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## (*N*-Pyrrolidinecarbodithioato-*S,S'*)bis(triphenylphosphine)silver(I)

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### Abstract

In the title compound, [Ag(C<sub>5</sub>H<sub>8</sub>NS<sub>2</sub>)(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>], the Ag atom is tetrahedrally surrounded by the two P atoms of the triphenylphosphine groups and the two S atoms of the bidentate pyrrolidinecarbodithioate ligand. The coordination polyhedron is severely distorted; the S—Ag—S angle is 68.15 (4)° and the remaining angles are in the range 107.23 (3)–124.43 (3)°. The pyrrolidine ring adopts an envelope conformation.

### Comment

We have recently reported the synthesis and crystal structure of the dimeric binuclear compound [(Ph<sub>3</sub>P)Ag(μ-CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>Ag(PPh<sub>3</sub>)] (Ng & Othman, 1995). This compound was formed in toluene and is rather unstable even in alcoholic solution, recrystallization from which resulted in dissociation to the monomeric form. We reacted the dimer with ammonium bis(2-hydroxyethyl)dithiocarbamate, which resulted in the formation of monomeric [bis(2-hydroxyethyl)dithiocarbamate]bis(triphenylphosphine)silver(I), (2) (Drew, Othman, Baba, Farina & Ng, 1995). Structural studies of the product of the reaction of the dimer with the 2-hydroxy-3,5-dinitrobenzoate anion, however, show that the binuclear structure of the parent acetate compound is retained (Othman, Effendy & White, 1995). The structural study of the title complex, (1), was undertaken as part of our studies on the reactions of the dimer.

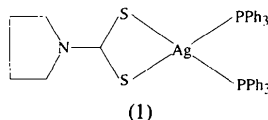


Fig. 1 shows a displacement ellipsoid plot of (1) with the numbering scheme. The Ag atom is in a tetrahedral environment with the two P atoms of the triphenylphosphine ligands and the S atoms of the biden-

tate pyrrolidinecarbodithioate ligand occupying the vertices of a distorted tetrahedron, the central core having quasi C<sub>2</sub> symmetry with the axis defined by the line containing the Ag, C37 and N1 atoms. The coordination polyhedron is severely distorted, the S1—Ag—S2 angle being 68.15 (4)° [67.82 (4)° in (2)]. The distortion is mainly due to the small bite of the carbodithioate ligand rather than electronic effects. There is also a large deviation of the P2—Ag—P1 angle [124.43 (3)°] from the ideal tetrahedral value [cf 118.96 (4)° in (2)]. The Ag—P bond distances of 2.4647 (8) and 2.4756 (8) Å [2.4385 (11) and 2.457 (2) Å in (2)] are within the expected range. Interligand interaction between phenyl groups is reduced by the widening of the P—Ag—P angle. The two C—S bond lengths are similar, with values of 1.701 (4) and 1.695 (4) Å [1.695 (4) and 1.730 (4) Å in (2)], but shorter than the sum of their covalent radii (1.82 Å), while the N1—C37 bond of 1.339 (5) Å is shorter than the single covalent bond distance of 1.47 Å (Pauling, 1960), suggesting the involvement of the N-atom lone pair in delocalized π bonding over the NCS<sub>2</sub> atoms. Despite the similar C—S bond distances, the Ag—S bond distances of 2.5689 (9) and 2.7082 (11) Å [2.5991 (12) and 2.6822 (13) Å in (2)] are significantly different and indicate unsymmetrical bidentate coordination of the carbodithioate ligand.

