

C1—Au—C5	179 (1)	N2—C5—Au	124 (2)
C1—S1—C2	98 (1)	S2—C5—Au	130 (1)
C5—S2—C6	97 (1)	C7—C6—S2	111 (2)
C1—N1—C3	117 (2)	C6—C7—N2	112 (2)
C5—N2—C7	115 (2)	C6—C7—C8	134 (3)
N1—C1—S1	103 (2)	N2—C7—C8	114 (2)
N1—C1—Au	128 (2)	C11 ^{''} —Zn—C11	108.2 (3)
S1—C1—Au	128 (2)	C11 ^{''} —Zn—C12 ^{''}	110.3 (4)
C3—C2—S1	108 (2)	C11 ^{''} —Zn—C12	108.7 (4)
C2—C3—N1	113 (2)	C11—Zn—C12 ^{''}	108.7 (4)
C2—C3—C4	133 (3)	C11—Zn—C12	110.3 (4)
N1—C3—C4	114 (2)	C12 ^{''} —Zn—C12	110.6 (3)
N2—C5—S2	106 (2)		

Symmetry codes: (i) $x, 1 - y, 1 - z$; (ii) $1 - x, y, \frac{1}{2} - z$.

The measured data set contained more than the unique set of reflections, including 306 Friedel pairs, allowing the eventual determination of the absolute configuration of the structure (CRYLSQ; Hall & Stewart, 1990). The substandard quality of the only available crystals suitable for structure determination required the use of restraints during refinement. After refinement with bond length and dihedral angle restraints [from 12 known structures from the Cambridge Structural Database (Allen *et al.*, 1979)] on the planar rings, difference maps showed two residual peaks with peak heights equivalent to C atoms. These peaks could be interpreted as the manifestation of a CH₂Cl₂ solvent molecule disordered across a twofold axis and were included in the model as C9 and C10, which were considered equivalent to Cl atoms at half weight. Non-restrained refinement of the light atoms (N, C, O, S) with a restricted set of reflection data (maximum $\sin\theta/\lambda = 0.30$) gave a better set of bonding parameters for the ring atoms. These parameters were used in subsequent restrained refinements with the full set of data. A final difference map was clean with no significant residual electron density peaks. Only the Au, Zn and Cl atoms were refined anisotropically as changes from isotropy for the lighter atoms did not result in improved agreement parameters. No H atoms were located and the low precision achieved did not warrant their inclusion in calculated positions.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Data reduction: ADDREF, ABSORB and SORTRF in Xtal3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: FOURR in Xtal3.0. Program(s) used to refine structure: CRYLSQ in Xtal3.0. Molecular graphics: ORTEP (Johnson, 1965) in Xtal3.0; SCHAKAL (Keller, 1988). Software used to prepare material for publication: BONDLA and CIFIO in Xtal3.0.

Lists of structure factors, anisotropic displacement parameters, and complete geometry, including contact distances, have been deposited with the IUCr (Reference: KH1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro(ethanedithioamide-S)bis(triphenylphosphine)silver(I)

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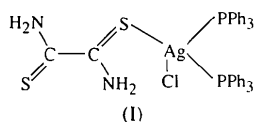
Abstract

The structure of the title compound, [AgCl(C₂H₄N₂S₂)-(C₁₈H₁₅P)₂], is reported. Dithiooxamide acts as a monodentate ligand coordinating *via* one S atom to Ag. The coordination polyhedron of the Ag atom is a distorted tetrahedron, with an Ag—S distance of 2.604 (1) Å and an Ag—Cl distance of 2.580 (1) Å.

Comment

Recent studies in our laboratory on copper(I) and silver(I) complexes and cluster compounds reveal that some substances, such as MO_nS_{4-n}²⁻ (M = Mo, W), containing polydentate ligands exhibit strong non-linear optical properties. The examples are MS₃OCu₂(PPh₃)₃ (M = Mo, W) (Shi, Hou & Xin, 1995) and Mo₂S₈Ag₄-(PPh₃)₄ (Ji *et al.*, 1995). An attempt to imitate the MO_nS_{4-n}²⁻ (M = Mo, W) structure with ethanedithioamide did not result in a polynuclear complex but

the monomeric title compound, (I). The X-ray crystal structure determination indicates that the central atom in the molecule is Ag, which has tetrahedral coordination involving Cl, P atoms from two PPh₃ ligands, and one S atom from dithiooxamide.



