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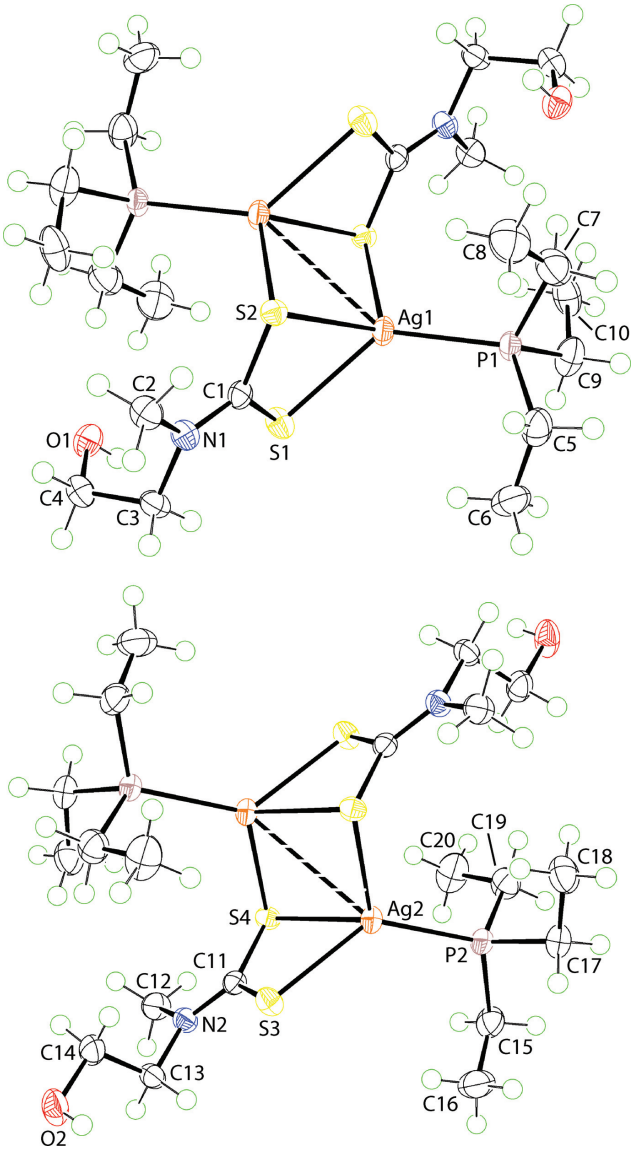
Crystal structure of bis[μ_2-(*N*-(2-hydroxyethyl)-*N*-methylcarbamodithioato-κ*S*:κ*S*,κ*S*′)]-bis(triethylphosphine-*P*)-di-silver(I), $C_{20}H_{46}Ag_2N_2O_2P_2S_4$



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Abstract

$C_{20}H_{46}Ag_2N_2O_2P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.3895(1)$ Å, $b = 13.1597(2)$ Å, $c = 13.1803(2)$ Å, $\alpha = 88.119(1)°$, $\beta = 86.601(1)°$, $\gamma = 70.173(1)°$, $V = 1529.22(4)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0162$, $wR_{ref}(F^2) = 0.0406$, $T = 100(2)$ K.

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The molecular structures are 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 prism
Size:	0.11 × 0.07 × 0.03 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	14.0 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	36269, 5464, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5242
$N(param)_{refined}$:	303
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

A solution of triethylphosphine (Sigma Aldrich; 1.0 M in THF, 0.25 mL, 0.25 mmol) was added to silver nitrate (Sigma Aldrich; 0.042 g, 0.25 mmol) in acetonitrile (10 mL), followed by the addition of ammonium *N*-(hydroxyethyl)-*N*-methyldithiocarbamate (0.042 g, 0.25 mmol) in acetonitrile (10 mL). The resulting mixture was stirred for 2 h and left for slow evaporation at room temperature, giving colourless crystals after 4 weeks. Yield: 0.066 g (71%). **M. pt** (Biobase automatic melting point apparatus MP450): 391–392 K. **Elemental Analysis** for $C_{20}H_{46}Ag_2N_2O_2P_2S_4$ (Leco TruSpec Micro CHN Elemental Analyser): C, 31.92; H, 6.16; N, 3.72%. Found:

