S(11)	0.33371 (7)	0.0973 (1)	0.28839 (8)	2.4 (1)
S(12)	0.35470 (7)	−0.1341 (1)	0.17584 (8)	2.7 (1)
S(13)	0.15972 (7)	0.1191 (1)	0.21790 (9)	3.2 (1)
S(14)	0.18234 (7)	−0.1633 (1)	0.08249 (8)	2.6 (1)
C(15)	0.3987 (3)	−0.0197 (4)	0.2609 (3)	2.1 (2)
C(16)	0.2468 (2)	0.0353 (4)	0.2126 (3)	1.9 (2)
C(17)	0.2568 (2)	−0.0733 (4)	0.1596 (3)	1.8 (2)
C(18)	0.0841 (2)	0.0005 (4)	0.1635 (3)	2.4 (2)
C(19)	0.0966 (2)	−0.0524 (4)	0.0695 (3)	2.1 (2)
S(21)	0.51910 (7)	0.0966 (1)	0.39283 (8)	2.6 (1)
S(22)	0.54725 (7)	−0.1350 (1)	0.28315 (9)	2.8 (1)
S(23)	0.68451 (7)	0.1207 (1)	0.50615 (8)	2.8 (1)
S(24)	0.71959 (7)	−0.1589 (1)	0.37375 (9)	2.8 (1)
C(25)	0.4787 (3)	−0.0200 (4)	0.3053 (3)	2.2 (2)
C(26)	0.6170 (2)	0.0351 (4)	0.4178 (3)	1.9 (2)
C(27)	0.6302 (2)	−0.0735 (4)	0.3659 (3)	2.1 (2)
C(28)	0.7720 (3)	0.0141 (5)	0.5264 (3)	2.6 (2)
C(29)	0.7924 (3)	−0.0406 (5)	0.4358 (3)	2.8 (2)
S(31)	0.39397 (7)	0.3753 (1)	0.49644 (9)	2.8 (1)
S(32)	0.41676 (7)	0.6252 (1)	0.39875 (9)	3.0 (1)
S(33)	0.21883 (7)	0.3589 (1)	0.41770 (8)	2.7 (1)
S(34)	0.24652 (8)	0.6586 (1)	0.30291 (9)	3.1 (1)
C(35)	0.4606 (2)	0.4995 (5)	0.4783 (3)	2.3 (2)
C(36)	0.3071 (3)	0.4489 (4)	0.4242 (3)	2.1 (2)
C(37)	0.3184 (3)	0.5616 (4)	0.3807 (3)	2.3 (2)
C(38)	0.1555 (3)	0.4345 (5)	0.3123 (3)	2.8 (2)
C(39)	0.1540 (3)	0.5824 (5)	0.3156 (3)	2.9 (2)