The Cl—Ag—S, S—Ag—P and Cl—Ag—P angles deviate from the tetrahedral value slightly (by no more than 6.2°), while the P—Ag—P angle is much larger (deviation 15.5°) owing to the interactions between the two bulky phosphine ligands. The average Ag—P and Ag—Cl distances are 2.468 (1) and 2.580 (1) Å, respectively, which are comparable with the values of 2.545 (1) and 2.552 (1) Å found in (Ph₃P)₃AgCl (Cassel, 1981), and 2.478 (3) and 2.517 (2) Å in (Ph₃P)₂Ag(py)Cl (Engelhardt, Healy, Skelton & White, 1991). The Ag—S distance [2.604 (1) Å] is of the order of the usual values found in silver(I) compounds containing phosphine ligands, such as Ag₃MoS₄I(PPh₃)₃ (Lang, Bao, Zhu & Xin, 1993) and (Et₄N)(PPh₃)₂AgS₃WOCu(CN) (Zhu, Du, Chen & Wu, 1992).

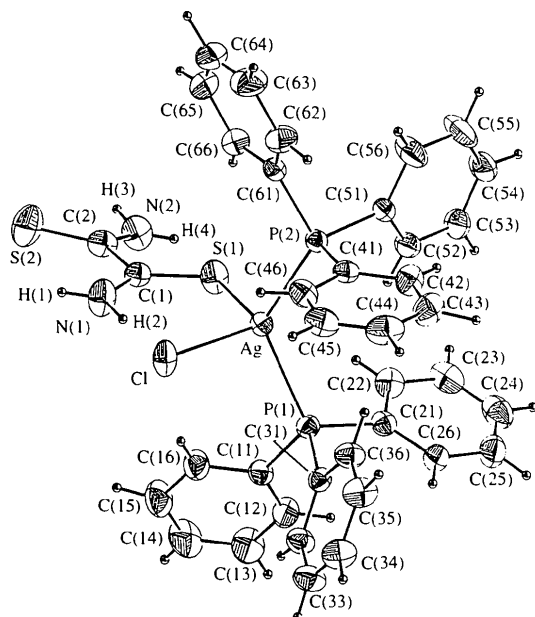


Fig. 1. View of the title compound. Displacement ellipsoids are shown at the 30% probability level. H atoms are omitted for clarity.

The dithiooxamide acts as a monodentate ligand through one S atom coordinating to Ag, and exhibits a *trans* configuration similar to that in (Ph₃P)₂Cu(C₂H₄N₂S₂)Cl (Ferrari, Fava, Pelizzi & Tarasconi, 1985). S(1)—C(1) is slightly longer than S(2)—C(2), showing the influence of coordination of S to Ag. The dithiooxamide molecule is approximately

planar; the coordinated S atom deviates slightly from the plane.

Intra- and intermolecular hydrogen-bond interactions exist between N(1), N(2) and the Cl atom: N(1)···Cl = 3.195 (4) Å, Cl···H(2)—N1 = 173 (4)°; N(2')···Cl = 3.150 (4) Å, Cl···H(3')—N(2') = 164 (6)° [symmetry code: (i) 1 + x, y, z]. AgSCNH···Cl rings are formed by N(1)···Cl and linked by N(2)···Cl hydrogen bonds in chains running along the *a* axis, in which the dithiooxamide molecule plays the role of a bridging group.

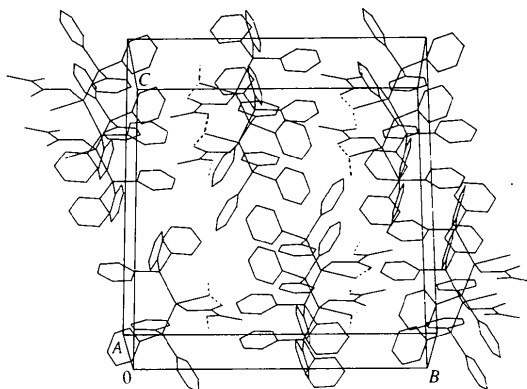


Fig. 2. Packing diagram viewed down the *a* axis. Note the hydrogen bonds running along the *a* axis.

Experimental

The title compound was prepared by the reaction of equimolar Ag(PPh₃)₂NO₃ with dithiooxamide and Me₄NCl in CH₂Cl₂. Single crystals were obtained by slow evaporation of the solvent.