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

Atom	x	y	z	U_{iso}*/U_{eq}
Ag1	0.52341(2)	1.03094(2)	0.11037(2)	0.01708(4)
S1	0.76308(5)	0.86071(3)	0.10134(3)	0.01963(9)
S2	0.70717(5)	1.02835(3)	−0.06253(3)	0.01501(8)
P1	0.44812(5)	1.18254(4)	0.22234(3)	0.01599(9)
O1	0.98993(15)	0.64786(10)	−0.06285(10)	0.0213(3)
H1O	0.962(3)	0.635(2)	−0.0038(10)	0.032*
N1	0.97498(17)	0.87435(12)	−0.03850(11)	0.0170(3)
C1	0.8298(2)	0.91455(14)	−0.00378(13)	0.0153(3)
C2	1.0360(2)	0.91967(16)	−0.12645(14)	0.0208(4)
H2A	1.036410	0.878416	−0.187090	0.031*
H2B	1.139865	0.915711	−0.114619	0.031*
H2C	0.972794	0.995275	−0.136622	0.031*
C3	1.0859(2)	0.77908(15)	0.00745(14)	0.0191(4)
H3A	1.046066	0.765770	0.075978	0.023*
H3B	1.181079	0.793953	0.015444	0.023*
C4	1.1202(2)	0.67829(15)	−0.05594(15)	0.0204(4)
H4A	1.157492	0.691974	−0.125097	0.024*
H4B	1.201313	0.618191	−0.024921	0.024*
C5	0.6012(2)	1.21496(17)	0.27823(16)	0.0273(4)
H5A	0.662676	1.235852	0.223151	0.033*
H5B	0.556501	1.277820	0.323263	0.033*
C6	0.7052(2)	1.12080(19)	0.33953(16)	0.0296(5)
H6A	0.648091	1.105849	0.399401	0.044*
H6B	0.790797	1.139905	0.361320	0.044*
H6C	0.743279	1.056433	0.297074	0.044*
C7	0.3403(2)	1.31193(17)	0.16267(17)	0.0311(5)
H7A	0.237735	1.311490	0.149770	0.037*
H7B	0.328583	1.370975	0.210562	0.037*
C8	0.4145(3)	1.33481(18)	0.06390(18)	0.0362(5)
H8A	0.512137	1.342169	0.077005	0.054*
H8B	0.348630	1.402011	0.033469	0.054*
H8C	0.430765	1.275090	0.017107	0.054*
C9	0.3272(2)	1.17574(18)	0.33458(16)	0.0279(4)
H9A	0.382920	1.113368	0.377470	0.033*
H9B	0.306615	1.241953	0.374702	0.033*
C10	0.1771(2)	1.16464(17)	0.31020(17)	0.0292(5)
H10A	0.116327	1.229653	0.273935	0.044*
H10B	0.122088	1.155704	0.373505	0.044*
H10C	0.196037	1.101399	0.267438	0.044*
Ag2	0.59852(2)	0.37598(2)	0.52495(2)	0.01719(4)
S3	0.75747(5)	0.40793(4)	0.36730(3)	0.01823(9)
S4	0.67709(5)	0.55883(3)	0.54196(3)	0.01562(9)
P2	0.65768(5)	0.24804(4)	0.66320(3)	0.01679(9)
O2	0.98458(18)	0.55427(11)	0.12046(10)	0.0278(3)
H2O	0.991(3)	0.4908(11)	0.108(2)	0.042*
N2	0.88884(17)	0.55412(12)	0.39628(11)	0.0173(3)
C11	0.78361(19)	0.51198(14)	0.43008(13)	0.0154(3)
C12	0.9157(2)	0.64414(15)	0.44582(15)	0.0218(4)
H12A	0.861516	0.712155	0.411166	0.033*
H12B	1.024544	0.632826	0.442081	0.033*
H12C	0.878915	0.647379	0.517204	0.033*
C13	0.9782(2)	0.51943(15)	0.30092(14)	0.0190(4)
H13A	0.997146	0.441603	0.291043	0.023*
H13B	1.077402	0.529872	0.304201	0.023*
C14	0.8948(2)	0.58390(16)	0.21205(15)	0.0246(4)
H14A	0.798056	0.570380	0.206531	0.029*
H14B	0.870983	0.661992	0.223693	0.029*
C15	0.8597(2)	0.18907(17)	0.68831(16)	0.0259(4)
H15A	0.896633	0.247113	0.708696	0.031*
H15B	0.872084	0.136982	0.745814	0.031*
C16	0.9563(2)	0.13136(18)	0.59629(19)	0.0343(5)
H16A	0.929710	0.067725	0.581444	0.051*
H16B	1.063781	0.108734	0.611042	0.051*
H16C	0.937423	0.180604	0.537336	0.051*
C17	0.6017(2)	0.12798(15)	0.65527(15)	0.0226(4)
H17A	0.665780	0.080436	0.601435	0.027*
H17B	0.620199	0.087447	0.720564	0.027*
C18	0.4359(2)	0.15580(18)	0.63213(17)	0.0289(4)
H18A	0.371616	0.196691	0.688582	0.043*
H18B	0.413824	0.089096	0.623303	0.043*
H18C	0.415507	0.199553	0.569589	0.043*
C19	0.5733(2)	0.30264(16)	0.78739(15)	0.0258(4)
H19A	0.463353	0.314146	0.789487	0.031*
H19B	0.618803	0.248727	0.840865	0.031*
C20	0.5954(3)	0.40875(18)	0.81107(17)	0.0351(5)
H20A	0.703955	0.397509	0.811748	0.053*
H20B	0.546734	0.434051	0.877758	0.053*
H20C	0.549566	0.462932	0.758927	0.053*

C, 31.81; H, 6.30; N, 3.85%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 3282 (br) ν(OH), 1456 (m) ν(C=N), 953 (m) ν(C-S).

