

Thiocyanatobis(triphenylphosphine)gold(I)

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(Received 16 September 1981; accepted 2 December 1981)

Abstract. $[\text{Au}(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{SCN})]$, $\text{C}_{37}\text{H}_{30}\text{AuNP}_2\text{S}$, is monoclinic, $P2_1/n$, $M_r = 779.6$, $a = 11.823$ (2), $b = 19.795$ (6), $c = 13.887$ (5) Å, $\beta = 91.73$ (5)°, $Z = 4$, $\mu(\text{Mo } K\alpha) = 4.52 \text{ mm}^{-1}$, $D_c = 1.594$, $D_x = 1.61$ (1) Mg m^{-3} , $V = 3248.6 \text{ Å}^3$. Final $R = 0.075$ for 3414 unique reflections. The complex crystallizes as a trigonal-planar, three-coordinate gold compound, similar to the analogous chloro complex.

Introduction. The title compound was obtained as part of a study of possible three- or four-coordinate gold complexes with thiocyanate and phosphine ligands. $[\text{Au}\{\text{P}(\text{cyclo-C}_6\text{H}_{11})_3\}_2][\text{SCN}]$ was shown to form a linear two-coordinate complex with an ionic thiocyanate anion (Muir, Muir & Lorca, 1980). In contrast, $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Cl}]$ forms a trigonal-planar three-coordinate complex (Baenziger, Dittmore & Doyle, 1974). In addition, preliminary results for $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3(\text{SCN})]$ show that it forms a four-coordinate complex having extremely long Au–P and Au–S distances (Muir, Muir, Arias, Campana & Dwight, 1981). It therefore seemed of interest to study related gold complexes, such as $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\text{SCN})]$, in order to understand better the structure and bonding involved.

The title compound was prepared, somewhat accidentally, using the method reported for $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3(\text{SCN})]$ (DeStefano & Burmeister, 1971). A solution of 0.32 g (4.0 mmol) of NaSCN in 20 ml of ethanol was added to 0.40 g (1.0 mmol) of $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ in 10 ml ethanol. After 10 min of stirring, NaCl was removed by filtration. A solution of 0.53 g (2.0 mmol) of triphenylphosphine in 30 ml ethanol was added to the blood-red filtrate, causing the mixture to become colorless. After stirring for 15 min, the solvent was then removed until crystals began to form. The product was filtered, washed with ethanol and ether and dried over CaSO_4 in vacuum. It is probable that reduction from Au^{III} to Au^{I} was due to reaction with SCN^- and not to reaction with phosphine, since both moles of phosphine were coordinated to the Au^{I} product. This is consistent with equilibrium data for reaction of AuCl_4^- with SCN^- (Elding, Gröning & Olsson, 1980).

Elemental analyses of 57.41% C, 3.99% H and 1.78% N were obtained. The theoretical composition includes 57.00% C, 3.88% H and 1.80% N. Pre-

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

	x	y	z	U_{eq}
Au	6571 (1)	4133 (1)	7236 (1)	40 (1)*
P(1)	7170 (3)	5138 (2)	7988 (3)	39 (2)*
P(2)	4712 (3)	3803 (2)	6818 (3)	37 (2)*
S(1)	7990 (4)	3309 (2)	6705 (4)	74 (3)*
C(1)	9250 (15)	3640 (9)	6924 (12)	66 (5)
N(1)	0129 (15)	3872 (9)	7103 (12)	102 (6)
C(111)	8157 (11)	5614 (7)	7286 (10)	42 (4)
C(112)	8274 (11)	5423 (7)	6332 (10)	42 (4)
C(113)	9028 (14)	5787 (9)	5764 (12)	69 (5)
C(114)	9639 (14)	6343 (9)	6143 (13)	70 (5)
C(115)	9502 (14)	6531 (8)	7103 (12)	66 (5)
C(116)	8775 (13)	6164 (8)	7684 (11)	59 (5)
C(121)	5964 (11)	5704 (7)	8180 (9)	42 (4)
C(122)	5077 (13)	5405 (7)	8682 (10)	53 (4)
C(123)	4105 (14)	5797 (8)	8827 (11)	64 (5)
C(124)	4014 (13)	6467 (7)	8477 (11)	52 (4)
C(125)	4928 (13)	6737 (8)	7990 (11)	57 (4)
C(126)	5902 (12)	6357 (7)	7827 (10)	49 (4)
C(131)	7802 (11)	5048 (7)	9195 (9)	36 (3)
C(132)	7760 (12)	5575 (7)	9854 (10)	46 (4)
C(133)	8291 (13)	5511 (8)	0770 (11)	57 (4)
C(134)	8867 (13)	4919 (8)	1017 (11)	56 (4)
C(135)	8890 (13)	4380 (8)	337 (11)	55 (4)
C(136)	8371 (12)	4444 (7)	9418 (10)	44 (4)
C(211)	3820 (11)	4535 (7)	6539 (9)	39 (3)
C(212)	2669 (11)	4538 (7)	6715 (9)	40 (3)
C(213)	2018 (12)	5127 (7)	6454 (10)	51 (4)
C(214)	2527 (14)	5670 (8)	6015 (11)	63 (5)
C(215)	3704 (14)	5659 (8)	5855 (11)	63 (5)
C(216)	4355 (12)	5086 (8)	6132 (11)	52 (4)
C(221)	4040 (11)	3336 (7)	7796 (9)	37 (3)
C(222)	4567 (11)	3378 (7)	8718 (10)	45 (4)
C(223)	4072 (12)	3017 (7)	9453 (10)	50 (4)
C(224)	3130 (13)	2618 (8)	9285 (11)	57 (4)
C(225)	2613 (12)	2588 (7)	8384 (10)	52 (4)
C(226)	3086 (11)	2934 (7)	7590 (10)	44 (4)
C(231)	4476 (12)	3246 (7)	5768 (10)	47 (4)
C(232)	5312 (12)	2742 (7)	5645 (10)	51 (4)
C(233)	5121 (13)	2291 (8)	4851 (11)	56 (4)
C(234)	4184 (13)	2354 (8)	4222 (11)	63 (5)
C(235)	3422 (15)	2843 (9)	4400 (13)	75 (5)
C(236)	3523 (12)	3315 (8)	5166 (11)	53 (4)

