

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

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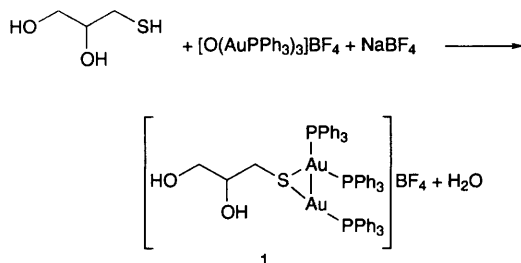
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Reaction of DL-3-sulfanylpropane-1,2-diol with  $[O(AuPPh_3)_3]BF_4$  afforded a dinuclear complex  $[Au_2(PPh_3)_3\{\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}\}]$  in which two gold environments, linear and trigonal planar, are present in 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,<sup>1</sup> gold thiolate drugs in chemotherapy,<sup>2</sup> gold-containing mesogenic compounds for liquid crystals,<sup>3</sup> and self-assembled monolayers for two-dimensional nanotechnology.<sup>4</sup> 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).<sup>5</sup> 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, monothio-glycerol (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]xonium 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  $\delta$  40.0 at room temperature, but at  $-60^\circ\text{C}$  this signal split into two peaks at  $\delta$  43.0 and 36.3



Scheme 1

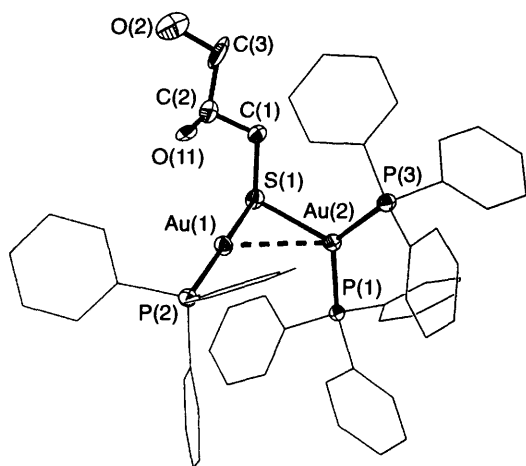
† To a solution of 3-sulfanylpropane-1,2-diol (0.15 mmol, 13.4 mm<sup>3</sup>) in dichloromethane (15 cm<sup>3</sup>) was added  $[O(AuPPh_3)_3]BF_4$  (0.10 mmol, 0.15 g) and a small amount of  $NaBF_4$ . After stirring for 1 h the mixture was filtered. Evaporation of the solvent from the filtrate *in vacuo* to a volume of ca. 5 cm<sup>3</sup> 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  $\delta$  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  $359.6^\circ$ ). 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  $-60^\circ\text{C}$ .

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,  $Z = 4$ ,  $U = 5134(1)$  Å<sup>3</sup>,  $D_c = 1.779$  g cm<sup>-3</sup>,  $F(000) = 2680.0$ ; Enraf-Nonius CAD4 diffractometer, Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å,  $-68^\circ\text{C}$ ). Data were corrected for Lorentz-polarization effects as well as for absorption [empirical,  $T_{min} = 0.5814$ ,  $T_{max} = 0.9996$ ,  $\mu(\text{Mo-K}\alpha) = 59.00$  cm<sup>-1</sup>]. 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  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $w = q / [\sigma^2(F_o^2) + (p)^2 + kp]$ ,  $p = [\max(F_o^2, 0) + 2F_c^2] / 3$ ;  $\rho_{\text{final}} = +4.88 / -1.59$  e Å<sup>-3</sup> located at the gold atoms. The structure was solved by direct methods and refined by full-matrix least-squares calculations (SHELXL 93<sup>6</sup>). 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,<sup>7</sup> 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<sub>3</sub>), but the angle P(1)–Au(2)–P(3) [134.71(7)°], the short S(1)–Au(2) and Au(1)–Au(2) distances and the small angle Au(1)–S(1)–Au(2) are all evidence that there is an intimate aggregation based on strong interactions associated within the Au(1)–S(1)–Au(2) triangle. There are no conspicuous intra- or inter-molecular contacts indicative of conventional hydrogen bonding. The origin of the third Ph<sub>3</sub>P molecule in **1** is not clear. No phosphine-deficient by-product could be isolated.

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