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Synthesis and Crystal Structure of $[\{Au_2(C_6H_4S_2\text{-}1,2)(PEt_3)\}_2]$

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Treatment of chloro(triethylphosphine)gold(I) with benzene-1,2-dithiol in the presence of a tertiary amine base affords $[\{Au_2(C_6H_4S_2\text{-}1,2)(PEt_3)\}_2]$ (60.4% Au by weight) which has a compact, centrosymmetric structure containing a rhomboid Au_4 unit supported by the sulfur and phosphorus ligands.

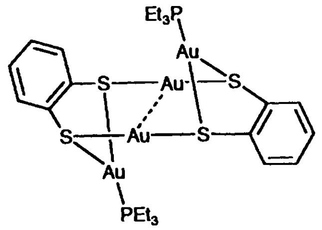
Gold(I) thiolate complexes have received continued interest in recent years owing to their widespread use in medicine,[1,2] electrical conductor and semiconductor technology,[3,4] and in the glass and ceramics industry,[5,6] *e.g.*, a (triethylphosphine)(thioglucose)gold(I) complex is one of the most successful drugs in the therapy of arthritis, and sulfur-rich liquid-gold pastes, largely based on natural products, are the traditional gold sources for the regioselective gilding of materials.

In the course of our studies on polynuclear gold(I) compounds with main-group element co-ordination centres[7,8] we have now obtained a novel tetranuclear complex with some interesting properties: (*i*) it is readily obtained in pure form; (*ii*) it is stable to air and water; (*iii*) it is soluble in polar organic solvents; (*iv*) it has an exceedingly high gold content (60.4% by weight), since half of the auxiliary phosphine ligand provided in the synthesis is not retained owing to the formation of a compact, thermally stable cluster structure.

Treatment of chloro(triethylphosphine)gold(I) with benzene-1,2-dithiol in the presence of triethylamine as a base in tetrahydrofuran at ambient temperature affords a light yellow crystalline product (m.p. 198 °C with decomposition) of stoichiometry $Au_2(C_6H_4S_2)(PEt_3)$ as determined by elemental analysis.† The bis(phosphine) complex $[Au_2(C_6H_4S_2\text{-}1,2)(PEt_3)_2]$ suggested by the stoichiometry of the reagents and a green compound identified as a mixed-valent salt $[Au(PEt_3)_2][Au(C_6H_2S_2\text{-}1,2)_2]$[9] (probably originating from partially oxidized dithiole) are by-products of the reaction [equation (1)]. Solutions of complex **1** in chloroform show a singlet

$$4[AuCl(PEt_3)] + 2C_6H_4(SH)_2\text{-}1,2 + 4NEt_3 \longrightarrow$$
$$4NHEt_3Cl + 2PEt_3 + \underset{\mathbf{1}}{[\{Au_2(C_6H_4S_2\text{-}1,2)(PEt_3)\}_2]} \quad (1)$$

resonance in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at δ 32.5. The ^1H NMR spectrum shows the pattern of an A_3B_2X spin system for the PEt_3 groups [δ 1.01 and 1.43, *J*(HH) 7.6, *J*(PH) 18.5 and 9.6 Hz, respectively] and of an ABB'A' spin system for the dithiolate group (δ 7.03 and 7.99). In the $^{13}C\text{-}\{^1H\}$ NMR spectrum, the carbon resonances appear at δ 9.0 (Me), 19.1 [CH_2, *J*(PC) 31.8 Hz], 125.3, 135.3 and 144.4 (C_6H_4). These data are distinct from those of the by-products (above).[9]



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According to fast atom bombardment mass spectrometry data (*m*-nitrobenzyl alcohol, *m*/*z* 1304), complex **1** forms a dimer the structure of which has been determined by single-crystal X-ray diffraction.‡

Crystals of **1** (from chloroform–*n*-hexane) are monoclinic,

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† To a solution of $[AuCl(PEt_3)]$ (0.65 g, 1.87 mmol) in tetrahydrofuran (10 cm^3) a mixture of $C_6H_4(SH)_2\text{-}1,2$ (0.13 g, 0.91 mmol) and NEt_3 (0.19 g, 1.87 mmol) in the same solvent (10 cm^3) was added dropwise at room temperature with stirring to give a faintly green solution and a white precipitate. The solvent was evaporated after 1 h, the residue was treated with water (20 cm^3) to remove $NHEt_3{}^+Cl^-$, collected by filtration and washed with water (2 × 10 cm^3) and diethyl ether (2 cm^3) to give 0.55 g of crude product. Crystallization from chloroform–hexane (1:1) afforded 0.21 g of pure material (35% yield). The by-products can be isolated from the mother-liquor[9] (Found: C, 22.05; H, 2.95; Au, 60.40; P, 4.75; S, 9.85. $C_{12}H_{19}Au_2PS_2$ requires C, 22.10; H, 2.95; Au, 60.40; P, 4.75; S, 9.85%).

