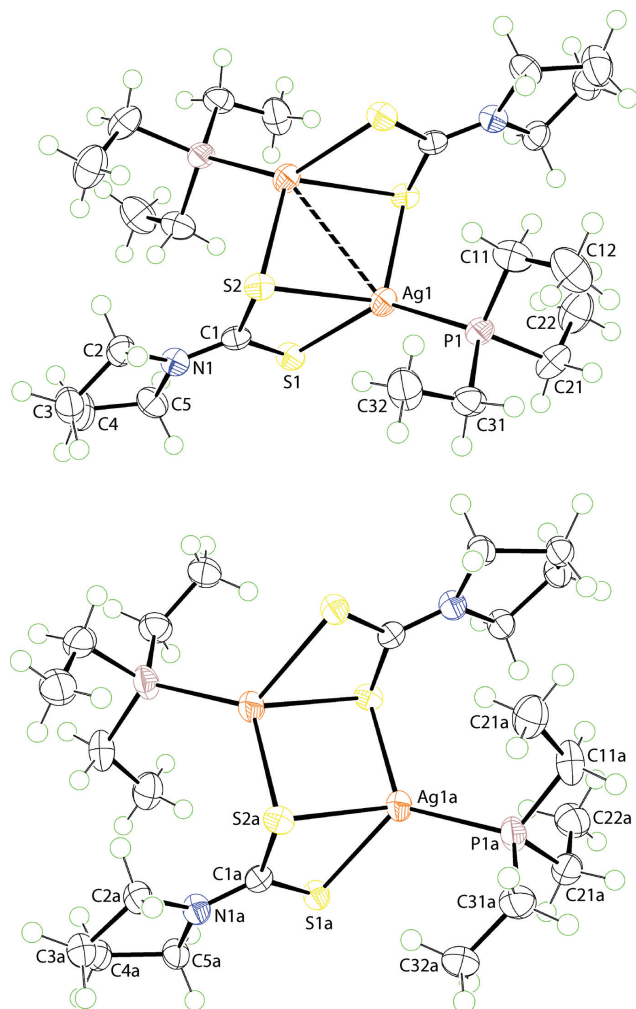




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Crystal structure of bis[μ_2 -(pyrrolidine-1-carbodithioato- $\kappa S:\kappa S,\kappa S'$)]-bis (triethylphosphine- κP)disilver(I), $C_{22}H_{46}Ag_2N_2P_2S_4$ **Abstract**

$C_{22}H_{46}Ag_2N_2P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 10.2008(3)$ Å, $b = 12.2058(3)$ Å, $c = 13.2466(4)$ Å, $\alpha = 88.155(2)^\circ$, $\beta = 87.256(2)^\circ$, $\gamma = 69.324(2)^\circ$, $V = 1541.12(8)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0237$, $wR_{ref}(F^2) = 0.0621$, $T = 100(2)$ K.

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The molecular structures of the two independent compounds of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.13 × 0.10 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	13.8 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	76.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	25450, 6430, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6034
$N(param)_{refined}$:	315
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

A solution of triethylphosphine solution (Sigma Aldrich; 1.0 M in THF, 1 mL, 1.0 mmol) was added to silver nitrate (Sigma Aldrich; 0.169 g, 1.0 mmol) in acetonitrile (10 mL), followed by the addition of ammonium pyrrolidinedithiocarbamate (Fluka; 0.164 g, 1.0 mmol) in acetonitrile (10 mL). The resulting mixture was stirred for 4 h and left for slow evaporation at room temperature, giving yellow crystals after 4 weeks. Yield: 0.197 g (53%). **M. pt** (Biobase automatic melting point apparatus MP450): 370 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm⁻¹): 1408 (s) $\nu(C=N)$, 985 (s) $\nu(C-S)$.

Experimental details

The H-atoms were placed in calculated positions ($C-H = 0.98-0.99$ Å) and were included in the refinement in the riding model approximation, with $U_{iso}(H)$ set to 1.2–1.5 $U_{eq}(C)$. The C31a-ethyl group was found to be disordered over two positions. Each component was refined independently

