

Fig. 1. Diagram of the structure showing the chain along the twofold screw axis.

forming a bridge between two Hg^{II} atoms related by the twofold screw axis. The ligand molecule is bidentate and is coordinated to Hg through N(1) from the pyridyl group and O from the acetyl group (Fig. 1). These two groups are planar within one standard deviation and the angle between them is 51.7° . The inclination of the acetyl group with respect to the pyridyl group is defined by the torsion angles N(1)–C(2)–N(2)–C(7) of 135.3° and C(2)–N(2)–C(7)–O of -8.8° . The average distances and angles agree well with the values for

similar compounds. There is a close intermolecular approach of $2.913(8) \text{ \AA}$ between O and N(2) ($-x, \frac{1}{2} + y, \frac{3}{2} - z$).

The angular geometry about the Hg atom is highly irregular, the X–Hg–Y angles ranging from $85.6(1)$ to $157.75(4)^\circ$. The coordination distances around the metal are less than 2.5 \AA , except for the Hg–O [$2.774(6) \text{ \AA}$]. One of the Br atoms is also close to another Hg atom of a neighbouring chain with Hg–Br(2) ($-x, 1-y, 1-z$) of $3.306(1) \text{ \AA}$. Fig. 1 gives the relevant bond distances and angles in the structure.

All computer calculations were performed using the *Enraf–Nonius Structure Determination Package*. The figure was drawn with the *ORTEP* program (Johnson, 1965).

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Bis(tricyclohexylphosphine)gold(I) Thiocyanate

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Abstract. $[\text{Au}\{\text{cyclo-C}_6\text{H}_{11}\}_3\text{P}\}_2]\text{SCN}$, $\text{C}_{36}\text{H}_{66}\text{Au-P}_2^+\text{SCN}^-$, orthorhombic, $M_r = 815.9$, $a = 25.151(19)$, $b = 15.737(14)$, $c = 9.630(9) \text{ \AA}$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 3.83 \text{ mm}^{-1}$, $F(000) = 1676$, $V = 3812 \text{ \AA}^3$, $T = 298 \pm 2 \text{ K}$. The complex forms an almost linear, two-coordinate gold compound, with both the bis(tricyclohexylphosphine)gold(I) cation and the thiocyanate anion located on the mirror plane in space group $Pnma$.

Introduction. The title compound was obtained during the attempted preparation of a gold cluster complex analogous to $[\text{Au}_{11}(\text{Ph}_3\text{P})_7](\text{SCN})_3$ (Cariati & Naldini, 1971). Similarly, in a recent report of an improved synthesis of $[\text{Au}_{11}(\text{Ph}_3\text{P})_7](\text{SCN})_3$, the isolation of

$[\text{Au}(\text{Ph}_3\text{P})_2]\text{SCN}$ was described (Vollenbroek, Bouten, Trooster, Van den Berg & Bour, 1978). $[\text{Au}\{\text{C}_6\text{H}_{11}\}_3\text{P}\}_2]\text{SCN}$ could be either linear with ionic thiocyanate or trigonal with the thiocyanate coordinated as in the case of $[\text{Au}(\text{Ph}_3\text{P})_2\text{Cl}]$ (Baenziger, Dittmore & Doyle, 1974). In order to include the compound in a series of complexes of Au^{I} to be studied by Mössbauer spectroscopy it was of interest to determine its coordination geometry. For this reason, and also since no structures of complexes of Au with $(\text{cyclo-C}_6\text{H}_{11})_3\text{P}$ were known, the structure determination of $[\text{Au}\{\text{cyclo-C}_6\text{H}_{11}\}_3\text{P}\}_2]\text{SCN}$ was undertaken.

The title compound was prepared during the reaction between (tricyclohexylphosphine)gold thiocyanate and sodium borohydride in ethanol solution. The reaction

mixture was taken to dryness, extracted with a benzene-CH₂Cl₂ solvent mixture, and separated by thin-layer chromatography into closely spaced deep-red and yellow-brown bands plus a residue. Single crystals of the material in both bands were recrystallized from ethyl acetate solution. The red crystals had a density of 1.99 (1) Mg m⁻³ while that of the yellow-brown crystals was 1.42 (1) Mg m⁻³ [by flotation in aqueous Hg(NO₃)₂ and Mn(NO₃)₂, respectively]. The yellow crystals yielded better single-crystal photographs, and are the subject of this investigation.

