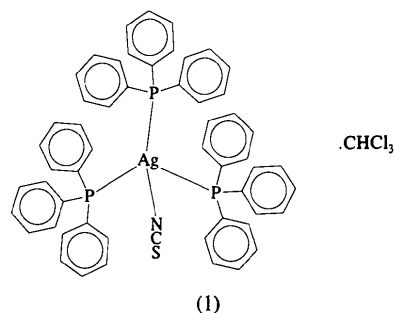


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Fun & Sivakumar, 1996), bis(2-hydroxyethyl)dithiocarbamate (Drew, Othman, Baba, Farina & Ng, 1996), 8-hydroxyquinoline (Othman, Goh, Fun & Sivakumar, 1996) and 2-hydroxy-3,5-dinitrobenzoate ligands, all of which are potentially bidentate (Othman, Effendy & White, 1996). Crystallographic studies of the products of these reactions showed that the Ag atoms are in tetrahedral environments except in the dimeric benzoate complex, in which the Ag atom is in a trigonal environment, essentially retaining the structure of the parent acetate. The title compound, (1), is the product of an attempt to prepare a complex between the dimer and thiosemicarbazide.



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(Thiocyanato-*N*)tris(triphenylphosphine)-silver(I) Chloroform Solvate

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Abstract

Crystals of $[\text{Ag}(\text{NCS})(\text{C}_{18}\text{H}_{15}\text{P})_3]\cdot\text{CHCl}_3$ consist of discrete $[\text{Ag}(\text{PPh}_3)_3(\text{NCS})]$ molecules, in which the Ag atom is tetrahedrally surrounded by three P atoms of the PPh_3 groups and the N atom of the isothiocyanate ligand, and chloroform molecules. The coordination polyhedron around the Ag atom is distorted with angles at Ag ranging from 102.58 (10) to 114.73 (3)°. The Ag—N—C angle is 159.6 (3)°.

Comment

During our study of the reactions of the dimer bis[acetato(triphenylphosphine)silver(I)], we have reacted the dimer with *N*-pyrrolidine carbodithioate (Othman,

The geometry about the Ag atom in (1) is tetrahedral, with three P atoms of the triphenylphosphine ligands and the N atom of the isothiocyanate ligand bonded to the Ag atom. The angles about the Ag atom deviate significantly from the ideal 109.5°, but to a lesser extent than those in $[\text{Ag}(\text{PPh}_3)_3\text{Cl}]$ (Cassel, 1981). The difference can be attributed to the different electronegativities of the N and Cl donor atoms of the anionic ligands, rather than to the Ag—N distance [2.319 (4) Å] being shorter than the Ag—Cl distance of 2.552 (1) Å. The π -acceptor nature of the NCS ligand enhances the bonding of the PPh_3 ligands to the Ag atom.

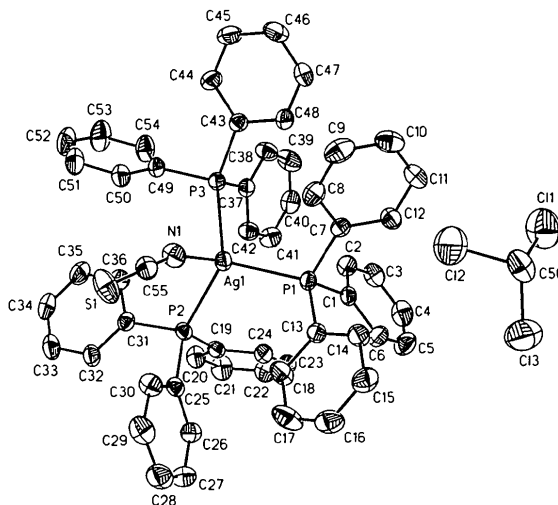


Fig. 1. A 30% displacement ellipsoid plot of (1) with the atomic numbering scheme.

The structures of other silver complexes of the type [Ag(PPh₃)₃X] (X = BF₄, I, Br, Cl), where the monodentate ligand X is bonded to the Ag atom, have been reported (Camalli & Caruso, 1987; Cassel, 1981; Engelhardt, Healy, Patrick & White, 1987). In these complexes, the Ag—P distances are usually close to 2.55 Å, irrespective of the anion or the values of the P—Ag—P angles; however, it should be noted that one of the Ag—P bonds in [Ag(PPh₃)₃I] is exceptionally long at 2.780 (2) Å. The Ag—P bond lengths in (1) are similar to those in the halide complexes, consistent with the anionic ligands exerting little or no electronic influence on the Ag—P bonds. However, structural and ³¹P NMR studies on [Ag(PPh₃)₃X] complexes (X = BF₄, I, Cl) have confirmed that the basicity of the anion can induce large variations in the geometry of the complexes (Camalli & Caruso, 1987).

