

Structure of the Monoclinic Form of Thiocyanatotris(triphenylphosphine)gold(I) Monohydrate

BY JAMES A. MUIR, MARIEL M. MUIR AND SONIA ARIAS

Departments of Physics and Chemistry, University of Puerto Rico, Rio Piedras, PR 00931, USA

AND CHARLES F. CAMPANA AND STEPHEN K. DWIGHT

Nicolet XRD Corporation, 10061 Bubb Road, Cupertino, CA 95014, USA

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Abstract. $[\text{Au}(\text{C}_{18}\text{H}_{15}\text{P})_3(\text{SCN})]\cdot\text{H}_2\text{O}$, $\text{C}_{55}\text{H}_{45}\text{AuN}_3\text{P}_3\text{S}\cdot\text{H}_2\text{O}$, monoclinic, $P2_1/n$, $M_r = 1059.9$, $a = 13.806$ (6), $b = 22.110$ (9), $c = 15.774$ (4) Å, $\beta = 94.68$ (4)°, $Z = 4$, $\mu(\text{Mo } K\alpha) = 3.24 \text{ mm}^{-1}$, $D_c = 1.462$, $D_m = 1.46$ (1) Mg m^{-3} , $V = 4799 \text{ Å}^3$. Final $R = R_w = 0.055$ for 4599 unique diffractometer-collected reflections. The complex crystallizes as a four-coordinate Au compound with an unusually long Au–S distance.

Introduction. The title compound was obtained during a study of possible three- or four-coordinate Au complexes with thiocyanate and phosphine ligands. It was prepared by reacting $[\text{AuL}_2\text{SCN}]$ ($L = \text{Ph}_3\text{P}$) with an eightfold excess of triphenylphosphine in benzene solution. The mixture was refluxed and crystals were then grown by evaporation. Elemental analyses of 63.65% C, 4.66% H, 1.25% N and 8.58% P were obtained. The theoretical composition includes 62.32% C, 4.47% H, 1.32% N and 8.77% P.

Preliminary examination of crystals by Weissenberg and precession techniques showed that two types of crystals were present. Most crystals were monoclinic with systematically absent reflections corresponding to space group $P2_1/n$. However, a few crystals from the same batch were found to be orthorhombic, with space group $P2_12_12_1$. Both types of crystals were subsequently shown to be modifications of the same title compound, although only the structure of the monoclinic modification is reported here.

For intensity-data collection a well formed transparent monoclinic crystal was mounted on a Nicolet R3m diffractometer equipped with a graphite-crystal monochromator set for Mo $K\alpha$ radiation. Accurate cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections. A total of 6613 non-zero reflections were measured for 2θ up to 45°. After L_p and empirical absorption corrections,

averaging equivalent reflections gave 4599 unique data with $F > 3\sigma(F)$.

The structure was solved by direct and heavy-atom methods, using *SHELXTL* (Sheldrick, 1979), and refined to $R = 0.071$ and $R_w = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.068$, for a model in which atoms not in the phenyl rings were anisotropic (Muir, Muir, Arias, Campana & Dwight, 1981). Neutral-atom scattering factors were used, and the weighting scheme was $w^{-1} = \sigma^2(F) + 0.001F^2$. At this point the Fourier difference synthesis was $< 1.4 \text{ e Å}^{-3}$ except for a single 2.5 e Å^{-3} peak located between the molecules of the complex. When this peak was included in the model as an O atom it gave a satisfactory temperature factor, and so the complex appears to be a hydrate. The final model, with H atoms riding on the corresponding C atom ($\text{C–H} = 0.96 \text{ Å}$ and $U_{\text{H}} = 0.06 \text{ Å}^2$) and with anisotropic temperature factors for all atoms except H and O, refined to $R = R_w = 0.055$. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The $[\text{Au}(\text{Ph}_3\text{P})_3(\text{SCN})]$ molecule is shown in Fig. 1. The coordination about the Au is fourfold. The Au–phosphine geometry is considerably distorted from trigonal planar, with the Au atom 0.38 Å out of the least-squares plane through the P atoms. This is about one half of the expected distance for an ideal tetrahedral AuL_4^+ geometry. Au–P distances are long: 2.384 (3), 2.401 (4) and 2.413 (3) Å (average 2.399 Å) and the P–Au–P angles are 113.8 (1), 116.7 (1) and 122.3 (1)°.