Crystal data

[AgCl(C₂H₄N₂S₂)-
(C₁₈H₁₅P)₂]
M_r = 788.09
Monoclinic
*P*2₁/*n*
a = 9.460 (2) Å
b = 19.572 (4) Å
c = 20.017 (6) Å
β = 92.58 (2)°
V = 3702 (2) Å³
Z = 4
D_x = 1.41 Mg m⁻³

Data collection

Enraf-Nonius CAD-4
diffractometer
ω/*θ* scans [speed < 5.49°
min⁻¹; *ω* width (0.45 +
0.35tan*θ*)°]
Absorption correction:
ψ scan (TEXSAN;
Molecular Structure
Corporation, 1987)
T_{min} = 0.90, *T_{max}* = 1.00
7157 measured reflections
6850 independent reflections

Mo K α radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 11.42–14.91°
μ = 0.833 mm⁻¹
T = 300 K
Pyramidal
0.35 × 0.25 × 0.20 mm
Red

5452 observed reflections
[*I* > 3 σ (*I*)]
R_{int} = 0.025
θ_{max} = 25°
h = 0 → 11
k = 0 → 23
l = -23 → 23
3 standard reflections
monitored every 300
reflections
intensity decay: 4.0%

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.11$
$R = 0.037$	$\Delta\rho_{\max} = 0.421 \text{ e } \text{\AA}^{-3}$
$wR = 0.049$	$\Delta\rho_{\min} = -0.743 \text{ e } \text{\AA}^{-3}$
$S = 1.35$	Extinction correction: none
5452 reflections	Atomic scattering factors
551 parameters	from <i>International Tables</i>
H atoms refined isotropically	for <i>X-ray Crystallography</i>
$w = 1/\sigma^2(F)$	(1974, Vol. IV)

P(2)—Ag—P(1)	125.01 (3)	C(41)—P(2)—C(51)	105.8 (2)
P(2)—Ag—Cl	108.71 (4)	C(41)—P(2)—C(61)	104.3 (2)
P(2)—Ag—S(1)	110.31 (4)	C(41)—P(2)—Ag	110.7 (1)
P(1)—Ag—Cl	103.74 (4)	C(51)—P(2)—C(61)	103.0 (2)
P(1)—Ag—S(1)	103.58 (4)	C(51)—P(2)—Ag	113.0 (1)
Cl—Ag—S(1)	103.38 (4)	C(61)—P(2)—Ag	118.8 (1)
C(1)—S(1)—Ag	113.9 (1)	N(1)—C(1)—C(2)	114.8 (3)
C(31)—P(1)—C(21)	104.2 (2)	N(1)—C(1)—S(1)	124.5 (3)
C(31)—P(1)—C(11)	105.0 (2)	C(2)—C(1)—S(1)	120.7 (3)
C(31)—P(1)—Ag	110.9 (1)	N(2)—C(2)—C(1)	113.7 (4)
C(21)—P(1)—C(11)	103.0 (2)	N(2)—C(2)—S(2)	124.8 (3)
C(21)—P(1)—Ag	117.3 (1)	C(1)—C(2)—S(2)	121.5 (3)
C(11)—P(1)—Ag	115.1 (1)		