In the majority of NCS complexes, the M—N—C angles lie between 150 and 180°. In (1), the Ag—N—C angle [159.6(3)°] lies within this range and correlates well with the N1—C55 [1.145(5) Å] and C55—S1 [1.635(4) Å] distances (Drew & Othman, 1975).

Chloroform molecules are found trapped in the cavities formed between the phenyl rings of adjacent complex molecules. They are stacked along the *c* axis with a minimum Cl⋯Cl interaction of 3.900(5) Å. No significant Cl⋯S interaction was observed, as this would result in further deviation of the M—N—C angle.

Experimental

The title compound was prepared by reacting bis[acetato-(triphenylphosphine)silver(I)] with a slight excess of thiosemicarbazide in ethanol. The mixture was heated and stirred. The resulting cloudy solution was filtered and a little chloroform added. Crystals of the product appeared on cooling to room temperature.

Crystal data

[Ag(NCS)(C ₁₈ H ₁₅ P) ₃].CHCl ₃	Mo K α radiation
$M_r = 1072.13$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 38 reflections
$P\bar{1}$	$\theta = 8-25^\circ$
$a = 13.329(2)$ Å	$\mu = 0.726$ mm ⁻¹
$b = 13.647(1)$ Å	$T = 293(2)$ K
$c = 14.467(1)$ Å	Prism
$\alpha = 89.70(1)^\circ$	$0.62 \times 0.52 \times 0.44$ mm
$\beta = 79.47(1)^\circ$	Colourless
$\gamma = 80.09(1)^\circ$	
$V = 2547.7(5)$ Å ³	
$Z = 2$	
$D_x = 1.398$ Mg m ⁻³	
D_m not measured	

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.0165$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 27.50^\circ$