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
Ag1	0.11287(2)	0.38539(2)	0.04670(2)	0.02312(5)
S1	0.08870(5)	0.61752(4)	0.07322(4)	0.01976(10)
S2	0.28321(5)	0.44607(4)	-0.07159(4)	0.02195(10)
P1	0.11511(6)	0.27387(5)	0.19974(4)	0.02173(11)
N1	0.29447(19)	0.65402(15)	-0.03537(13)	0.0204(3)
C1	0.2285(2)	0.57957(18)	-0.01394(15)	0.0185(4)
C2	0.2592(2)	0.76924(18)	0.01227(17)	0.0237(4)
H2A	0.242764	0.763538	0.086196	0.028*
H2B	0.174868	0.827643	-0.017022	0.028*
C3	0.3879(3)	0.8011(2)	-0.0119(2)	0.0311(5)
H3A	0.459906	0.766976	0.038945	0.037*
H3B	0.363696	0.887093	-0.014625	0.037*
C4	0.4388(3)	0.7479(2)	-0.1152(2)	0.0373(6)
H4A	0.539577	0.734981	-0.127840	0.045*
H4B	0.384637	0.799075	-0.169576	0.045*
C5	0.4136(2)	0.6316(2)	-0.10896(17)	0.0258(4)
H5A	0.389642	0.610892	-0.175560	0.031*
H5B	0.497238	0.567470	-0.084992	0.031*
C11	-0.0605(3)	0.3141(2)	0.2600(2)	0.0315(5)
H11A	-0.102585	0.400667	0.260675	0.038*
H11B	-0.118589	0.285914	0.217213	0.038*
C12	-0.0707(3)	0.2684(3)	0.3676(2)	0.0441(7)
H12A	-0.018218	0.183941	0.370676	0.066*
H12B	-0.169283	0.283441	0.387268	0.066*
H12C	-0.031145	0.308403	0.413942	0.066*
C21	0.1745(3)	0.1139(2)	0.18877(19)	0.0317(5)
H21A	0.273785	0.084626	0.164135	0.038*
H21B	0.169629	0.078820	0.256629	0.038*
C22	0.0883(3)	0.0740(2)	0.1177(2)	0.0382(6)
H22A	-0.008759	0.097361	0.144448	0.057*
H22B	0.127832	-0.011407	0.112069	0.057*
H22C	0.090222	0.110306	0.050875	0.057*
C31	0.2243(2)	0.2895(2)	0.29976(17)	0.0271(5)
H31A	0.207233	0.247577	0.361315	0.032*
H31B	0.324263	0.252447	0.278236	0.032*
C32	0.1954(3)	0.4170(2)	0.3252(2)	0.0365(6)
H32A	0.206916	0.460123	0.263692	0.055*
H32B	0.261431	0.420905	0.375092	0.055*
H32C	0.099266	0.452066	0.353054	0.055*
Ag1A	0.39068(2)	0.02426(2)	0.60657(2)	0.02487(5)
S1A	0.35714(5)	-0.02768(4)	0.41435(4)	0.01889(10)
S2A	0.42601(5)	-0.19830(4)	0.58892(4)	0.02034(10)
P1A	0.20415(6)	0.15836(5)	0.70428(5)	0.02621(12)
N1A	0.40529(19)	-0.25486(15)	0.40062(13)	0.0203(3)
C1A	0.3976(2)	-0.16928(17)	0.46324(15)	0.0178(4)
C2A	0.3859(2)	-0.23945(18)	0.29079(16)	0.0219(4)
H2A1	0.461930	-0.217914	0.256495	0.026*
H2A2	0.294527	-0.178292	0.276083	0.026*
C3A	0.3909(2)	-0.35979(19)	0.25767(17)	0.0240(4)
H3A1	0.430488	-0.376205	0.187753	0.029*
H3A2	0.296213	-0.365221	0.261521	0.029*
C4A	0.4868(2)	-0.44421(18)	0.33353(16)	0.0225(4)
H4A1	0.470312	-0.519456	0.337988	0.027*
H4A2	0.586819	-0.459647	0.314921	0.027*
C5A	0.4441(2)	-0.37810(18)	0.43252(16)	0.0226(4)

Table 2 (continued)

Atom	x	y	z	U _{iso} */U _{eq}
H5A1	0.363528	-0.393168	0.466775	0.027*
H5A2	0.523069	-0.400786	0.478745	0.027*
C11A	0.1867(3)	0.3134(2)	0.70350(18)	0.0304(5)
H11C	0.095625	0.359732	0.736590	0.036*
H11D	0.262055	0.322363	0.743102	0.036*
C12A	0.1950(3)	0.3614(2)	0.59675(19)	0.0338(5)
H12D	0.283764	0.314390	0.563000	0.051*
H12E	0.189872	0.442930	0.599890	0.051*
H12F	0.116604	0.357781	0.558670	0.051*
C21A	0.2090(3)	0.1181(2)	0.8390(2)	0.0307(5)
H21C	0.129401	0.176732	0.875537	0.037*
H21D	0.196980	0.041261	0.847313	0.037*
C22A	0.3452(3)	0.1110(2)	0.8859(2)	0.0336(5)
H22D	0.424704	0.054770	0.848823	0.050*
H22E	0.344337	0.085324	0.956743	0.050*
H22F	0.354356	0.188331	0.882453	0.050*
C31A ^a	0.0280(3)	0.1738(4)	0.6652(3)	0.0294(8)
H31C ^a	-0.041031	0.207216	0.721192	0.035*
H31D ^a	0.002937	0.228671	0.606598	0.035*
C32A ^a	0.0212(3)	0.0554(3)	0.6363(3)	0.0344(10)
H32D ^a	0.085450	0.024530	0.578154	0.052*
H32E ^a	-0.074634	0.065686	0.618658	0.052*
H32F ^a	0.048563	0.000417	0.693602	0.052*
C31B ^b	0.0328(13)	0.1251(16)	0.7013(14)	0.030(4)
H31E ^b	0.050216	0.042369	0.721004	0.036*
H31F ^b	-0.038940	0.175998	0.748910	0.036*
C32B ^b	-0.0161(13)	0.1479(16)	0.5963(11)	0.042(5)
H32G ^b	-0.047741	0.232266	0.581571	0.063*
H32H ^b	-0.094065	0.119837	0.589167	0.063*
H32I ^b	0.061091	0.106788	0.548934	0.063*

^aOccupancy: 0.797(9), ^bOccupancy: 0.203(9).

with the major component having a site occupancy factor = 0.797(9).