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Ag	0.81829 (3)	0.13777 (1)	0.24959 (1)	3.54 (1)
Cl	0.94701 (9)	0.25367 (5)	0.26134 (6)	5.39 (5)
S(1)	0.5528 (1)	0.17027 (6)	0.25805 (6)	5.42 (5)
S(2)	0.3424 (1)	0.36309 (7)	0.25055 (8)	7.77 (8)
P(1)	0.8770 (1)	0.07966 (5)	0.35725 (4)	3.45 (4)
P(2)	0.8603 (1)	0.09027 (4)	0.13860 (4)	3.35 (4)
N(1)	0.6239 (4)	0.2994 (2)	0.2682 (2)	5.9 (2)
N(2)	0.2780 (4)	0.2351 (3)	0.2724 (2)	6.0 (2)
C(1)	0.5246 (4)	0.2534 (2)	0.2635 (2)	3.9 (2)
C(2)	0.3747 (4)	0.2816 (2)	0.2626 (2)	4.5 (2)
C(11)	0.8037 (4)	0.1198 (2)	0.4309 (2)	3.9 (2)
C(12)	0.7697 (5)	0.0838 (2)	0.4866 (2)	5.1 (2)
C(13)	0.7141 (6)	0.1169 (3)	0.5407 (3)	6.8 (3)
C(14)	0.6917 (6)	0.1849 (3)	0.5388 (3)	7.6 (3)
C(15)	0.7244 (6)	0.2222 (3)	0.4834 (3)	7.0 (3)
C(16)	0.7798 (5)	0.1899 (2)	0.4289 (2)	5.2 (2)
C(21)	0.8231 (4)	-0.0093 (2)	0.3648 (2)	3.8 (1)
C(22)	0.6813 (5)	-0.0247 (2)	0.3501 (2)	4.9 (2)
C(23)	0.6338 (6)	-0.0919 (3)	0.3539 (2)	6.0 (3)
C(24)	0.7249 (7)	-0.1427 (3)	0.3718 (2)	6.5 (3)
C(25)	0.8633 (7)	-0.1284 (2)	0.3860 (3)	6.2 (3)
C(26)	0.9147 (5)	-0.0619 (2)	0.3830 (2)	4.7 (2)
C(31)	1.0667 (4)	0.0781 (2)	0.3748 (2)	3.5 (1)
C(32)	1.1306 (4)	0.0990 (2)	0.4343 (2)	4.6 (2)
C(33)	1.2768 (5)	0.0986 (3)	0.4440 (2)	5.6 (2)
C(34)	1.3586 (5)	0.0764 (3)	0.3944 (2)	6.0 (2)
C(35)	1.2974 (5)	0.0543 (3)	0.3343 (2)	5.8 (2)
C(36)	1.1525 (4)	0.0560 (2)	0.3246 (2)	4.7 (2)
C(41)	1.0462 (4)	0.0713 (2)	0.1308 (2)	3.7 (1)
C(42)	1.1018 (5)	0.0064 (2)	0.1262 (2)	5.1 (2)
C(43)	1.2463 (5)	-0.0038 (3)	0.1262 (2)	6.2 (2)
C(44)	1.3361 (5)	0.0502 (3)	0.1299 (2)	6.4 (3)
C(45)	1.2844 (5)	0.1154 (3)	0.1342 (2)	5.8 (2)
C(46)	1.1400 (4)	0.1255 (2)	0.1352 (2)	4.9 (2)
C(51)	0.7670 (4)	0.0102 (2)	0.1224 (2)	3.7 (1)
C(52)	0.7166 (4)	-0.0246 (2)	0.1761 (2)	4.4 (2)
C(53)	0.6401 (5)	-0.0842 (2)	0.1679 (2)	5.3 (2)
C(54)	0.6107 (6)	-0.1090 (2)	0.1058 (2)	6.2 (2)
C(55)	0.6599 (8)	-0.0752 (3)	0.0521 (3)	8.7 (3)
C(56)	0.7357 (7)	-0.0158 (3)	0.0597 (2)	7.0 (3)
C(61)	0.8127 (4)	0.1412 (2)	0.0648 (2)	4.0 (2)
C(62)	0.8943 (6)	0.1450 (3)	0.0091 (2)	5.7 (2)
C(63)	0.8453 (8)	0.1833 (3)	-0.0465 (3)	7.6 (3)
C(64)	0.7194 (8)	0.2160 (3)	-0.0470 (3)	7.4 (3)
C(65)	0.6382 (7)	0.2126 (3)	0.0079 (3)	7.2 (3)
C(66)	0.6843 (5)	0.1756 (2)	0.0639 (2)	5.3 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ag—P(2)	2.458 (1)	P(1)—C(11)	1.833 (4)
Ag—P(1)	2.477 (1)	P(2)—C(41)	1.811 (4)
Ag—Cl	2.580 (1)	P(2)—C(51)	1.819 (3)
Ag—S(1)	2.604 (1)	P(2)—C(61)	1.821 (4)
S(1)—C(1)	1.654 (4)	N(1)—C(1)	1.301 (5)
S(2)—C(2)	1.640 (4)	N(2)—C(2)	1.312 (6)
P(1)—C(31)	1.814 (4)	C(1)—C(2)	1.521 (5)
P(1)—C(21)	1.822 (4)		

The structure was solved by direct methods. The Ag atom was located in an E map and the remaining non-H atoms were deduced from successive Fourier syntheses. The structure was refined by full-matrix least-squares techniques. H atoms were positioned geometrically and refined isotropically. All calculations were performed on a MicroVAX3100 computer.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1987). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: KH1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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