of gold atoms,[17] and in the pentanuclear complex [(Ph$_2$PCH$_2$PPh$_2$)$_3$(Ph$_2$PCHPPh$_2$)Au$_5$]$^{2+}$, with the extra gold atom attached to the basic Au$_4$ tetrahedron via tentacles of the bis(diphenylphosphino)methan(id)e ligands.[18] Owing to the changes in stoichiometry, structure, and symmetry, these compounds are less adequate as models for the [Au$_4$]$^{2+}$ unit, and theoretical treatment will be much facilitated for the high-symmetry species now available.

Unfortunately, there is not yet a rational synthesis for compound **1**. Experiments aiming at a controlled reduction of (^{t}Bu)$_3$PAuCl by Na[BH$_4$]/Na[BF$_4$] in a number of polar solvents did not give any tetranuclear gold clusters. Efforts in this direction will be continued.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, bond lengths and angles, and H-atom parameters (17 pages). Ordering information is given on any current masthead page.

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