

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
C20—H20...O3	1.02 (4)	2.46 (4)	3.457 (6)	165 (3)
C2—H2...O5 <sup>i</sup>	0.90 (3)	2.52 (3)	3.291 (5)	144 (2)
N3—H1N3...O5 <sup>i</sup>	0.88 (3)	1.99 (3)	2.859 (5)	168 (3)
C3—H3...O4 <sup>ii</sup>	0.95 (4)	2.47 (4)	3.377 (9)	160 (3)
C13—H13...O5 <sup>iii</sup>	0.85 (5)	2.55 (4)	3.352 (6)	157 (4)
C14—H14...O2 <sup>iv</sup>	0.92 (4)	2.58 (4)	3.334 (4)	140 (3)
N6—H1N6...O2 <sup>iv</sup>	0.78 (3)	1.98 (3)	2.763 (4)	176 (3)

Symmetry codes: (i)  $2 - x, 1 - y, -z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $x - 1, y, z$ ; (iv)  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. Atoms C22 and C23 of the propionate group showed very high disorder with unreliable C—C bond lengths. Hence, it was decided to consider the propionate group as two entities with different orientations for the bonds C21—C22 and C22—C23. The occupancies of C22 and C23 were initially refined and then fixed at 0.45 for C22A/C23A and 0.55 for C22B/C23B. The O atoms of the disordered nitrate group were divided into two sets with occupancies of 0.78 and 0.22. All the disordered atoms were refined anisotropically with C—C, N—O and O—O distances involving the disordered atoms restrained. The H atoms of C22A, C22B, C23A and C23B were fixed geometrically and allowed to ride on the atoms to which they are attached. All other H atoms were located from a difference Fourier map and refined isotropically.

Data collection, cell refinement and data reduction: X-SCANS (Siemens, 1994); structure solution and molecular graphics: SHELXTL/PC (Sheldrick, 1990); structure refinement: SHELXL93 (Sheldrick, 1993); geometrical calculations: PARST (Nardelli, 1983, 1995).

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## $\mu$ -(2-Thioxo-1,3-dithiole-4,5-dithiolato)-bis{[tris(*p*-methoxyphenyl)phosphine]-gold(I)}

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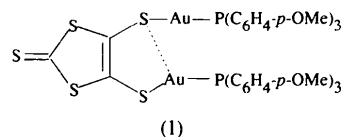
## Abstract

The molecule  $[\text{Au}_2(\mu\text{-C}_3\text{S}_5)\{\text{P}(\text{C}_6\text{H}_4\text{OCH}_3)_3\}_2]$  consists of two AuPR<sub>3</sub> fragments bridged by one dmit group. Although the Au—S [2.327 (2) and 2.331 (2) Å] and Au—P [2.264 (2) and 2.265 (2) Å] bond lengths are similar to those observed in related dithiolate complexes, the intramolecular Au...S [3.013 (2) Å] and Au...Au [3.2217 (8) Å] contacts are longer.

## Comment

Dinuclear gold(I) complexes have been studied extensively during recent years (Melnik & Parish, 1986; Usón & Laguna, 1986; Mingos, 1984; Jones, 1981) because they provide a good basis for the study of weak metal–metal interactions (Schmidbaur *et al.*, 1989; Schmidbaur, 1990). Such interactions are often observed in polynuclear gold(I) derivatives and arise from relativistic effects (Pyykkö, 1988).

Interest in metal thiolate chemistry has increased because of the widespread applications of some of these compounds, *e.g.* for modelling protein sites, as anti-arthritis drugs, and in catalytic processes (Blower & Dilworth, 1987; Holm *et al.*, 1990; Wright *et al.*, 1990; Dance, 1986; Kuchn & Isied, 1980). In particular, several examples of complexes containing bridging dithiolate ligands coordinated to gold(I)–PR<sub>3</sub> units have been reported (Dávila *et al.*, 1993, 1994; Nakamoto *et al.*, 1993; Gimeno *et al.*, 1994; Cerrada *et al.*, 1996). We report here a dinuclear gold(I) derivative, (1), containing 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) as the bidentate ligand, which is an example of a so-called 'open-ring' complex (Dávila *et al.*, 1994).



