P(1)	0.1615 (3)	0.5874 (1)	0.1600 (1)	0.0554
P(2)	0.3103 (3)	0.1465 (1)	0.1111 (1)	0.0539
C(111)	0.2059 (9)	0.6582 (5)	0.2069 (5)	0.0483
C(112)	0.226 (1)	0.7128 (5)	0.1724 (5)	0.0567
C(113)	0.258 (1)	0.7666 (5)	0.2089 (6)	0.0606
C(114)	0.2735 (10)	0.7663 (6)	0.2816 (6)	0.0610
C(115)	0.254 (1)	0.7123 (6)	0.3158 (5)	0.0627
C(116)	0.2214 (10)	0.6588 (5)	0.2793 (6)	0.0558
C(117)	0.309 (1)	0.8262 (6)	0.3215 (6)	0.0965
C(121)	0.0572 (10)	0.6103 (5)	0.0773 (5)	0.0512
C(122)	−0.079 (1)	0.6229 (6)	0.0767 (5)	0.0690
C(123)	−0.161 (1)	0.6405 (6)	0.0161 (7)	0.0807
C(124)	−0.109 (1)	0.6455 (5)	−0.0450 (6)	0.0677
C(125)	0.029 (1)	0.6362 (7)	−0.0431 (6)	0.1111
C(126)	0.111 (1)	0.6179 (7)	0.0178 (6)	0.0984
C(127)	−0.197 (1)	0.6636 (6)	−0.1139 (6)	0.0971
C(131)	0.3212 (10)	0.5573 (5)	0.1368 (5)	0.0521
C(132)	0.438 (1)	0.5909 (5)	0.1363 (6)	0.0654
C(133)	0.558 (1)	0.5663 (6)	0.1195 (6)	0.0719
C(134)	0.561 (1)	0.5065 (6)	0.0991 (5)	0.0587
C(135)	0.444 (1)	0.4720 (5)	0.0975 (6)	0.0725
C(136)	0.326 (1)	0.4970 (6)	0.1154 (6)	0.0724
C(137)	0.692 (1)	0.4770 (6)	0.0830 (6)	0.0934
C(211)	0.3993 (10)	0.0764 (5)	0.1380 (5)	0.0506
C(212)	0.510 (1)	0.0565 (7)	0.1066 (6)	0.0865
C(213)	0.578 (1)	0.0024 (7)	0.1269 (8)	0.0935
C(214)	0.539 (1)	−0.0318 (6)	0.1787 (7)	0.0759
C(215)	0.434 (1)	−0.0114 (6)	0.2114 (5)	0.0752
C(216)	0.367 (1)	0.0416 (6)	0.1926 (6)	0.0687
C(217)	0.616 (1)	−0.0916 (6)	0.1991 (7)	0.1208
C(221)	0.142 (1)	0.1271 (6)	0.0643 (5)	0.0572
C(222)	0.073 (1)	0.0740 (6)	0.0747 (6)	0.0822
C(223)	−0.060 (1)	0.0632 (7)	0.0398 (7)	0.0939
C(224)	−0.126 (1)	0.1054 (7)	−0.0046 (6)	0.0738
C(225)	−0.059 (1)	0.1595 (7)	−0.0129 (6)	0.0971
C(226)	0.071 (1)	0.1689 (6)	0.0209 (6)	0.0930
C(227)	−0.269 (1)	0.0932 (7)	−0.0447 (6)	0.1047
C(231)	0.2738 (10)	0.1817 (4)	0.1905 (5)	0.0457
C(232)	0.3779 (10)	0.2063 (5)	0.2363 (6)	0.0643
C(233)	0.354 (1)	0.2368 (5)	0.2953 (6)	0.0642
C(234)	0.223 (1)	0.2472 (6)	0.3089 (5)	0.0610
C(235)	0.119 (1)	0.2226 (6)	0.2623 (6)	0.0864
C(236)	0.141 (1)	0.1907 (6)	0.2046 (5)	0.0773
C(237)	0.195 (1)	0.2811 (6)	0.3714 (6)	0.0915

Table 2. *Selected geometric parameters* (Å, °)