‡ *Crystal data.* $C_{24}H_{38}Au_4P_2S_4$, $M_r = 1304.64$, colourless crystals (0.25 × 0.30 × 0.35 mm), monoclinic, space group $P2_1/n$ (no. 14), $a = 9.866(2)$, $b = 13.274(1)$, $c = 12.776(2)$ Å, $\beta = 103.46(2)°$, $U = 1627.2$ Å^3, $Z = 2$, $D_c = 2.662$ g cm^{-3}, $F(000) = 1184$. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 182.81 cm^{-1}, $T = 22$ °C, θ–2θ scan mode. During data collection three standard reflections were periodically measured as a general check of crystal and instrument stability. No significant change was observed. Reduced-cell calculations (DELOS, LAPAGE)[10,11] did not indicate any higher symmetry. Intensity data were corrected for absorption effects (DIFABS).[12] The structure was solved by direct methods and refined by full-matrix least-squares calculations (SHELXS 86,[13] SHELX 76[14]). Of 4248 measured reflections, 3292 were unique, and 2412 were considered 'observed' [$F_o \geqslant 4.0\sigma(F_o)$] and used for refinement. Thermal motion was treated anisotropically for all non-hydrogen atoms except for carbon atoms C(22) and C(32) of two of the ethyl groups, which were disordered in split positions with site-occupancy factors of 0.5:0.5 and 0.6:0.4 for C(22):C(222) and C(32):C(322), respectively. Hydrogen atoms of ethyl groups were neglected, ring hydrogen atoms were placed in calculated fixed positions with isotropic displacement parameters ($U_{iso} = 0.05$ Å^2). Number of refined parameters 152. The functions minimized were $R = \Sigma(||F_o| - |F_c||)/|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$. Final *R* and *R'* values are 0.061 and 0.075, respectively. Residual electron density is in the range +3.72 to −4.42 e Å^{-3} (near the gold atoms). Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

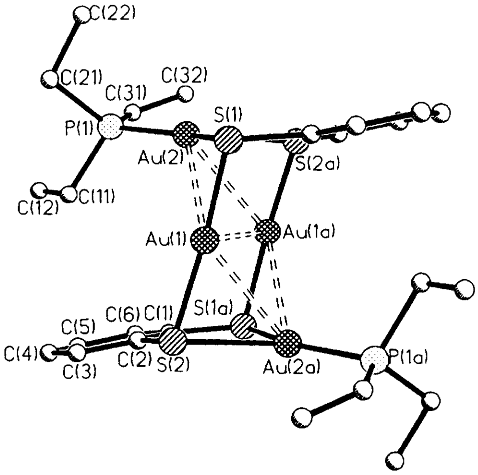

Fig. 1 Molecular structure of $[\{Au_2(C_6H_4S_2\text{-}1,2)(PEt_3)\}_2]$ with atomic numbering (the molecule has a centre of inversion). Selected bond lengths (Å) and angles (°): Au(1)···Au(1a) 3.114(1), Au(1)···Au(2) 3.052(1), Au(1)···Au(2a) 3.129(1), Au(1)–S(1) 2.311(5), Au(1)–S(2) 2.294(4), Au(2)–S(1) 2.407(5), Au(2)–S(2a) 2.625(4), Au(2)–P(1) 2.224(6); Au(1)–S(1)–Au(2) 80.6(1), Au(1)–S(2)–Au(2a) 78.7(1), Au(1)···Au(2)···Au(1a) 60.5(1), Au(2)···Au(1)···Au(2a) 119.5(1), S(1)–Au(1)–S(2) 173.3(1), S(1)–Au(2)–P(1) 149.1(2), S(2a)–Au(2)–P(1) 126.5(2), S(1)–Au(2)–S(2a) 84.4(1)

space group $P2_1/n$, with two molecules in the unit cell. There is no solvent contained in the crystals. The structure of the complex is shown in Fig. 1. The molecule has a crystallographic centre of inversion which relates the two chelating benzene-1,2-dithiolato ligands and the two triethylphosphine units. The four gold atoms are arranged in the form of a parallelogram with Au···Au edges of 3.052(1) and 3.129(1) Å, and a short transannular Au···Au distance of 3.114(1) Å. The gold atoms at the wide-angle vertices of the parallelogram (119.5°) are two-co-ordinate with S–Au–S angles of 173.3°, while those at the acute-angle vertices (60.5°) are three-co-ordinate in a quasi-planar environment of one phosphorus and two sulfur atoms. Each of the bidentate dithiolate ligands is bridging three gold atoms, while the triethylphosphines are monodentate. There is a slight disorder of the ethyl groups of these units in the crystal, which, however, could be accounted for by a suitable computational model.

With $[AuCl(PPh_3)]$ instead of $[AuCl(PEt_3)]$ as the starting material, no PPh_3 is lost under similar reaction conditions to those used above,[9] and a complex $[Au_2(C_6H_4S_2\text{-}1,2)(PPh_3)_2]$ is obtained as the sole product. Studies with a variety of other ligands have therefore been initiated in order to investigate the influence of electronic and/or steric effects on the stoichiometry of the reaction. (*Note added at proof.* For a methyl homologue, derived from toluene-3,4-dithiol, see ref. 15).

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