

Mixed co-ordination numbers and geometries of gold(I) in a dinuclear complex of thioglycerol

José M. López-de-Luzuriaga, Alexander Sladek and Hubert Schmidbaur*

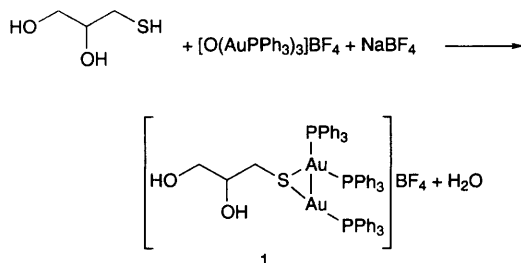
Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Reaction of DL-3-sulfanylpropane-1,2-diol with $[O(AuPPh_3)_3]BF_4$ afforded a dinuclear complex $[Au_2(PPh_3)_3\{SCH_2CH(OH)CH_2OH\}]$ in which two gold environments, linear and trigonal planar, are present in the same molecule; the complex has been structurally characterized.

Gold usage in advanced technology is based predominantly on sulfur compounds of univalent gold. Prominent examples are 'liquid golds' used in gilding processes,¹ gold thiolate drugs in chemotherapy,² gold-containing mesogenic compounds for liquid crystals,³ and self-assembled monolayers for two-dimensional nanotechnology.⁴ Many of these applications require high solubility of the thiolates in suitable solvents, preferentially aqueous solvents, and a high net gold content.

We have therefore become engaged in the chemistry of sulfur-functional polyols and have chosen various thioglycerols as ligands for gold(I).⁵ Tri- and di-thioglycerols were shown to form a number of polynuclear compounds, where all sulfur atoms are clustering centres for $[(R_3P)Au]^+$ units. Accordingly, monothioglycerol (DL-3-sulfanylpropane-1,2-diol) was expected to give rise to a dinuclear species with a hydrophilic diol chain dangling from the sulfur atom. Indeed treatment of it with tris[(triphenylphosphine)aurio]oxonium tetrafluoroborate in dichloromethane in the presence of sodium tetrafluoroborate afforded a dinuclear complex as a crystalline white solid in 40% yield † (Scheme 1).

Very surprisingly, however, the compound showed elemental analysis and spectroscopic data which require three instead of two PPh_3 ligands. The ^{31}P - $\{^1H\}$ NMR spectrum (in $CDCl_3$) showed only one broad signal at δ 40.0 at room temperature, but at $-60^\circ C$ this signal split into two peaks at δ 43.0 and 36.3



Scheme 1

† To a solution of 3-sulfanylpropane-1,2-diol (0.15 mmol, 13.4 mm³) in dichloromethane (15 cm³) was added $[O(AuPPh_3)_3]BF_4$ (0.10 mmol, 0.15 g) and a small amount of $NaBF_4$. After stirring for 1 h the mixture was filtered. Evaporation of the solvent from the filtrate *in vacuo* to a volume of ca. 5 cm³ and addition of pentane led to the precipitation of the complex as a white solid. Yield 40% (Found: C, 48.15; H, 3.65. Calc. for $C_{57}H_{52}Au_2BF_4O_2P_3S$: C, 49.8; H, 3.8%). Mass spectrum (positive ion FAB): $m/z = 1025.6$ ($[M - PPh_3]^+$, 36.6%).

of relative intensity 2:1. The 1H NMR spectrum in the same solvent showed three multiplets in the aliphatic region at δ 3.25, 3.67 and 3.81, corresponding to the three non-equivalent groups of protons of the glycerol unit, with no major temperature dependence. This behaviour suggested a fluxional structure with three phosphine units competing for co-ordination sites at two gold atoms attached to the sulfur end of the glycerol.

Crystals of complex **1** obtained from dichloromethane solution by layering with pentane were found to be monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The lattice contains independent tetrafluoroborate anions and dinuclear complex cations. ‡ In the cation the two gold atoms are attached to the mercaptide sulfur atom converting it into a pyramidal sulfonium centre (Fig. 1). The Au-S-Au angle of only $75.95(5)^\circ$ is associated with a short Au-Au contact of 3.0162(5) Å. Together with the angles C(1)-S(1)-Au(1) [$108.78(3)^\circ$] and C(1)-S(1)-Au(2) [$108.2(3)^\circ$], these data are very similar to those from the structural chemistry of other diaurated monosulfonium salts. However, the co-ordination spheres of the two gold atoms are entirely different. One of them, Au(1), features the conventional linear two-co-ordination [S(1)-Au-P(2) $175.86(7)^\circ$], while the other, Au(2), has a distorted trigonal-planar co-ordination by one sulfur and two phosphorus atoms (sum of angles 359.6°). This different co-ordination is reflected in different Au-S distances: Au(2)-S 2.575(2) Å and Au(1)-S 2.316(2) Å. In solution there appears to be a rapid exchange of phosphine ligands between Au(1) and Au(2) rendering these ligands equivalent on the NMR time-scale. The structure requires the two phosphines at the three-co-ordinate gold atom to be diastereotopic, but their ^{31}P resonances are not resolved at $-60^\circ C$.