Elemental analyses yielded 7.68% P, 3.74% S, 54.33% C, and 8.05% H and 25.40% Au for the yellow residue. The theoretical composition includes 7.59% P, 3.93% S, 54.47% C, 8.15% H, and 24.14% Au. Preliminary analyses of crystals by Weissenberg and precession techniques showed systematically absent reflections in the *Ok*l zone when *k* + *l* = 2*n* + 1 and in the *hk*0 zone when *h* = 2*n* + 1, indicating space groups *Pnma* or *Pn*2₁*a*.

For the intensity-data collection, a well formed needle-shaped crystal in the form of a triangular prism was mounted with the *c* axis parallel to the ω axis of a Pailred semi-automatic diffractometer equipped with a graphite monochromator and Mo *K* α radiation. 2084 independent non-zero reflections were measured on layers *hk*0–10, of which 1289 had an intensity which exceeded three times the standard deviation and were included in subsequent analyses. The 640 reflection was measured after each layer of data was collected and was found to remain constant to $\pm 3\%$, although the pale-yellow crystals gradually became transparent. Accurate cell parameters were determined by a graphical fitting to the setting angles of appropriate sets of axial reflections. Cell faces were identified and accurately measured for absorption correction, with the transmission factors varying from 0.68 to 0.80.

A three-dimensional Patterson synthesis revealed the location of the Au atom. Least-squares refinement and difference Fourier syntheses were begun in the non-centrosymmetric space group *Pn*2₁*a*, starting with an *R* value of 0.22 for the single, isotropic Au atom, and proceeding with some difficulty to final values of *R* = 0.079 and *R'* = $\sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.076$, for a model in which the Au, P and S atoms were anisotropic, and 183 parameters were refined (Muir & Muir, 1976). This model was unsatisfactory in several respects; C–C distances ranged from 1.24 to 1.83 Å, the P–C distances ranged from 1.77 to 2.03 Å, one or both of the P atoms became non-positive definite, and the thiocyanate ion was non-linear.

Refinement was thus attempted in the centrosymmetric space group *Pnma*, in which both the cation and the anion lie on the mirror plane at *y* = $\frac{3}{4}$. Subsequent full-matrix least-squares refinement of the model with anisotropic Au, P and S atoms, and with only 115 parameters refined in this space group, yielded

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Au(1)	-689 (1)	7500	-506 (2)	42 (1)
P(1)	182 (4)	7500	214 (11)	36 (6)
P(2)	-1580 (5)	7500	-1121 (13)	52 (6)
C(1)	314 (15)	8425 (25)	1293 (38)	77 (7)
C(2)	877 (14)	8666 (25)	1527 (36)	74 (7)
C(3)	953 (15)	9445 (25)	2640 (38)	98 (8)
C(4)	492 (14)	9832 (25)	3267 (39)	94 (8)
C(5)	-43 (13)	9548 (24)	3000 (31)	76 (7)
C(6)	-145 (13)	8773 (25)	2108 (33)	86 (7)
C(7)	679 (20)	7500	-1134 (41)	61 (8)
C(8)	595 (14)	6711 (23)	-2041 (36)	74 (7)
C(9)	1010 (13)	6678 (24)	-3283 (37)	80 (7)
C(10)	939 (19)	7500	-4206 (46)	78 (8)
C(11)	-1891 (13)	6558 (24)	-372 (39)	82 (7)
C(12)	-2468 (12)	6356 (22)	-924 (30)	65 (7)
C(13)	-2700 (14)	5532 (25)	-253 (38)	99 (8)
C(14)	-2412 (15)	5054 (26)	655 (40)	102 (8)
C(15)	-1896 (14)	5305 (24)	1108 (35)	78 (7)
C(16)	-1649 (13)	6122 (25)	728 (36)	93 (7)
C(17)	-1647 (16)	7500	-3019 (39)	42 (8)
C(18)	-1373 (11)	8297 (21)	-3693 (34)	57 (7)
C(19)	-1447 (11)	8272 (20)	-5228 (32)	54 (7)
C(20)	-1175 (19)	7500	-5936 (44)	71 (8)
S(1)	-2839 (7)	7500	-7101 (19)	137 (8)
C(21)	-2888 (24)	7500	-5592 (58)	99 (9)
N(1)	-2957 (18)	7500	-4643 (47)	84 (8)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