Au(1)—Cl(1)	2.255 (3)	P(1)—C(121)	1.812 (10)
Au(1)—P(1)	2.201 (3)	P(1)—C(131)	1.794 (9)
Au(2)—Cl(2)	2.256 (3)	P(2)—C(211)	1.78 (1)
Au(2)—P(2)	2.208 (3)	P(2)—C(221)	1.786 (10)
P(1)—C(111)	1.79 (1)	P(2)—C(231)	1.783 (9)
Cl(1)—Au(1)—P(1)	178.1 (1)	C(121)—P(1)—C(131)	105.5 (4)
Cl(2)—Au(2)—P(2)	179.6 (1)	Au(2)—P(2)—C(211)	112.7 (3)
Au(1)—P(1)—C(111)	113.8 (4)	Au(2)—P(2)—C(221)	113.0 (4)
Au(1)—P(1)—C(121)	113.6 (3)	Au(2)—P(2)—C(231)	112.9 (3)
Au(1)—P(1)—C(131)	111.5 (4)	C(211)—P(2)—C(221)	108.0 (5)
C(111)—P(1)—C(121)	105.3 (5)	C(211)—P(2)—C(231)	105.4 (5)
C(111)—P(1)—C(131)	106.5 (5)	C(221)—P(2)—C(231)	104.1 (4)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(triethylphosphine)gold(I) Bis(1,2-benzenedithiolato-*S*,*S'*)gold(III), [Au{$P(C_2H_5)_3$}$_2$][Au($S_2C_6H_4$)$_2$]

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Abstract

The structure of the title compound consists of [Au(PEt_3)$_2$]$^+$ cation and [Au($S_2C_6H_4$)$_2$]$^-$ anion pairs. The gold(I) cations exhibit linear coordination to two PEt_3 ligands. The geometry of the gold(III) anions is square planar with four S atoms coordinated to the Au center. Typical Au—S and Au—P distances are observed.

Comment

Square-planar gold(III) bis(dithiolate) complexes are well known (Puddephatt, 1987) and have been studied for their electron-transfer capabilities (Eisenberg, 1970; McCleverty, 1968). Gold(II) complexes have also been obtained from these square-planar species by reduction (Waters & Gray, 1965).

The generation of mixed-valence Au^{III}/Au^{I} species has been observed in the disproportionation reactions of dinuclear Au^{II} species (Khan, Wang & Fackler, 1989). It has been reported that the addition of halides to dinuclear gold(I) dithiolate rings of the type [Au(μ-dithiolato)]$_2$ produces unstable gold(II)

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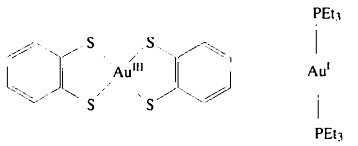
species which decompose to give the mixed-valence compounds.

We have recently reported the synthesis and characterization of dinuclear 1,2-dithiolene 'open-ring' gold(I) complexes (Dávila, Elduque, Grant, Staples & Fackler, 1993) of the type $[\mathrm{Au_2}(\mu\text{-}1,2\text{-dithiolene})(\mathrm{P}R_3)_2]$. The reaction of 1,2-benzenedithiolate with trialkylphosphine gold chlorides occurs with oxidation of one of the gold(I) centers to gold(III), producing mixed-valence $\mathrm{Au^{III}/Au^{I}}$ species. We believe that these complexes are formed from the disproportionation of unstable dinuclear gold(II) 1,2-(aromatic)dithiolene$(\mathrm{P}R_3)_2$ complexes. Here we report the structure of $[\mathrm{Au^{I}(PEt_3)_2}][\mathrm{Au^{III}(S_2C_6H_4)_2}]$, (I), produced from the reaction of 1,2-benzenedithiol with $\mathrm{Au(PEt_3)Cl}$.



(I)

The structure of $[\mathrm{Au(PEt_3)_2}][\mathrm{Au(S_2C_6H_4)_2}]$ (Fig. 1) is formed by $[\mathrm{Au(PEt_3)_2}]^+$ cation and $[\mathrm{Au(S_2C_6H_4)_2}]^-$ anion pairs. The $[\mathrm{Au(PEt_3)_2}]^+$ cation shows distorted linear coordination of two $\mathrm{PEt_3}$ units to the gold(I) center with a P(1)—Au(1)—P(2) angle of 169.9 (1)°.

Two chelating 1,2-benzenedithiolate units coordinate to the gold(III) center of the anion in a square-planar fashion. The average Au—S distance is 2.314 Å. There are no metal–metal interactions in the structure. Au(2) and Au(3) both lie on inversion centers, hence the structure contains two independent and exactly centrosymmetric types of anion.