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

Br(1)—Cu	2.407 (2)	S(23)—C(26)	1.734 (5)
Br(2)—Cu	2.421 (2)	S(23)—C(28)	1.810 (5)
S(11)—C(15)	1.723 (5)	S(24)—C(27)	1.731 (5)
S(11)—C(16)	1.741 (4)	S(24)—C(29)	1.807 (5)
S(12)—C(15)	1.721 (5)	C(26)—C(27)	1.370 (6)
S(12)—C(17)	1.742 (4)	C(28)—C(29)	1.508 (7)
S(13)—C(16)	1.723 (4)	S(31)—C(35)	1.750 (5)
S(13)—C(18)	1.805 (5)	S(31)—C(36)	1.766 (5)
S(14)—C(17)	1.738 (4)	S(32)—C(35)	1.755 (5)
S(14)—C(19)	1.818 (5)	S(32)—C(37)	1.758 (5)
C(15)—C(25)	1.367 (6)	S(33)—C(36)	1.741 (5)
C(16)—C(17)	1.365 (6)	S(33)—C(38)	1.808 (5)
C(18)—C(19)	1.495 (6)	S(34)—C(37)	1.756 (5)
S(21)—C(25)	1.742 (5)	S(34)—C(39)	1.797 (5)
S(21)—C(26)	1.739 (5)	C(36)—C(37)	1.332 (6)
S(22)—C(25)	1.726 (5)	C(38)—C(39)	1.501 (7)
S(22)—C(27)	1.739 (5)	C(35)—C(35^{i})	1.343 (8)
Br(1)—Cu—Br(2)	90.00 (2)	S(21)—C(26)—S(23)	114.8 (2)
C(15)—S(11)—C(16)	96.4 (2)	S(21)—C(26)—C(27)	116.2 (3)
C(15)—S(12)—C(17)	96.3 (2)	S(23)—C(26)—C(27)	129.0 (3)
C(16)—S(13)—C(18)	101.0 (2)	S(22)—C(27)—S(24)	115.7 (3)
C(17)—S(14)—C(19)	101.3 (2)	S(22)—C(27)—C(26)	116.5 (3)
S(11)—C(15)—S(12)	114.9 (3)	S(24)—C(27)—C(26)	127.8 (3)
S(11)—C(15)—C(25)	121.3 (3)	S(23)—C(28)—C(29)	114.8 (3)
S(12)—C(15)—C(25)	123.8 (3)	S(24)—C(29)—C(28)	113.4 (3)
S(11)—C(16)—S(13)	114.5 (2)	C(35)—S(31)—C(36)	95.5 (2)
S(11)—C(16)—C(17)	116.1 (3)	C(35)—S(32)—C(37)	94.7 (2)
S(13)—C(16)—C(17)	129.4 (3)	C(36)—S(33)—C(38)	99.8 (2)
S(12)—C(17)—S(14)	116.1 (2)	C(37)—S(34)—C(39)	101.5 (2)
S(12)—C(17)—C(16)	116.4 (3)	S(31)—C(35)—S(32)	114.8 (3)
S(14)—C(17)—C(16)	127.5 (3)	S(31)—C(35)—C(35^{i})	123.2 (5)
S(13)—C(18)—C(19)	113.1 (3)	S(32)—C(35)—C(35^{i})	122.0 (5)
S(14)—C(19)—C(18)	113.6 (3)	S(31)—C(36)—S(33)	114.2 (2)
C(25)—S(21)—C(26)	96.4 (2)	S(31)—C(36)—C(37)	116.3 (3)
C(25)—S(22)—C(27)	96.6 (2)	S(33)—C(36)—C(37)	129.5 (4)
C(26)—S(23)—C(28)	101.9 (2)	S(32)—C(37)—S(34)	113.2 (3)
C(27)—S(24)—C(29)	101.3 (2)	S(32)—C(37)—C(36)	118.5 (4)
C(15)—C(25)—S(21)	121.5 (3)	S(34)—C(37)—C(36)	128.3 (4)
C(15)—C(25)—S(22)	124.1 (4)	S(33)—C(38)—C(39)	114.1 (3)
S(21)—C(25)—S(22)	114.4 (3)	S(34)—C(39)—C(38)	113.9 (4)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

The atomic coordinates given by Mori *et al.* (1987) were used as starting values for the refinement and the atom-labelling scheme employed is the same as that used by Hebrard *et al.* (1994). All non-H atoms were refined anisotropically. H atoms were placed at calculated positions (C—H = 1.0 Å); these positions were allowed to vary during the last few cycles. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (Enraf–Nonius, 1985). Program used to refine structure: *SHELXS*86 (Sheldrick, 1985).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and plots of the structure and the crystal packing have been deposited with the IUCr (Reference: MU1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro[tri(*p*-tolyl)phosphine]gold(I)

P. D. Cookson and E. R. T. Tiekink

Department of Chemistry, The University of Adelaide, Adelaide, SA 5005, Australia

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Abstract

The Au atom in each of the two molecules that comprise the asymmetric unit of chloro[tris(4-methylphenyl)phosphine]gold(I), $[AuCl(C_{21}H_{21}P)]$, ex-

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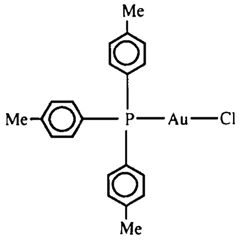
ists in a linear coordination geometry; the Au—Cl distances are 2.255 (3) and 2.256 (3) Å, the Au—P distances 2.201 (3) and 2.208 (3) Å, and the Cl—Au—P angles are 178.1 (1) and 179.6 (1)°.