Compound **1** may also be described as an addition compound of $HOCH_2CH(OH)CH_2SAuL$ and $[AuL_2]BF_4$ ($L =$

‡ Crystal data: $C_{57}H_{52}Au_2BF_4O_2P_3S$ **1**, $M_r = 1374.70$, monoclinic, space group $P2_1/c$, $a = 10.634(1)$, $b = 23.390(2)$, $c = 20.641(2)$ Å, $\beta = 90.43(1)^\circ$, crystal dimensions $0.22 \times 0.30 \times 0.40$ mm, $Z = 4$, $U = 5134(1)$ Å³, $D_c = 1.779$ g cm⁻³, $F(000) = 2680.0$; Enraf-Nonius CAD4 diffractometer, Mo-K α radiation ($\lambda = 0.71069$ Å, $-68^\circ C$). Data were corrected for Lorentz-polarization effects as well as for absorption [empirical, $T_{min} = 0.5814$, $T_{max} = 0.9996$, $\mu(Mo-K\alpha) = 59.00$ cm⁻¹]. 10 488 Reflections measured, 9915 unique, 7959 'observed' [$F_o \geq 4\sigma(F_o)$]. Hydrogen atoms [except at C(2) and at the disordered oxygen atom at C(2) (site occupation factor 0.5/0.5)] were calculated in idealized geometry and included with isotropic contributions [riding model, $U_{iso(H)} = 1.5U_{eq(C)}$]. Non-H atoms were refined with anisotropic displacement parameters. 640 Refined parameters, $wR2$ [R based on F (OMIT4)] = 0.1068 [0.0449], $l = 0.0331$, $k = 48.4410$, where $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $w = q / [\sigma^2(F_o^2) + (p)^2 + kp]$, $p = [\max(F_o^2, 0) + 2F_c^2] / 3$; $\rho_{final} = +4.88 / -1.59$ e Å⁻³ located at the gold atoms. The structure was solved by direct methods and refined by full-matrix least-squares calculations (SHELXL 93⁶). Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/320.

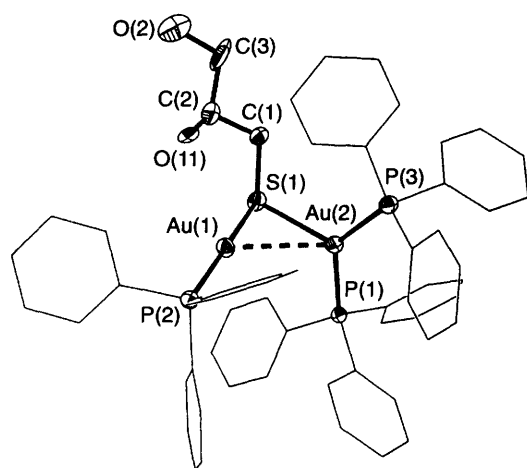


Fig. 1 Molecular structure of the cation of compound **1** with atomic numbering [ORTEP,⁷ hydrogen atoms omitted, s.o.f. = 0.5 for O(11)]. Selected bond lengths (Å) and angles (°): Au(1)–Au(2) 3.0162(5), Au(1)–S(1) 2.316(2), Au(2)–S(1) 2.575(2), Au(1)–P(2) 2.269(2), Au(2)–P(1) 2.357(2) and Au(2)–P(3) 2.324(2); S(1)–Au(1)–P(2) 175.86(7), S(1)–Au(2)–P(1) 104.26(6), S(1)–Au(2)–P(3) 120.64(7), P(1)–Au(2)–P(3) 134.71(7), Au(1)–S(1)–Au(2) 75.95(5), Au(1)–S(1)–C(1) 108.7(3), Au(2)–S(1)–C(1) 108.2(3)

PPh_3), but the angle $\text{P}(1)\text{--Au}(2)\text{--P}(3)$ [$134.71(7)^\circ$], the short $\text{S}(1)\text{--Au}(2)$ and $\text{Au}(1)\text{--Au}(2)$ distances and the small angle $\text{Au}(1)\text{--S}(1)\text{--Au}(2)$ are all evidence that there is an intimate aggregation based on strong interactions associated within the $\text{Au}(1)\text{--S}(1)\text{--Au}(2)$ triangle. There are no conspicuous intra- or inter-molecular contacts indicative of conventional hydrogen bonding. The origin of the third Ph_3P molecule in **1** is not clear. No phosphine-deficient by-product could be isolated.

Acknowledgements

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