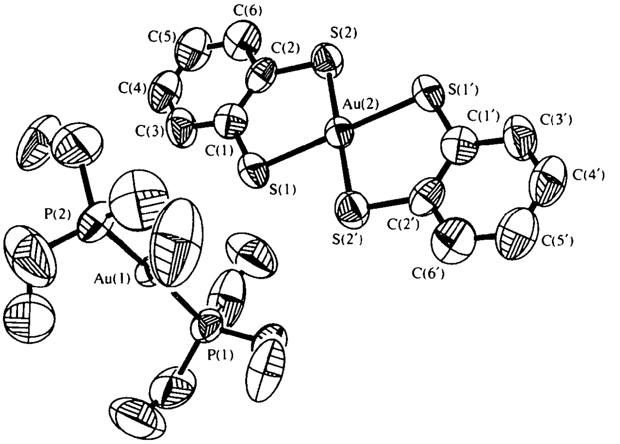


Fig. 1. The structure of $[\mathrm{Au(PEt_3)_2}][\mathrm{Au(S_2C_6H_4)_2}]$ showing displacement ellipsoids at the 50% probability level. Primed atoms are related to the corresponding unprimed atoms by the center of symmetry.

An analogous structure to that of the aromatic dithiolene–gold(III) anion has been reported for the toluenedithiol derivative (Mazid, Tahir Razi & Sadler, 1981). The structure of the gold(IV) analog of the bis(1,2-benzenedithiolate) anion has also been reported, and displays the same square-planar coordination (Rindorf, Thorup, Bjørnholm & Bechgaard, 1990).

Experimental

1,2-Benzenedithiol (32.8 µl, 0.0286 mmol) was added to a MeOH solution of KOH (1.96 ml, 0.571 mmol). This colorless solution was transferred to a Schlenk tube containing an acetone solution of $\mathrm{Au(PEt_3)Cl}$ (0.2001 g, 0.5714 mmol), which then turned green. After 2 h the solvent was evaporated off and $\mathrm{CH_2Cl_2}$ was added. The solution was filtered, concentrated under vacuum and the product was precipitated upon addition of $\mathrm{Et_2O}$ to the concentrated solution. A light-green solid was recovered (0.141 g, 21%). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR $\mathrm{CDCl_3}$: 33.85 p.p.m. ^{1}H NMR $\mathrm{CDCl_3}$: δ = 1.91 (*m*, $\mathrm{PCH_2C}H_3$, $J_{\mathrm{H-H}}$ 7.62, $J_{\mathrm{P-H}}$ 17.9 Hz), 2.46 (*m*, $\mathrm{PC}H_2\mathrm{CH_3}$, $J_{\mathrm{P-H}}$ 8.33 Hz), 7.53, 8.57 p.p.m. (AA′, BB′ $J_{\mathrm{H-H}}$ 2.38 Hz, $J_{\mathrm{H-H}}$ 5.86 Hz). Crystals of the title compound were obtained by the slow diffusion of a layer of $\mathrm{Et_2O}$ into a $\mathrm{CH_2Cl_2}$ solution of the compound.

Crystal data

$[\mathrm{Au(C_6H_{15}P)_2}]$-$[\mathrm{Au(C_6H_4S_2)_2}]$
M_r = 910.71
Triclinic
$P\overline{1}$
a = 9.532 (4) Å
b = 12.696 (5) Å
c = 13.116 (4) Å
α = 86.13 (3)°
β = 84.09 (3)°
γ = 80.51 (3)°
V = 1555 (1) Å^3
Z = 2
D_x = 1.945 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 9.780 mm^{-1}
T = 298 K
Needle
0.5 × 0.3 × 0.1 mm
Green

Data collection

Nicolet $R3m/E$ diffractometer
ω scans
Absorption correction: empirical
T_{min} = 0.432, T_{max} = 0.947
4562 measured reflections
2874 independent reflections
2708 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$

R_{int} = 0.0367
θ_{max} = 22.5°
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections intensity variation: <1%

Refinement

Refinement on F
R = 0.0350
wR = 0.0395
S = 1.218

$(\Delta/\sigma)_{\mathrm{max}}$ = 0.003
$\Delta\rho_{\mathrm{max}}$ = 0.89 e Å^{-3}
$\Delta\rho_{\mathrm{min}}$ = −1.14 e Å^{-3}
Extinction correction: none