* Lists of structure factors, anisotropic temperature factors and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36776 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

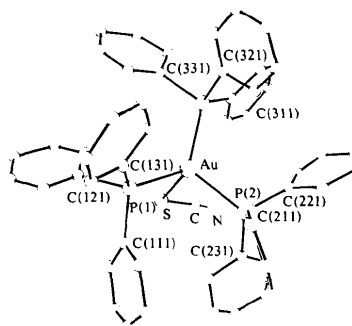
	x	y	z	U_{eq}^*
Au	908 (1)	1471 (1)	2524 (1)	53 (1)
P(1)	9300 (3)	1585 (2)	2977 (2)	53 (1)
P(2)	2181 (3)	1748 (2)	3593 (2)	55 (1)
P(3)	1251 (2)	1591 (1)	1077 (2)	47 (1)
S	894 (3)	229 (1)	2839 (2)	76 (1)
C	1998 (11)	35 (5)	2927 (7)	78 (5)
N	2818 (10)	-146 (5)	2958 (8)	116 (6)
C(111)	9247 (9)	1485 (6)	4120 (7)	59 (5)
C(112)	9147 (9)	925 (6)	4450 (7)	79 (5)
C(113)	9214 (10)	839 (6)	5331 (8)	95 (6)
C(114)	9362 (11)	1307 (6)	5861 (8)	102 (6)
C(115)	9474 (10)	1881 (7)	5545 (8)	95 (6)
C(116)	9430 (9)	1965 (6)	4674 (7)	75 (5)
C(121)	8363 (8)	1068 (5)	2551 (6)	56 (4)
C(122)	7433 (8)	1058 (7)	2836 (8)	84 (5)
C(123)	6729 (10)	666 (6)	2474 (8)	92 (6)
C(124)	6974 (11)	262 (6)	1854 (10)	104 (7)
C(125)	7888 (11)	268 (7)	1570 (10)	114 (7)
C(126)	8566 (10)	671 (6)	1911 (8)	82 (5)
C(131)	8771 (7)	2323 (4)	2747 (6)	54 (4)
C(132)	9157 (8)	2686 (5)	2144 (6)	62 (4)
C(133)	8752 (9)	3245 (6)	1928 (8)	85 (5)
C(134)	7951 (11)	3449 (5)	2311 (9)	101 (6)
C(135)	7568 (11)	3083 (6)	2899 (9)	97 (6)
C(136)	7966 (8)	2544 (5)	3121 (8)	76 (5)
C(211)	1892 (8)	2407 (5)	4202 (7)	59 (4)
C(212)	2128 (9)	2451 (6)	5077 (7)	71 (5)
C(213)	1853 (9)	2957 (6)	5523 (8)	83 (5)
C(214)	1354 (9)	3408 (6)	5111 (10)	92 (6)
C(215)	1111 (8)	3384 (5)	4238 (8)	75 (5)
C(216)	1384 (7)	2886 (5)	3805 (7)	64 (4)
C(221)	3312 (7)	1953 (5)	3173 (6)	54 (4)
C(222)	3757 (7)	2512 (5)	3293 (6)	66 (4)
C(223)	4607 (8)	2630 (6)	2922 (7)	79 (5)
C(224)	5043 (8)	2208 (8)	2456 (7)	102 (7)
C(225)	4594 (8)	1662 (7)	2338 (9)	101 (6)
C(226)	3750 (9)	1537 (5)	2667 (7)	71 (5)
C(231)	2535 (10)	1198 (5)	4391 (7)	71 (5)
C(232)	1808 (11)	943 (6)	4842 (7)	91 (6)
C(233)	2057 (17)	529 (8)	5471 (10)	137 (10)
C(234)	2960 (15)	350 (7)	5659 (9)	153 (9)
C(235)	3662 (18)	579 (9)	5200 (11)	149 (11)
C(236)	3459 (12)	1008 (7)	4592 (8)	99 (6)
C(311)	1335 (7)	2389 (4)	794 (5)	45 (3)
C(312)	933 (9)	2635 (5)	32 (7)	75 (5)
C(313)	1032 (11)	3244 (6)	-131 (10)	97 (6)
C(314)	1492 (11)	3620 (6)	421 (10)	99 (6)
C(315)	1889 (10)	3388 (5)	1162 (8)	90 (6)
C(316)	1820 (9)	2777 (5)	1367 (7)	72 (5)
C(321)	2374 (7)	1274 (4)	758 (6)	53 (4)
C(322)	2962 (7)	1566 (5)	246 (8)	71 (5)
C(323)	3748 (9)	1273 (6)	-49 (10)	103 (7)
C(324)	3984 (8)	706 (6)	193 (9)	95 (6)
C(325)	3420 (9)	406 (5)	728 (8)	89 (5)
C(326)	2601 (9)	687 (5)	1031 (7)	71 (5)
C(331)	385 (7)	1282 (4)	267 (6)	52 (4)
C(332)	9414 (9)	1403 (7)	279 (8)	73 (6)
C(333)	8728 (8)	1186 (6)	-319 (7)	74 (5)
C(334)	9006 (8)	815 (6)	-942 (8)	85 (5)
C(335)	9963 (10)	708 (7)	8995 (10)	124 (8)
C(336)	640 (9)	937 (7)	-395 (8)	101 (6)
O	4733 (13)	-416 (8)	2509 (11)	232 (7)†

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

† Isotropic.