Absorption correction:	$h = -1 \rightarrow 17$
none	$k = -17 \rightarrow 17$
13 101 measured reflections	$l = -18 \rightarrow 18$
11 600 independent reflections	3 standard reflections monitored every 97 reflections
8877 observed reflections [$I > 2\sigma(I)$]	intensity decay: <3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0513$	$\Delta\rho_{\text{max}} = 1.55$ e Å ⁻³
$wR(F^2) = 0.1641$	$\Delta\rho_{\text{min}} = -1.06$ e Å ⁻³
$S = 1.059$	Extinction correction: none
11 600 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
586 parameters	
H-atom parameters not refined	
$w = 1/[\sigma^2(F_o^2) + (0.1084P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{eq}
Ag1	0.24382 (2)	0.69426 (2)	0.70424 (2)	0.04329 (10)
P1	0.24790 (7)	0.51601 (6)	0.75764 (6)	0.0406 (2)
P2	0.13834 (7)	0.82887 (6)	0.82711 (6)	0.0421 (2)
P3	0.20026 (7)	0.72535 (6)	0.54053 (6)	0.0401 (2)
C1	0.1184 (3)	0.4823 (2)	0.7859 (2)	0.0425 (7)
C2	0.0536 (3)	0.5070 (3)	0.7223 (3)	0.0542 (9)
C3	-0.0460 (3)	0.4843 (3)	0.7389 (4)	0.0651 (11)
C4	-0.0807 (4)	0.4381 (4)	0.8205 (4)	0.0757 (13)
C5	-0.0153 (4)	0.4133 (4)	0.8845 (4)	0.0738 (13)
C6	0.0819 (3)	0.4361 (3)	0.8683 (3)	0.0586 (10)
C7	0.3164 (3)	0.4212 (3)	0.6692 (2)	0.0417 (7)
C8	0.4069 (3)	0.4382 (3)	0.6116 (3)	0.0618 (10)
C9	0.4600 (4)	0.3659 (4)	0.5443 (4)	0.0775 (14)
C10	0.4260 (4)	0.2806 (4)	0.5330 (3)	0.0689 (12)
C11	0.3370 (4)	0.2618 (3)	0.5907 (3)	0.0653 (11)
C12	0.2830 (3)	0.3321 (3)	0.6589 (3)	0.0544 (9)
C13	0.3068 (3)	0.4790 (3)	0.8595 (2)	0.0452 (7)
C14	0.3514 (4)	0.3809 (3)	0.8723 (3)	0.0582 (10)
C15	0.3927 (4)	0.3565 (4)	0.9526 (3)	0.0706 (12)
C16	0.3905 (4)	0.4270 (4)	1.0195 (3)	0.0764 (14)
C17	0.3459 (5)	0.5257 (5)	1.0079 (4)	0.091 (2)
C18	0.3056 (4)	0.5513 (3)	0.9274 (3)	0.0692 (12)
C19	0.0013 (3)	0.8204 (3)	0.8647 (2)	0.0445 (7)
C20	-0.0769 (3)	0.9020 (3)	0.8745 (3)	0.0601 (10)
C21	-0.1810 (3)	0.8893 (4)	0.8991 (4)	0.0738 (13)
C22	-0.2049 (4)	0.7970 (4)	0.9130 (4)	0.0728 (13)
C23	-0.1278 (4)	0.7152 (4)	0.9044 (3)	0.0657 (11)
C24	-0.0254 (3)	0.7258 (3)	0.8807 (3)	0.0560 (9)
C25	0.1887 (3)	0.8236 (2)	0.9358 (3)	0.0466 (8)
C26	0.1279 (4)	0.8195 (3)	1.0245 (3)	0.0598 (10)
C27	0.1724 (5)	0.8148 (4)	1.1042 (3)	0.0758 (13)
C28	0.2730 (5)	0.8167 (4)	1.0972 (4)	0.087 (2)
C29	0.3364 (4)	0.8219 (4)	1.0107 (4)	0.0779 (14)
C30	0.2942 (3)	0.8243 (3)	0.9296 (3)	0.0621 (10)
C31	0.1305 (3)	0.9604 (3)	0.7974 (3)	0.0454 (8)
C32	0.1398 (3)	1.0327 (3)	0.8598 (3)	0.0586 (10)
C33	0.1260 (4)	1.1325 (3)	0.8347 (4)	0.0728 (13)
C34	0.1019 (4)	1.1582 (3)	0.7493 (4)	0.0729 (13)
C35	0.0936 (4)	1.0866 (3)	0.6865 (4)	0.0710 (12)
C36	0.1088 (4)	0.9871 (3)	0.7095 (3)	0.0610 (10)
C37	0.0639 (3)	0.7195 (2)	0.5426 (2)	0.0429 (7)
C38	0.0284 (4)	0.6867 (4)	0.4663 (3)	0.0662 (11)
C39	-0.0765 (4)	0.6780 (4)	0.4760 (4)	0.0799 (15)
C40	-0.1440 (3)	0.7041 (3)	0.5580 (4)	0.0671 (11)
C41	-0.1090 (3)	0.7388 (4)	0.6342 (3)	0.0650 (11)
C42	-0.0055 (3)	0.7458 (3)	0.6259 (3)	0.0544 (9)

C43	0.2658 (3)	0.6479 (3)	0.4375 (2)	0.0441 (7)
C44	0.3089 (4)	0.6858 (3)	0.3535 (3)	0.0674 (12)
C45	0.3596 (5)	0.6227 (4)	0.2784 (3)	0.081 (2)
C46	0.3674 (4)	0.5218 (4)	0.2859 (3)	0.0734 (13)
C47	0.3254 (4)	0.4837 (3)	0.3689 (3)	0.0693 (12)
C48	0.2741 (4)	0.5455 (3)	0.4434 (3)	0.0563 (9)
C49	0.2171 (3)	0.8495 (3)	0.5004 (3)	0.0481 (8)
C50	0.3020 (3)	0.8856 (3)	0.5212 (3)	0.0568 (9)
C51	0.3242 (4)	0.9765 (3)	0.4851 (4)	0.0762 (14)
C52	0.2611 (5)	1.0304 (4)	0.4326 (5)	0.088 (2)
C53	0.1760 (5)	0.9970 (4)	0.4146 (5)	0.093 (2)
C54	0.1535 (4)	0.9060 (3)	0.4487 (4)	0.0725 (13)
N1	0.4128 (3)	0.7185 (3)	0.6988 (3)	0.0641 (9)
C55	0.4835 (3)	0.7397 (3)	0.7230 (3)	0.0559 (9)
S1	0.58586 (10)	0.76794 (10)	0.75668 (12)	0.0858 (4)
C56	0.4851 (5)	0.0321 (4)	0.7830 (5)	0.093 (2)
C11	0.3948 (2)	0.0104 (2)	0.7154 (2)	0.1388 (8)
C12	0.5300 (2)	0.1431 (2)	0.7405 (2)	0.1490 (9)
C13	0.4293 (4)	0.0500 (3)	0.8981 (2)	0.231 (2)