2708 reflections
292 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00042F_o^2]$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Au(1)	0.2782 (1)	0.2152 (1)	0.2508 (1)	0.063 (1)
Au(2)	0	0	0	0.051 (1)
Au(3)	1/2	1/2	1/2	0.076 (1)
S(1)	0.1317 (3)	0.1174 (2)	0.0590 (3)	0.072 (1)
S(2)	0.0309 (3)	0.0763 (2)	−0.1641 (2)	0.072 (1)
S(3)	0.5391 (4)	0.4228 (3)	0.3422 (3)	0.097 (2)
S(4)	0.3302 (4)	0.6326 (3)	0.4339 (3)	0.094 (1)
P(1)	0.0615 (3)	0.3148 (3)	0.3069 (3)	0.074 (1)
P(2)	0.4860 (3)	0.0952 (3)	0.2187 (3)	0.079 (1)
C(1)	0.1871 (12)	0.1890 (8)	−0.0537 (10)	0.067 (5)
C(2)	0.1448 (11)	0.1718 (8)	−0.1497 (9)	0.063 (4)
C(3)	0.2758 (14)	0.2660 (10)	−0.0499 (12)	0.085 (6)
C(4)	0.3212 (14)	0.3200 (10)	−0.1364 (14)	0.091 (7)
C(5)	0.2828 (15)	0.3038 (10)	−0.2287 (13)	0.098 (7)
C(6)	0.1912 (14)	0.2291 (10)	−0.2358 (10)	0.091 (6)
C(7)	−0.0667 (12)	0.2277 (11)	0.3410 (11)	0.091 (6)
C(8)	−0.0249 (16)	0.1369 (13)	0.4145 (15)	0.144 (10)
C(9)	0.0749 (17)	0.3924 (14)	0.4175 (14)	0.140 (9)
C(10)	0.1665 (22)	0.3442 (17)	0.4956 (14)	0.181 (13)
C(11)	−0.0259 (18)	0.4269 (13)	0.2207 (18)	0.158 (11)
C(12)	−0.0534 (22)	0.4001 (16)	0.1291 (14)	0.170 (12)
C(13)	0.5756 (18)	0.1037 (15)	0.0851 (14)	0.145 (9)
C(14)	0.6390 (17)	0.1988 (13)	0.0609 (15)	0.144 (10)
C(15)	0.4500 (19)	−0.0373 (12)	0.2093 (15)	0.156 (10)
C(16)	0.3605 (21)	−0.0848 (14)	0.2832 (20)	0.216 (15)
C(17)	0.6135 (20)	0.0949 (19)	0.3003 (17)	0.207 (14)
C(18)	0.5730 (19)	0.1065 (16)	0.4027 (13)	0.143 (10)
C(19)	0.4123 (13)	0.5062 (9)	0.2698 (11)	0.079 (6)
C(20)	0.3242 (13)	0.5931 (9)	0.3078 (10)	0.075 (5)
C(21)	0.2263 (14)	0.6533 (10)	0.2459 (13)	0.084 (6)
C(22)	0.2158 (16)	0.6286 (11)	0.1478 (13)	0.095 (7)
C(23)	0.3089 (16)	0.5424 (13)	0.1074 (12)	0.100 (7)
C(24)	0.4044 (15)	0.4795 (10)	0.1683 (13)	0.091 (6)

Table 2. *Selected geometric parameters* (Å, °)

Au(1)—P(1)	2.315 (3)	Au(2)—S(2)	2.311 (3)
Au(1)—P(2)	2.311 (3)	Au(3)—S(3)	2.319 (4)
Au(2)—S(1)	2.317 (3)	Au(3)—S(4)	2.324 (3)
P(1)—Au(1)—P(2)	169.9 (1)	S(3)—Au(3)—S(4)	89.6 (1)
S(1)—Au(2)—S(2)	90.0 (1)		

Computations were performed using the *SHELXTL* program package (Sheldrick, 1986).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms, and a packing diagram have been deposited with the IUCr (Reference: MU1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Monomeric (Dipropionato-*O*)(dithiourea-*S*)-zinc(II)

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Abstract

Zinc(II) propionate reacts with thiourea in water to form the title monomeric colourless zinc(II) complex, $[Zn(C_3H_5O_2)_2(CH_4N_2S)_2]$. Two thiourea S atoms and two propionate O atoms form a distorted tetrahedron around the Zn^{II} atom with Zn—S bonds of 2.320 (1) and 2.341 (2) Å and Zn—O bonds of 1.959 (3) and 1.988 (2) Å. One carboxylate group forms two intermolecular hydrogen bonds to two different amino groups and these, together with other intermolecular hydrogen bonds, distort the tetrahedron.

Comment

Both anhydrous zinc(II) acetate (Capilla, 1979) and zinc(II) propionate (Goldschmied, Rae & Stephenson, 1977) form polymeric structures, the former a three-