Experimental details

The carbon-bound 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 1.2–1.5U_{eq}(C). The O-bound H atoms were refined with O—H = 0.84 ± 0.01 Å, and with 1.5U_{eq}(O).

Comment

Herein, the crystal structure determination of a binuclear phosphanesilver(I) dithiocarbamate derivative, $\{Et_3PAg[S_2CN(Me)CH_2CH_2OH]\}_2$, (I), featuring hydrogen bonding functionality in the dithiocarbamate ligand, is described. Related compounds have attracted interest owing to their anti-bacterial activity and encouraging pharmacokinetic profiles [5]. Complimentary crystal structure investigations reveal three structural motifs for compounds of the general formula $R_3PAg(S_2CNR'R'')$. There is a single example of a one-dimensional coordination polymer, i.e. in the crystal of $[Ph_2(Me)PAg(S_2CNEt_2)]_n$ [6], where the presence of a tridentate, μ_2-bridging dithiocarbamate ligand links

adjacent silver(I) atoms. A similar mode of coordination of the dithiocarbamate ligand is found in the remaining two structural motifs. There is a single example of a binuclear structure where the bridging dithiocarbamate ligands lie to the same side of the central Ag_2S_2 core, namely in the crystal of $\{Cy_3PAg[S_2CN(CH_2)_4]\}_2$ [5]. The remaining $R_3PAg(S_2CNR'R'')$ structures have the dithiocarbamate ligands lying to opposite sides of the central Ag_2S_2 plane [5–11]. The structure of (I) conforms to the common binuclear structural motif.

There are two half molecules of (I) in the crystallographic asymmetric unit with the full molecule completed by the application of a centre of inversion in each case, as shown in the figure (70% displacement ellipsoids; the unlabelled atoms in the upper and lower images are related by the symmetry operations (i) $1-x, 2-y, -z$ and (ii) $1-x, 1-y, 1-z$, respectively). The anticipated tridentate, μ_2-bridging mode of coordination of the dithiocarbamate ligand is present whereby the ligand chelates the Ag1 atom while at the same time connects to the centrosymmetrically related $Ag1^i$ atom, forming Ag1—S1, S2, $S2^i$ bond lengths of 2.5812(4), 2.7695(4) and 2.6522(4) Å, respectively. The four-coordinate geometry is completed by the phosphane ligand [Ag1—P1 = 2.4022(4) Å] and a transannular Ag1···$Ag1^i$ contact [3.1419(2) Å] is noted. The comparable bond lengths for the second independent molecule are Ag2—S3, S4, $S4^{ii}$, P2, $Ag2^{ii}$ = 2.5927(4), 2.7648(4), 2.6315(4), 2.3974(4) and 3.2275(2) Å, respectively. Reflecting the fact the S2 atom is engaged in two Ag1—S2 bonds compared to one for the S1 atom, the C1—S2 bond length [1.7399(18) Å] is significantly longer than the C1—S1 bond [1.7169(18) Å]; C11—S3, S4 = 1.7164(17) and 1.7382(18) Å. The resulting PS_3 donor set is highly distorted owing to the restricted bite distance of the chelate angle [S1—Ag1—S2 = 67.420(13)°] and the close approach of the $Ag1^i$ atom; the widest angle of 131.272(15)° is for S1—Ag1—P1; S3—Ag2—S4 = 67.542(13)° and S3—Ag2—P2 = 132.573(16)°.

The most recognisable feature of the molecular packing is the formation of hydroxyl-O—H···O (hydroxyl) hydrogen bonds [O1—H1o···O2: H1o···O2 = 1.905(17) Å, O1···O2 = 2.6813(19) Å with angle at H1o = 154(3)° and O2—H2o···$O1^{iii}$: H2o···$O1^{iii}$ = 1.885(17) Å, O2···$O1^{iii}$ = 2.7182(19) Å with angle at H2o = 173(3)° for (iii): $1-x, 2-y, -z$]. The hydroxyl groups assemble to form eight-membered $\{\cdots OH\}_4$ synthons leading to supramolecular layers parallel to (1 1 1). The layers are sandwiched by hydrogen-rich substituents and stack without directional interactions between them.

Finally, the Hirshfeld surfaces and two-dimensional fingerprint plots were calculated for each of the independent molecules in order to see if there were any distinguishing features between them; calculations were performed with Crystal Explorer 17 [12] in accord with standard protocols [13]. For the Ag1-molecule, H···H [76.5%] and H···S/S···H [13.2%] account for almost 90% of all surface contacts. The next most significant contribution comes from H···O/O···H contacts, at 4.6% with the decomposed fingerprint featuring sharp spikes corresponding to the O—H···O hydrogen bonding. A similar but, nevertheless distinct distribution of surface contacts is noted for the Ag2-molecule, i.e. H···H [74.6%], H···S/S···H [13.9%] and H···O/O···H [5.8%].

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