Au(1)–P(1)	2.295 (11)	P(1)–C(7)	1.801 (45)
Au(1)–P(2)	2.316 (13)	P(2)–C(11)	1.824 (36)
P(1)–C(1)	1.819 (38)	P(2)–C(17)	1.835 (39)
S(1)–C(21)	1.46 (5)	C(21)–N(1)	0.93 (6)
P(1)–C(1)–C(2)	117.7 (28)	Au(1)–P(2)–C(17)	110.1 (14)
P(1)–C(1)–C(6)	116.9 (26)	P(1)–Au(1)–P(2)	177.2 (4)
P(1)–C(7)–C(8)	108.4 (25)	P(2)–C(11)–C(12)	115.1 (24)
Au(1)–P(1)–C(1)	110.3 (12)	P(2)–C(11)–C(16)	119.8 (27)
Au(1)–P(1)–C(7)	116.3 (15)	P(2)–C(17)–C(18)	111.8 (20)
Au(1)–P(2)–C(11)	108.2 (12)	S(1)–C(21)–N(1)	174 (7)

an *R* of 0.084 and an *R'* of 0.078. These slightly higher *R* values are not surprising in view of the large decrease in the number of parameters refined. In any event, the model, as refined in *Pnma*, is clearly superior.

The weighting scheme used was $w = 1/\sigma_F^2$, where σ_F was derived from counting statistics only. Neutral-atom scattering factors (Cromer & Mann, 1968) were used, and corrected for anomalous dispersion (Cromer & Liberman, 1970). A final difference Fourier map showed two peaks near the Au and one peak near the N with peak heights in the range 1–1.5 e \AA^{-3} . None of these could be correlated with any of the solvent molecules with which the title compound has been in contact during its preparation or crystal growth. The analysis of variance was flat. The atomic coordinates

and thermal parameters are given in Table 1, and the resulting interatomic distances and angles in Table 2.*

Discussion. The coordination about the Au atom is shown in Fig. 1; the Au and P atoms are located on the mirror plane, as are C(7), C(10), C(17), and C(20). The Au is linearly coordinated, with $P(1)-Au-P(2) = 177.2(4)^\circ$. The Au-P distances, 2.295(11) and 2.316(13) Å, are nearly equal, as are the P-C distances, which range from 1.80(4) to 1.83(4) Å. The C-C distances in the cyclohexyl rings range from 1.36(5) to 1.64(5) Å.

Au-P distances in linear complexes depend on the ligand *trans* to the phosphine. For $[Au(MePh_2P)_2]PF_6$, with *trans* phosphine, the Au-P distance is 2.316(4) Å (Guy, Jones & Sheldrick, 1976), which is very close to the values reported here. The Au-P value is 2.279(8) Å for $[AuMe(Ph_3P)]$ (Gavens, Guy, Mays & Sheldrick, 1977) and 2.235(3) Å for $[Au(Ph_3P)Cl]$ (Baenziger, Bennett & Soboroff, 1976). The tricyclohexylphosphine groups are approximately eclipsed. The SCN⁻ ion, which also lies on the mirror plane, is nearly linear, with an S-C-N angle of $174(7)^\circ$. The same basic conclusions were earlier obtained from the model refined in *Pr2,a*, but with considerably greater e.s.d.'s.

Studies of Mössbauer spectra of gold complexes have been reported recently in which a correlation of isomer shift and quadrupole splitting is found to be very sensitive to the coordination geometry. The complexes $[AuL_2]ClO_4$, with $L = Ph_3P, MePh_2P, EtPh_2P,$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34974 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

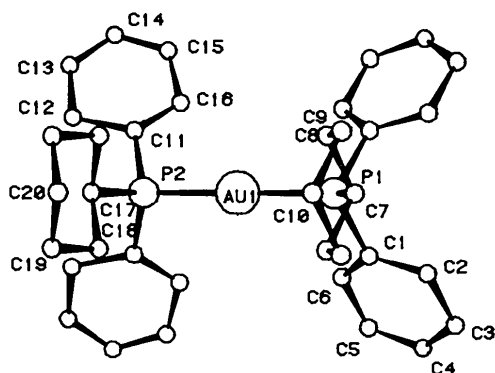


Fig. 1. View of the cation showing the horizontal mirror plane.

$Me_2PhP,$ and $Et_2PhP,$ all fit the correlation for linear complexes but the trigonal complex $[Au(Ph_3P)_2Cl]$ does not (McAuliffe, Parish & Randall, 1977). Similarly, the complexes $[AuL_2]PF_6$, for a wide variety of ligands including $L = (C_6H_{11})_3P$ as well as other phosphines, fit the correlation for linear complexes (Jones, Maddock, Mays, Muir & Williams, 1977), while $[Au(Ph_3P)_2(SCN)]$ was assigned as three coordinate (Jones, Jones, Maddock, Mays, Vergnano & Williams, 1977).

It is interesting that the coordination geometry of the complexes $[AuL_2]SCN$ is apparently trigonal for $L = Ph_3P$ but has been shown in this work to be linear for $L = (C_6H_{11})_3P$. A structural study of the Ph_3P complex would be of interest.

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