Comment

Linear geometry about the Au atom is found in each of the two independent molecules of [{(*p*-tolyl)$_3$P}AuCl], (I), that comprise the asymmetric unit. There are no significant intermolecular contacts in the lattice; the closest contact of 3.42 (3) Å occurs between atoms C(223) and C(223′)($-x$, $-y$, $-z$). The closest Au···Au contact in the lattice is 7.3284 (9) Å and occurs between Au(1) and Au(2″)($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$). Small differences in the orientation of the *p*-tolyl groups give rise to the two independent molecules. The most significant difference can be seen in the Au(1)—P(1)—C(131)—C(132) torsion angle of −142.6 (8)° compared with an angle of 121.2 (9)° for Au(2)—P(2)—C(231)—C(236) in the second molecule. The two independent Au—P distances are equal within experimental error, as are the Au—Cl bond lengths.



(I)

Linear Au-atom coordination geometries are found in related [(R_3P)AuCl] systems. The Au—P distances of 2.201 (3) and 2.208 (3) Å in the present structure are significantly shorter than the Au—P distance of 2.235 (3) Å found in [(Ph$_3$P)AuCl] (Baenziger, Bennett & Soboroff, 1976). Similarly, the Au—Cl distances of 2.255 (3) and 2.256 (3) Å are shorter than the comparable distance of 2.279 (3) Å found in the Ph$_3$P analogue. Clearly, the steric profiles of the two phosphine ligands are essentially the same in the two structures and, in the absence of significant intermolecular interactions, the different bond lengths may be related to the different electron-donating abilities of the phosphine ligands.

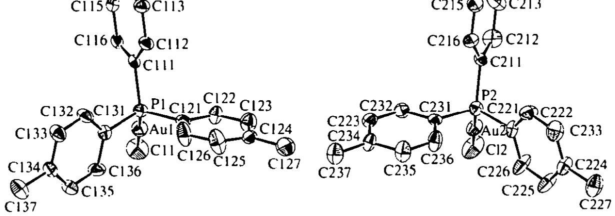


Fig. 1. Molecular structure (*ORTEP*II; Johnson, 1976) of the two independent molecules of [{(*p*-tolyl)$_3$P}AuCl] showing the crystallographic numbering scheme and ellipsoids drawn at the 25% probability level.

Experimental

The title compound was prepared according to the literature procedure of Al-Saády, McAuliffe, Parish & Sandbank (1985) and crystals suitable for the X-ray study were grown by the slow evaporation of a chloroform solution of the compound held at 277 K (m.p. 459–460 K).

Crystal data

[AuCl($C_{21}H_{21}P$)]
$M_r = 536.79$
Monoclinic
$P2_1/c$
$a = 9.674$ (2) Å
$b = 21.597$ (6) Å
$c = 19.174$ (2) Å
$\beta = 98.84$ (1)°
$V = 3958$ (1) Å^3
$Z = 8$
$D_x = 1.801$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 12.7$–17.1°
$\mu = 7.625$ mm^{-1}
$T = 293$ K
Needle
0.42 × 0.13 × 0.13 mm
Colourless

Data collection

AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.897$, $T_{\max} = 1.035$
7921 measured reflections
7461 independent reflections
3487 observed reflections [$I \geq 3\sigma(I)$]

$R_{\text{int}} = 0.059$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 28$
$l = -25 \rightarrow 25$
3 standard reflections monitored every 400 reflections
intensity variation: 0.35%

Refinement

Refinement on F
$R = 0.0360$
$wR = 0.0290$
$S = 1.340$
3487 reflections
433 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.0020$
$\Delta\rho_{\max} = 0.565$ e Å^{-3}
$\Delta\rho_{\min} = -0.543$ e Å^{-3}
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)

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

	x	y	z	U_{eq}
Au(1)	0.05758 (5)	0.51914 (2)	0.21966 (2)	0.0644
Au(2)	0.43135 (5)	0.20720 (2)	0.05019 (2)	0.0650
Cl(1)	−0.0441 (3)	0.4468 (2)	0.2798 (2)	0.1058
Cl(2)	0.5560 (3)	0.2693 (2)	−0.0115 (2)	0.1092

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: *SHELXS86* (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($S_2C_6H_4$)$_2$]

Rosa M. Dávila, Richard J. Staples and John P. Fackler Jr*

Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA

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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)