Table 2. Selected geometric parameters (Å, °)

Ag1—N1	2.319 (4)	P2—C25	1.816 (4)
Ag1—P1	2.5431 (9)	P2—C31	1.833 (4)
Ag1—P2	2.5967 (9)	P3—C37	1.828 (4)
Ag1—P3	2.5561 (9)	P3—C43	1.824 (4)
P1—C1	1.837 (4)	P3—C49	1.825 (4)
P1—C7	1.824 (4)	N1—C55	1.145 (5)
P1—C13	1.823 (4)	C55—S1	1.635 (4)
P2—C19	1.832 (4)		
N1—Ag1—P1	103.36 (10)	C43—P3—Ag1	122.95 (11)
N1—Ag1—P3	107.89 (10)	C49—P3—Ag1	112.07 (13)
P1—Ag1—P3	114.73 (3)	C2—C1—P1	117.2 (3)
N1—Ag1—P2	102.58 (10)	C6—C1—P1	123.9 (3)
P1—Ag1—P2	114.73 (3)	C12—C7—P1	122.5 (3)
P3—Ag1—P2	112.12 (3)	C8—C7—P1	118.7 (3)
C7—P1—C1	102.4 (2)	C18—C13—P1	118.5 (3)
C13—P1—C1	104.6 (2)	C14—C13—P1	122.3 (3)
C13—P1—C7	102.4 (2)	C20—C19—P2	123.0 (3)
C1—P1—Ag1	112.83 (11)	C24—C19—P2	118.3 (3)
C7—P1—Ag1	114.74 (11)	C26—C25—P2	123.7 (3)
C13—P1—Ag1	118.08 (12)	C30—C25—P2	117.7 (3)
C25—P2—C19	104.1 (2)	C32—C31—P2	122.9 (3)
C25—P2—C31	102.7 (2)	C36—C31—P2	117.4 (3)
C19—P2—C31	101.6 (2)	C38—C37—P3	123.0 (3)
C19—P2—Ag1	115.47 (11)	C42—C37—P3	117.8 (3)
C25—P2—Ag1	112.16 (12)	C44—C43—P3	123.5 (3)
C31—P2—Ag1	118.91 (12)	C48—C43—P3	118.6 (3)
C43—P3—C37	102.6 (2)	C54—C49—P3	123.6 (3)
C49—P3—C37	105.6 (2)	C50—C49—P3	117.1 (3)
C43—P3—C49	101.8 (2)	C55—N1—Ag1	159.6 (3)
C37—P3—Ag1	110.18 (12)	N1—C55—S1	178.8 (4)

The H atoms were placed in calculated positions and subsequently constrained to ride on the atoms to which they are attached. The extreme values in the final difference map occur around the Cl atoms of the chloroform molecule; otherwise the map is featureless.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990) (direct methods). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC, PARST (Nardelli, 1983). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1253). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Molecular Adducts of Inorganic Salts. VI. The Dimorphism of Cd(ReO₄)₂·2tu (tu = Thiourea)

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Abstract

The title compound, cadmium tetraoxorhenium bis(thiourea), Cd(ReO₄)₂·2CH₄N₂S, forms two polymorphs: monoclinic, (I), and triclinic, (II). Both are built up from infinite chains in which the Cd atoms are hexacoordinate. In (I), the centrosymmetric CdO₄S₂ octahedra are interlinked by double ReO₄ bridges, while in (II), CdO₃S₃ octahedra are connected by alternating double ReO₄ and S bridges. The Cd—S coordination bond length is 2.495 (2) Å in (I) and ranges from 2.576 (2) to 2.719 (2) Å in (II). The hydrogen bonding between chains is more developed in compound (II).