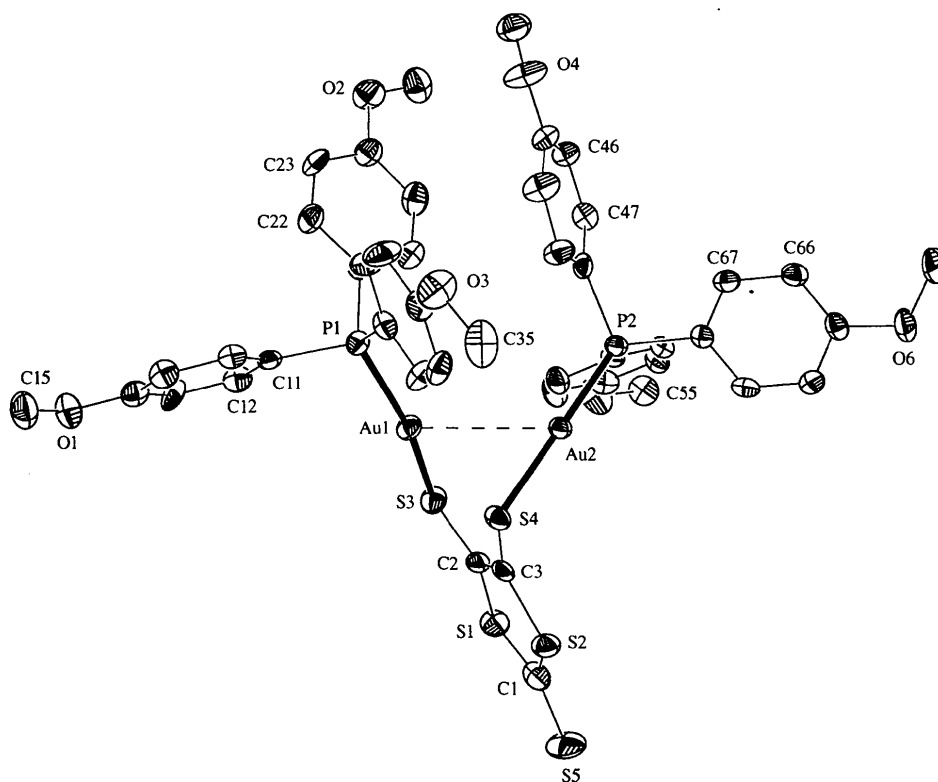


Fig. 1. The molecular structure of the title compound shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The structure of [Au<sub>2</sub>(μ-dmit){P(*p*-C<sub>6</sub>H<sub>4</sub>OMe)<sub>3</sub>}]<sub>2</sub>, (1), is shown in Fig. 1. In the molecule, the dmit ligand acts as a μ<sub>2</sub> bridge to the two gold(I) centres via the S atoms. The mode of coordination is clearly non-symmetric: the linear coordination at Au2 is usual in gold(I) complexes [P2—Au2—S4 174.89 (8)°], but the angle P1—Au1—S3 [160.14 (8)°] deviates from linearity, which is associated with an extra interaction Au1···S4 of 3.013 (2) Å and an intramolecular Au···Au contact of 3.2217 (8) Å. The PPh<sub>3</sub> analogue [Au<sub>2</sub>(μ-dmit)(PPh<sub>3</sub>)<sub>2</sub>] (Cerrada *et al.*, 1996) shows similar features, though the distortion of the threefold coordination is more marked [the angle P—Au—S is 159.32 (8)° and the extra Au···S interaction is 2.823 (1) Å] and the Au···Au contact is shorter [3.0681 (8) Å]. These differences have been analysed for other dithiolate–gold complexes (Dávila *et al.*, 1994) and explained mainly by steric factors. In the cases of (1) and the PPh<sub>3</sub> analogue, considering that the two phosphines, PPh<sub>3</sub> and P(*p*-PhOMe)<sub>3</sub>, have similar cone angles (145 and 141°, respectively) (Tolman, 1977), the differences between them should be attributed to the more basic character of the P(*p*-PhOMe)<sub>3</sub> ligand (Hartley, 1990; Angelici & Bush, 1988). Complex (1) shows slightly shorter Au—S lengths [Au1—S3 2.327 (2) and Au2—S4 2.331 (2) Å] than the PPh<sub>3</sub> derivative [average Au—S 2.345 (1) Å], whereas the Au—P lengths [Au1—P1 2.264 (2) and

Au2—P2 2.265 (2) Å] are closer to those of the PPh<sub>3</sub> complex [average Au—P 2.256 (1) Å].