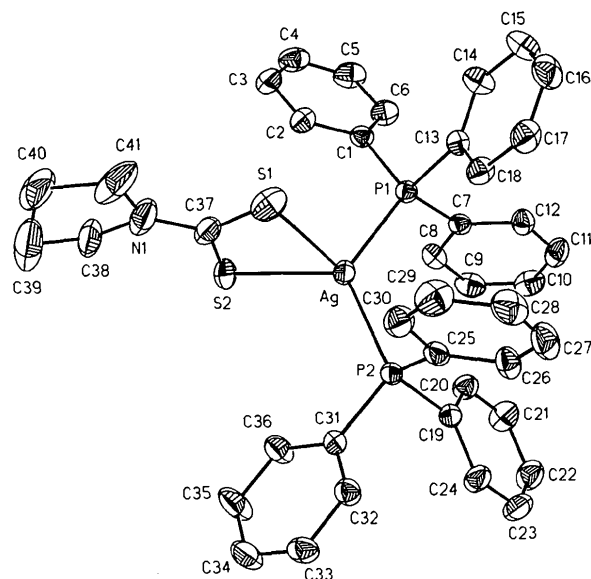


Fig. 1. A 30% displacement ellipsoid plot of the title compound.

The pyrrolidine ring has an envelope conformation; asymmetry parameter ΔC<sub>5</sub>(C39) = 0.011 (3) (Nardelli, 1983a). The crystal structure is stabilized by van der Waals interactions.

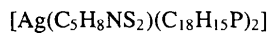
### Experimental

The title compound was prepared by mixing stoichiometric quantities of bis[acetato(triphenylphosphine)silver(I)] with ammonium pyrrolidinecarbodithioate in absolute ethanol. The

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mixture was stirred and warmed on a hot plate. The resulting clear solution was filtered and allowed to cool. Colourless crystals were obtained after a few days.

### Crystal data



$M_r = 778.65$

Monoclinic

$P2_1/c$

$a = 14.040(1) \text{ \AA}$

$b = 10.222(1) \text{ \AA}$

$c = 25.699(3) \text{ \AA}$

$\beta = 93.63(1)^\circ$

$V = 3680.8(6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.405 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 8-25^\circ$

$\mu = 0.778 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Block

$0.58 \times 0.48 \times 0.42 \text{ mm}$

Colourless

### Data collection

Siemens P4 diffractometer

$\theta/2\theta$  scans

Absorption correction:

none

10 421 measured reflections

8396 independent reflections

6459 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0384$

$\theta_{\text{max}} = 27.51^\circ$

$h = -3 \rightarrow 18$

$k = -1 \rightarrow 13$

$l = -33 \rightarrow 33$

3 standard reflections

monitored every 97

reflections

intensity decay:  $< 3\%$

### Refinement

Refinement on  $F^2$

$R(F) = 0.0410$

$wR(F^2) = 0.1763$

$S = 1.032$

8368 reflections

544 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2$

$+ 0.6219P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.74 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

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

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
Ag	0.25708 (2)	0.30870 (2)	0.151034 (8)	0.04152 (9)
S1	0.07409 (7)	0.29559 (12)	0.11118 (5)	0.0698 (3)
S2	0.18483 (7)	0.53704 (9)	0.13468 (4)	0.0626 (3)
P1	0.25871 (6)	0.23417 (8)	0.24274 (3)	0.0376 (2)
P2	0.36071 (6)	0.21987 (7)	0.08565 (3)	0.0378 (2)
N1	0.0118 (3)	0.5358 (5)	0.09110 (15)	0.0888 (13)
C1	0.1919 (2)	0.3331 (3)	0.28710 (12)	0.0426 (7)
C2	0.1149 (3)	0.4043 (4)	0.2666 (2)	0.0566 (9)
C3	0.0628 (3)	0.4829 (4)	0.2988 (2)	0.0694 (11)
C4	0.0881 (3)	0.4898 (4)	0.3510 (2)	0.0696 (12)
C5	0.1642 (3)	0.4201 (4)	0.3715 (2)	0.0689 (11)
C6	0.2166 (3)	0.3406 (4)	0.34021 (14)	0.0553 (8)
C7	0.3767 (2)	0.2199 (3)	0.27691 (11)	0.0391 (6)
C8	0.4293 (3)	0.3339 (4)	0.28534 (13)	0.0501 (8)
C9	0.5226 (3)	0.3280 (5)	0.3066 (2)	0.0618 (10)
C10	0.5635 (3)	0.2113 (5)	0.3193 (2)	0.0651 (11)
C11	0.5127 (3)	0.0986 (5)	0.31124 (15)	0.0591 (9)
C12	0.4191 (3)	0.1016 (3)	0.29020 (13)	0.0480 (7)
C13	0.2100 (2)	0.0694 (3)	0.24583 (12)	0.0426 (6)
C14	0.1675 (3)	0.0188 (4)	0.2885 (2)	0.0635 (10)
C15	0.1363 (4)	-0.1106 (5)	0.2877 (2)	0.0778 (13)
C16	0.1465 (4)	-0.1865 (4)	0.2451 (2)	0.0745 (12)