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

Au-P(1)	2.401 (4)	Au-P(2)	2.413 (3)
Au-P(3)	2.384 (3)	Au-S	2.791 (3)
P(1)-C(111)	1.824 (12)	P(1)-C(121)	1.813 (11)
P(1)-C(131)	1.812 (11)	P(2)-C(211)	1.807 (12)
P(2)-C(221)	1.803 (11)	P(2)-C(231)	1.791 (12)
P(3)-C(311)	1.826 (10)	P(3)-C(321)	1.809 (11)
P(3)-C(331)	1.812 (10)	S-C	1.577 (15)
C-N	1.199 (20)	N-O	2.85 (2)
P(1)-Au-P(2)	113.8 (1)	P(1)-Au-P(3)	122.3 (1)
P(2)-Au-P(3)	116.7 (1)	Au-P(1)-C(111)	113.2 (4)
Au-P(1)-C(121)	118.1 (4)	C(111)-P(1)-C(121)	101.9 (5)
Au-P(1)-C(131)	113.7 (4)	C(111)-P(1)-C(131)	105.1 (5)
C(121)-P(1)-C(131)	103.3 (5)	Au-P(2)-C(211)	113.4 (4)
Au-P(2)-C(221)	114.3 (3)	C(211)-P(2)-C(221)	103.2 (5)
Au-P(2)-C(231)	117.4 (4)	C(211)-P(2)-C(231)	103.5 (5)
C(221)-P(2)-C(231)	103.5 (6)	Au-P(3)-C(311)	111.3 (3)
Au-P(3)-C(321)	117.7 (3)	C(311)-P(3)-C(321)	103.5 (5)
Au-P(3)-C(331)	117.5 (4)	C(311)-P(3)-C(331)	104.1 (4)
C(321)-P(3)-C(331)	100.9 (5)		
S-C-N	175.4 (1.1)	Au-S-C	105.2 (4)
S-Au-P(1)	91.8 (1)	S-Au-P(2)	98.1 (1)
S-Au-P(3)	106.6 (1)		

Fig. 1. The $[\text{Au}(\text{Ph}_3\text{P})_3(\text{SCN})]$ molecule.

The SCN^- ligand is also coordinated to the Au atom, so the resulting geometry is trigonal pyramidal. The Au-S distance is unusually long, 2.791 (4) \AA , and the S-Au-P angles vary considerably: 91.8 (1), 98.1 (1) and 106.6 (1) $^\circ$. By comparison, $[\text{L}_2\text{AuSCN}]$ is three-coordinate with almost ideal trigonal-planar geometry (Muir, Muir & Arias, 1982). It has more normal interatomic distances: Au-P is 2.348 \AA (average), while Au-S is 2.468 (4) \AA , 0.32 \AA less than for $[\text{L}_3\text{AuSCN}]$. Other L_3Au complexes are known, $[\text{L}_3\text{Au}][\text{B}_9\text{H}_{12}\text{S}]$ (Guggenberger, 1974) and the analogous tetraphenylborate derivative (Jones, 1980a), but both of these are ionic with trigonal-planar cations and having normal interatomic distances.

The water molecule is located in a small hole near the N end of the SCN^- ligand. The N-O bond distance is 2.85 (2) \AA .

Few other four-coordinate Au^{I} complexes are known. The cation in $[\text{Au}(\text{pdma})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ [pdma = *o*-phenylenebis(dimethylarsine)] displays fourfold geometry, with As-Au-As 87 (1) or 122 (1) $^\circ$ for angles within or between the bidentate chelate groups (Usón, Laguna, Vicente, García, Jones &

Table 3. Comparison of Au—P and Au—S bond lengths (Å) in some Au^I complexes

Compound (L = Ph ₃ P)	Au—P	Au—S
[L ₂ AuSCN]	2.348 (2)*	2.468 (4)
[L ₃ AuSCN]·H ₂ O	2.399 (15)*	2.791 (4)
[L ₃ Au][BPh ₄]·L·CHCl ₃	2.402 (9)*	(Au—P in non-bonded L is 3.95 Å)
[L ₄ Au][BPh ₄]·EtOH, disordered structure	2.447 (14)*	(Trigonal site)
[(MePh ₂ P) ₃ Au][PF ₆]	2.606 (6)*	(Tetrahedral site)
	2.449 (1)	

* Average bond lengths are given, together with the sample standard deviation.