* U_{eq} is $\frac{1}{3}$ of the trace of the orthogonalized U matrix.

Table 2. Bond lengths (Å) and angles (°)

Au(1)–P(1)	2.346 (4)	Au(1)–P(2)	2.349 (4)	Au(1)–S(1)	2.468 (4)	S(1)–C(1)	1.647 (18)
C(1)–N(1)	1.157 (20)	P(1)–C(111)	1.808 (14)	P(1)–C(121)	1.839 (13)	P(1)–C(131)	1.824 (13)
P(2)–C(211)	1.826 (13)	P(2)–C(221)	1.843 (13)	P(2)–C(231)	1.842 (14)		
P(1)–Au(1)–P(2)	127.8 (1)	P(1)–Au(1)–S(1)	119.6 (1)	P(2)–Au(1)–S(1)	112.4 (1)	Au(1)–S(1)–C(1)	107.6 (1)
S(1)–C(1)–N(1)	178.2 (1.8)	Au(1)–P(1)–C(111)	113.1 (5)	Au(1)–P(1)–C(121)	110.9 (4)	Au(1)–P(1)–C(131)	115.9 (4)
Au(1)–P(2)–C(211)	111.2 (4)	Au(1)–P(2)–C(221)	112.3 (4)	Au(1)–P(2)–C(231)	118.7 (5)		

Ring	C–C bond lengths			C–C–C bond angles		
	Min	Max	Mean	Min	Max	Mean
11	1.389 (17)	1.413 (19)	1.403 (18)	118.5 (13)	121.2 (13)	120.0 (13)
12	1.383 (18)	1.416 (20)	1.402 (19)	117.7 (14)	122.4 (13)	120.0 (14)
13	1.388 (17)	1.425 (19)	1.404 (18)	118.1 (13)	121.5 (12)	120.0 (13)
21	1.383 (19)	1.437 (18)	1.405 (19)	118.6 (12)	121.8 (13)	120.0 (13)
22	1.377 (19)	1.426 (18)	1.397 (19)	116.5 (12)	123.3 (12)	120.0 (12)
23	1.349 (21)	1.430 (19)	1.400 (20)	115.8 (14)	124.6 (16)	120.0 (15)

liminary analyses of crystals by Weissenberg and precession techniques showed systematically absent reflections of $k = 2n + 1$ in the $0k0$ zone with $h + l = 2n + 1$ in the $h0l$ zone, indicating space group $P2_1/n$.

For intensity-data collection a colorless plate-like crystal having approximate dimensions $0.20 \times 0.10 \times 0.05$ mm was mounted with its b axis parallel to the φ axis of an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected and reduced to structure factors by the Molecular Structure Corporation, College Station, Texas. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 24 reflections.

4381 unique reflections were collected, of which 3414 had non-zero intensities and were included in the final refinement. As a check on the stability of the crystal and the electronics, three check reflections were measured every 41 min, and their intensities were found to remain constant within experimental error. Lp corrections were applied, as was an empirical absorption correction based on a series of ψ scans.

A three-dimensional Patterson synthesis revealed the location of the Au atom. Least-squares refinement and difference Fourier syntheses were applied, beginning with an R value of 0.22 for the single, isotropic Au atom, and proceeding without difficulty to final isotropic values of $R = 0.081$ and $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.067$. When the Au, P and S atoms were allowed to refine anisotropically, final values of $R = 0.075$ and $R' = 0.061$ were reached. At this point the highest remaining peaks in a difference Fourier map not associated with the Au atom were approximately $1.0 e \text{ \AA}^{-3}$, and were identified as H-atom peaks about the phenyl rings.