C17	0.1874 (3)	-0.1376 (4)	0.2021 (2)	0.0671 (10)
C18	0.2187 (3)	-0.0100 (3)	0.20225 (15)	0.0535 (8)
C19	0.4854 (2)	0.1953 (3)	0.10727 (11)	0.0409 (6)
C20	0.5135 (3)	0.2204 (4)	0.15900 (13)	0.0507 (8)
C21	0.6078 (3)	0.2095 (4)	0.1775 (2)	0.0654 (10)
C22	0.6755 (3)	0.1728 (5)	0.1440 (2)	0.0669 (10)
C23	0.6492 (3)	0.1471 (5)	0.0924 (2)	0.0702 (11)
C24	0.5559 (3)	0.1595 (4)	0.07402 (14)	0.0575 (9)
C25	0.3177 (2)	0.0602 (3)	0.06374 (12)	0.0434 (7)
C26	0.3693 (3)	-0.0550 (3)	0.07098 (14)	0.0547 (8)
C27	0.3291 (4)	-0.1744 (4)	0.0565 (2)	0.0685 (12)
C28	0.2384 (4)	-0.1809 (4)	0.0352 (2)	0.0732 (12)
C29	0.1861 (4)	-0.0677 (5)	0.0271 (2)	0.0746 (12)
C30	0.2248 (3)	0.0524 (4)	0.0419 (2)	0.0602 (9)
C31	0.3695 (2)	0.3095 (3)	0.02455 (11)	0.0399 (6)
C32	0.3876 (2)	0.2496 (3)	-0.02213 (12)	0.0457 (7)
C33	0.4006 (3)	0.3232 (4)	-0.06657 (12)	0.0535 (8)
C34	0.3941 (3)	0.4567 (4)	-0.0645 (2)	0.0678 (11)
C35	0.3735 (5)	0.5167 (4)	-0.0188 (2)	0.085 (2)
C36	0.3626 (3)	0.4439 (4)	0.0260 (2)	0.0618 (10)
C37	0.0837 (3)	0.4609 (4)	0.11061 (13)	0.0589 (10)
C38	0.0141 (5)	0.6804 (6)	0.0889 (2)	0.119 (3)
C39	-0.0502 (6)	0.7183 (9)	0.0444 (2)	0.157 (4)
C40	-0.1243 (4)	0.6132 (9)	0.0452 (3)	0.133 (3)
C41	-0.0765 (4)	0.4827 (8)	0.0651 (2)	0.131 (3)

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

Ag—P2	2.4647 (8)	P2—C25	1.817 (3)
Ag—P1	2.4756 (8)	P2—C19	1.820 (3)
Ag—S2	2.5689 (9)	P2—C31	1.829 (3)
Ag—S1	2.7082 (11)	N1—C37	1.339 (5)
S1—C37	1.695 (4)	N1—C41	1.474 (7)
S2—C37	1.701 (4)	N1—C38	1.479 (8)
P1—C13	1.821 (3)	C38—C39	1.464 (8)
P1—C1	1.827 (3)	C39—C40	1.497 (11)
P1—C7	1.831 (3)	C40—C41	1.564 (10)
P2—Ag—P1	124.43 (3)	P1—Ag—S1	107.23 (3)
P2—Ag—S2	117.85 (3)	S2—Ag—S1	68.15 (4)
P1—Ag—S2	114.52 (3)	C37—S1—Ag	83.10 (13)
P2—Ag—S1	108.11 (3)	C37—S2—Ag	87.46 (14)