### Experimental

Sodium metal (9 mg, 0.4 mmol) and 4,5-bis(thiobenzoyl)-1,3-dithiole-2-thione (81 mg, 0.2 mmol) were dissolved under nitrogen atmosphere in methanol (20 ml) to form a dark red solution of Na<sub>2</sub>C<sub>3</sub>S<sub>5</sub>, to which was added AuCl(PPh<sub>3</sub>) (233 mg, 0.4 mmol). A yellow solid precipitated immediately, which was collected by filtration, washed with methanol and dried *in vacuo* (yield: 90%). <sup>1</sup>H NMR: δ(Me) 3.75 p.p.m. (s). P NMR: 32.4 p.p.m. (s). Yellow rectangular crystals of the complex were obtained from the slow diffusion of an OEt<sub>2</sub> layer into a CH<sub>2</sub>Cl<sub>2</sub> solution.

### Crystal data

[Au<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>)(C<sub>21</sub>H<sub>21</sub>O<sub>3</sub>P)<sub>2</sub>]

*M<sub>r</sub>* = 1294.96

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 13.776 (3) Å

*b* = 13.262 (3) Å

*c* = 24.964 (10) Å

β = 94.54 (4)°

*V* = 4547 (2) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.892 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 47

reflections

θ = 8–15°

μ = 6.794 mm<sup>-1</sup>

*T* = 173 (2) K

Tablet

0.42 × 0.19 × 0.19 mm

Yellow

**Data collection**

Stoe Siemens AED-2 diffractometer  
 $\omega/\theta$  scans  
 Absorption correction:  $\psi$  scans (XEMP; Siemens 1990a)  
 $T_{\min} = 0.142$ ,  $T_{\max} = 0.275$   
 8726 measured reflections  
 8023 independent reflections

6280 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.058$   
 $\theta_{\max} = 25.01^\circ$   
 $h = 0 \rightarrow 16$   
 $k = -15 \rightarrow 1$   
 $l = -29 \rightarrow 29$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.100$   
 $S = 1.048$   
 8021 reflections  
 547 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 26.1665P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$   
 $\Delta\rho_{\max} = 2.322 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -2.049 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Au1—P1	2.264 (2)	S1—C2	1.756 (8)
Au1—S3	2.327 (2)	S2—C1	1.739 (9)
Au1...Au2	3.2217 (8)	S2—C3	1.754 (8)
Au2—P2	2.265 (2)	S3—C2	1.739 (9)
Au2—S4	2.331 (2)	S4—C3	1.750 (8)
S1—C1	1.722 (11)	S5—C1	1.649 (9)
P1—Au1—S3	160.14 (8)	C2—S3—Au1	107.2 (3)
P2—Au2—S4	174.89 (8)	C3—S4—Au2	102.6 (3)

The significant residual electron density is in the heavy-atom region; the distance of the maximum peak,  $2.322 \text{ e } \text{\AA}^{-3}$ , to the nearest atom (Au2) is  $1.11 \text{ \AA}$ . H atoms of the methyl groups were refined as rigid groups; others were included using a riding model.

Data collection: DIF4 (Stoe, 1987a). Cell refinement: DIF4. Data reduction: REDU4 (Stoe, 1987b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1990b). Software used to prepare material for publication: SHELXL93.

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**$\mu$ -[7,8-Bis(diphenylphosphino)-7,8-dicarbonyl-undecaborato-1 $\kappa$ P,2 $\kappa$ P']](pentafluorophenyl-1 $\kappa$ C)(triphenylphosphine-2 $\kappa$ P)-digold(I) Dichloromethane Solvate**

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**Abstract**

The title compound,  $[\text{Au}_2(\text{C}_{26}\text{H}_{30}\text{B}_9\text{P}_2)(\text{C}_6\text{F}_5)(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot\text{CH}_2\text{Cl}_2$ , has a dinuclear structure with the diphosphinocarbaborane moiety bridging the two Au atoms. There is a short intramolecular Au...Au contact of  $2.9885(8) \text{ \AA}$ . The linear coordination at the Au<sup>I</sup> atoms is highly distorted: P—Au—C  $166.6(2)$  and P—Au—P