The weighting scheme used was $w^{-1} = \sigma_F^2$, where σ_F was derived from counting statistics only. Neutral-atom scattering factors were used, except for Au¹. 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 geometry is close to ideal trigonal planar – the Au atom is only 0.04 Å out of the least-squares plane through the P and S atoms, while the P–Au–P angle is 127.8 (1)°. Au–P distances are 2.346 (4) and 2.349 (4) Å while Au–S is 2.468 (4). $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Cl}]$ is very similar, with the Au atom 0.01 Å from the plane, and Au–P distances of 2.323 (4) and 2.339 (4) Å. The geometry is less ideal, since the P–Au–P angle is now 132.1 (1)°. Ionic trigonal-planar complexes with three identical phosphine ligands are also similar: $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]^- [\text{B}(\text{C}_6\text{H}_5)_4]^+$ has Au–P 2.365, 2.384, 2.403 Å, P–Au–P 115.2, 119.3, 125.4°, the Au atom lies 0.06 Å

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36581 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

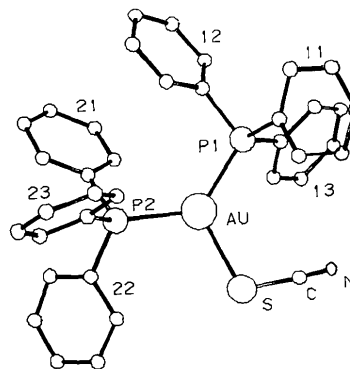


Fig. 1. The $[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\text{SCN})]$ molecule. Phenyl rings are labelled as in Table 2.

out of the P_3 plane (Jones, 1980), while $[Au\{P(C_6H_5)_3\}_3][B_9H_{12}S]$ has Au—P 2.345, 2.384, 2.389 Å, P—Au—P 112.3, 121.5, 124.1°, the Au atom lies 0.2 Å out of the P_3 plane (Guggenberger, 1974). In contrast to all of these $[Au\{P(C_6H_5)_3\}_3(SCN)]$ displays four-coordinate geometry, with much longer Au—P distances (2.384, 2.401 and 2.413 Å), and a very much longer Au—S distance of 2.791 Å. The similarity in structure of the trigonal $[Au\{P(C_6H_5)_3\}_2(SCN)]$ and $[Au\{P(C_6H_5)_3\}_2Cl]$ in contrast to the linear $[Au\{cyclo-C_6H_{11}\}_3\}_2[SCN]$ suggests that the steric requirements of the phosphine are the determining factor in the structure.

Computer programs used included *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978).

We are grateful to the University of Puerto Rico Computing Service for generous grants of time on the IBM 370/148 computer, and to L. Bird for helpful discussions. Research was supported in part by grant RR-8102 from the Division of Research Resources, National Institutes of Health.

Acta Cryst. (1982). **B38**, 1320–1323

The Structure of μ -Thio-bis[tribenzylgermanium(IV)]

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(Received 2 November 1981; accepted 2 December 1981)

Abstract. $C_{42}H_{42}Ge_2S$, monoclinic, $C2/c$, $a = 25.448$ (7), $b = 9.344$ (2), $c = 17.304$ (3) Å, $\beta = 118.31$ (2)°, $U = 3622.6$ Å³, $M_r = 724.04$, $D_c = 1.327$ Mg m⁻³ for $Z = 4$, $F(000) = 1496$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, μ (Mo $K\alpha$) = 1.674 mm⁻¹; $R = 0.0861$ for 1512 reflections. The structure consists of molecules lying across the twofold axes of the unit cell: the GeSGe angle is 106.6 (2)° and the Ge—S distance 2.233 (4) Å.

Introduction. As part of a study of hexa-organo substituted triatomics, $X(R_3M)_2$, we have previously reported the structures of $O(Ph_3Ge)_2$ (Glidewell & Liles, 1978a) and $O[(PhCH_2)_3Ge]_2$ (Glidewell & Liles,

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1979a). The structure of $S(Ph_3Ge)_2$ has also been reported (Krebs & Korte, 1979). $O(Ph_3Ge)_2$ and $O[(PhCH_2)_3Ge]_2$ both have very wide GeOGe angles, 135.2 (2) and 180.0 (0)° respectively: the former can be ascribed to a 'hard atom' contact between the Ge atoms (Glidewell & Liles, 1978a) and the latter can be accounted for in terms of a second-order Jahn–Teller effect (Glidewell, 1978a,b). To test whether a similar effect could be observed when the central O atom was replaced by an S atom – thus reducing the electronegativity difference between the central atom and the $(PhCH_2)_3Ge$ groups – we have determined the structure of $S[(PhCH_2)_3Ge]_2$.

$S[(PhCH_2)_3Ge]_2$ was prepared from $(PhCH_2)_3GeBr$ (Bauer & Burschkies, 1934) by the action of Na_2S in ethanol solution (Burschkies, 1935). Crystals suitable for X-ray examination were obtained from 60–80 petrol solution.

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