The phenyl H atoms were located from difference Fourier maps and refined isotropically. The pyrrolidine H atoms were fixed geometrically and allowed to ride on their respective parent atoms.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990b). Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983b).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1228). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Bis(*O*-cyclohexyl dithiocarbonato)dimethyltin(IV)

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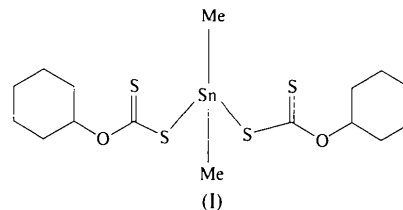
### Abstract

In  $[\text{Sn}(\text{CH}_3)_2(\text{C}_7\text{H}_{11}\text{OS}_2)_2]$ , the environment about the Sn atom is distorted tetrahedral, defined by the donor S atoms of the two monodentate dithiocarbonato (xanthate) ligands and by the two methyl C atoms. The second S atom of each xanthate ligand is twisted towards the Sn atom, in the so-called *S,S* orientation.

### Comment

The solid-state structures of metal xanthates have been reviewed (Tiekink & Winter, 1992; Winter, 1980). An interesting feature of the dithiocarbonato (xanthate) ligand ( $-\text{S}_2\text{COR}$ ) is shown in its monodentate coordination mode. The second non-coordinating S atom has two possible orientations: towards the central metal atom (the *S,S* mode) or away from it (by a rotation about the coordinated S—C bond), in which case the xanthate O atom is directed towards the central metal atom (the *S,O* mode). Structural studies of gold(I) xanthates have suggested that the presence of bulky substituents on the central atom would favour the former mode of orien-

tation while in cases where there is little or no steric hindrance, the latter mode would be adopted (Siasios & Tiekink, 1993). This paper reports the structure of an organotin xanthate complex, (I), in which the monodentate xanthate ligands adopt the *S,S* orientation even though the two methyl groups are not sterically demanding.



A displacement ellipsoid plot of the molecule with the atom-numbering scheme is shown in Fig. 1. The molecule is symmetrical about the C1—Sn—C2 plane, one half being related to the other by a mirror plane normal to **b**. This is in contrast to other diorganotin bis(xanthate) compounds which have no imposed symmetry (Dakternieks, Hoskins, Tiekink & Winter, 1984; Donoghue & Tiekink, 1991; Donoghue, Tiekink & Webster, 1993). The Sn atom has distorted tetrahedral coordination with angles of 134.7(1) and 87.2(1)°. Both these angles are significantly larger than those of previously reported structures. The large difference in the C3—S2 [1.630(7) Å] and C3—S1 [1.731(7) Å] bond lengths suggests that the xanthate is essentially monodentate. In the present structure, the second S atom of each xanthate ligand is directed towards the central Sn atom in the *S,S* orientation. The Sn...S2 distance of 3.072(2) Å is greater than the sum of the covalent radii (2.42 Å) of the Sn and S atoms, but less than the sum of the van der Waals radii (4.00 Å) (Bondi, 1964), indicating a weak interaction. This *S,S* mode is unexpected as the Sn<sup>IV</sup> ion, being a 'hard' acid, would be expected to be attracted to the 'hard' O atom rather than the 'soft' S atom. Furthermore, the methyl groups on the central Sn atom are not expected to offer substantial steric hindrance so as to force an *S,S* orientation mode.

The remaining parameters defining the xanthate ligands are normal and agree with those of previous examples. The C—C bond distances in the cyclohexyl ring [1.45(1)–1.51(1) Å] are less than the normal values; their apparent shortness may be attributed to high thermal vibrations. The cyclohexyl ring adopts a chair

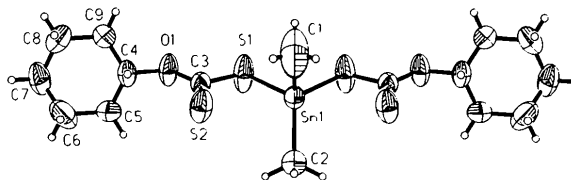


Fig. 1. A 50% probability displacement ellipsoid plot of the title molecule with the atom-numbering scheme.

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