Sheldrick, 1981). [L₄Au][BPh₄] has been studied in powder form (Malatesta, Naldini, Simonetta & Cariati, 1966), and more recently has been crystallized as a variety of solvates. None of these (Jones, 1980b, 1982) show the sought-after regular tetrahedral geometry: the chloroform solvate contains a trigonal-planar cation with three short Au—P bonds (average 2.402 Å), and a very remote (3.95 Å) Ph₃P ligand, while the ethanol and acetonitrile analogs are disordered between tetrahedral and trigonal components. The ethanol analog has average Au—P bond lengths of 2.447 Å (trigonal component) and 2.606 Å (tetrahedral component).

The only monodentate four-coordinate Au^I complex which shows nearly regular tetrahedral geometry in the solid state is [Au(Ph₂Me)₄][PF₆] (Elder, Zeiher, Onady & Whittle, 1981). Here the Au atom occupies a site of 4 symmetry and the coordination about the Au is close to ideal tetrahedral, with Au—P 2.449 (1) Å and P—Au—P angles of 105.24 (4) and 118.32 (4)°. The Au—P bonds in [L₃AuSCN]·H₂O are thus longer than those of [L₂AuSCN], the same in length as those of

[L₃Au][BPh₄]·L·CHCl₃, shorter than those found for [(Ph₂MeP)₄Au][PF₆], and much shorter than those found for either site in [L₄Au][BPh₄]·EtOH. As can be seen from Table 3, there is clearly some correlation of both Au—P and Au—S bond lengths with degree of steric crowding about the Au atom.

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References

- ELDER, R. C., ZEIHNER, E. H. K., ONADY, M. & WHITTLE, R. R. (1981). *J. Chem. Soc. Chem. Commun.* pp. 900–901.
- GUGGENBERGER, L. J. (1974). *J. Organomet. Chem.* **81**, 271–280.
- JONES, P. G. (1980a). *Acta Cryst.* **B36**, 3105–3107.
- JONES, P. G. (1980b). *J. Chem. Soc. Chem. Commun.* pp. 1031–1033.
- JONES, P. G. (1982). *Gold Bull.* **14**, 102–118.
- MALATESTA, L., NALDINI, L., SIMONETTA, G. & CARIATI, F. (1966). *Coord. Chem. Rev.* **1**, 1966.
- MUIR, J. A., MUIR, M. M. & ARIAS, S. (1982). *Acta Cryst.* **B38**, 1318–1320.
- MUIR, J. A., MUIR, M. M., ARIAS, S., CAMPANA, C. F. & DWIGHT, S. K. (1981). *Acta Cryst.* **A37**, C227.
- SHELDRICK, G. M. (1979). *SHELXTL*. An integrated system for solving, refining and displaying crystal structures from diffraction data. Univ. of Göttingen, Federal Republic of Germany.
- USÓN, R., LAGUNA, A., VICENTE, J., GARCÍA, J., JONES, P. G. & SHELDRICK, G. M. (1981). *J. Chem. Soc. Dalton Trans.* pp. 655–657.

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Structure of the 1:1 Complex of Mercury(II) Trifluoroacetate with 2,2'-Bipyridyl*

BY JOAN HALFPENNY

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

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Abstract. [Hg(C₂F₃O₂)₂]₂(C₁₀H₈N₂)₂·C₂₈H₁₆F₁₂Hg₂N₄·O₈, triclinic, *P*1, *a* = 12.59 (1), *b* = 16.07 (2), *c* = 9.73 (1) Å, α = 109.1 (1), β = 113.9 (1), γ = 73.4 (1)°, *U* = 1673.78 Å³, *F*(000) = 1087.96, *Z* = 2, *D*_x = 2.309, *D*_m = 2.318 Mg m⁻³. The structure, determined from 2496 observed diffractometer-

measured intensities (*R* = 0.057), shows two independent Hg each coordinated to one 2,2'-bipyridyl: Hg(1)—N = 2.24 (2), 2.36 (2) Å; Hg(2)—N = 2.30 (2), 2.28 (2) Å. Each Hg is also coordinated to two trifluoroacetate groups: Hg(1)—O = 2.21 (1), 2.53 (2), 2.58 (2), 2.81 (2), 2.88 (2) Å; Hg(2)—O = 2.23 (1), 2.35 (2), 2.78 (3), 2.82 (2) Å.

* Recommended IUPAC name: catena-poly {[2,2'-bipyridyl](trifluoroacetato-*O,O'*)mercury}-μ-(trifluoroacetato-*O,O'*:*O'*)-[2,2'-bipyridyl](trifluoroacetato-*O,O'*)mercury}-μ-(trifluoroacetato-*O*:*O'*).

Introduction. It has been shown (Halfpenny, Small & Thorpe, 1978; Halfpenny & Small, 1980, 1981) that