Comment

In connection with recent anti-bacterial screening and pharmacokinetic studies of binuclear phosphanesilver(I) dithiocarbamates, {Cy₃PAg(S₂CNRR')}₂, complementary crystallographic studies revealed a novel conformation for one of the derivatives [5]. The common feature of the solid-state structures are μ₂-bridging dithiocarbamate ligands and a central Ag₂S₂ core, with the distinction arising in terms of the relative disposition of the dithiocarbamate ligands. In three of the structures, i.e. with R = R' = Et and CH₂CH₂OH, and R = Me, R' = CH₂CH₂OH, the dithiocarbamate ligands lie to either side of the core, i.e. adopt an anti-conformation. The unusual structure was observed when NRR' = N(CH₂)₄, which has a *syn* conformation as the dithiocarbamate ligands are orientated to the same side of the Ag₂S₂ core. The majority of related structures adopt the *anti*-conformation [6–11], with the only other exceptional structure being that

of $\{Ph_2(Me)PAG(S_2CNET_2)\}_n$, which, although having a similar mode of coordination of the dithiocarbamate ligand, is a one-dimensional coordination polymer in the solid-state [9]. In continuation of studies in this area, herein, the results of the crystal structure determination of $\{Et_3PAG[S_2CN(CH_2)_4]\}_2$, (I), are described.

The molecular structures of the two independent binuclear molecules of (I) are shown in the figure (70% displacement ellipsoids; the unlabelled atoms in the upper and lower images are generated by the application of the symmetry operations (i) $-x, 1-y, -z$ and (ii) $1-x, -y, 1-z$, respectively). As each binuclear complex is disposed about a centre of inversion, the asymmetric unit comprises two half complexes. The dithiocarbamate ligand is tridentate, simultaneously chelating the Ag1 atom [Ag1–S1 = 2.7882(5) Å and Ag1–S2 = 2.5683(5) Å] and bridging the Ag1ⁱ atom [Ag1ⁱ–S1 = 2.6684(5) Å]; the fourth position in the PS₃ coordination geometry is occupied by the phosphane-P1 atom [Ag1–P1 = 2.4017(5) Å]. The Ag1a atom exhibits the same general features but, in this case, the shortest Ag–S bond involves the S1aⁱⁱ atom which links the monomeric units into the dimer [Ag1a–S1a, S2a, S1aⁱⁱ & P1 = 2.7097(5), 2.6278(5), 2.5890(5) & 2.3825(5) Å, respectively]. The four-coordinate geometry defined by the PS₃ donor set is highly distorted as seen in the range of angles subtended at the Ag1 atom, i.e. 67.791(15)°, for the S1–Ag1–S2 chelate angle, to 139.496(19)° for S2–Ag1–P1. The range is reduced for the Ag1a atom, i.e. 68.334(15) Å for S1a–Ag1a–S2a to 125.188(19)° for S1aⁱⁱ–Ag1a–P1a. An intramolecular Ag1ⁱ···Ag1ⁱ [3.1876(3) Å] contact is noted but, the equivalent separation for the Ag1a-complex is considerably longer at 3.4451(4) Å. This represents the greatest difference between the independent complexes.

In the crystal, weak P-methylene-C–H···S(bridging) interactions [C21–H21b···S1a: H21b···S1a = 2.86 Å, C21···S1a = 3.649(3) Å with angle at H21b = 137° and C21a–H21c···S1ⁱⁱⁱ: H21c···S1ⁱⁱⁱ = 2.78 Å, C21a···S1ⁱⁱⁱ = 3.738(3) Å with angle at H21c = 163° for (iii) $-x, 1-y, 1-z$]. As these occur between the independent molecules comprising the asymmetric unit and each of these forms two donor and two acceptor interactions that extend laterally, the complexes are assembled into a two-dimensional array parallel to (110). The layers stack without directional interactions between them.

Using Crystal Explorer 17 [12] and following standard protocols [13], the Hirshfeld surfaces and two-dimensional fingerprint plots were calculated for each of the independent complexes. There are two dominant surface contacts for the Ag1-complex, namely H···H and H···S/S···H contributing 77.8 and 18.5%, respectively, the latter, in part, reflecting the H···S contacts discussed above. A similar dominance is observed for the Ag1a-complex (major component; no significant difference was noted for the minor component),

but, with distinct percentage contributions to the Hirshfeld surface, i.e. 80.7 and 17.2%.

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