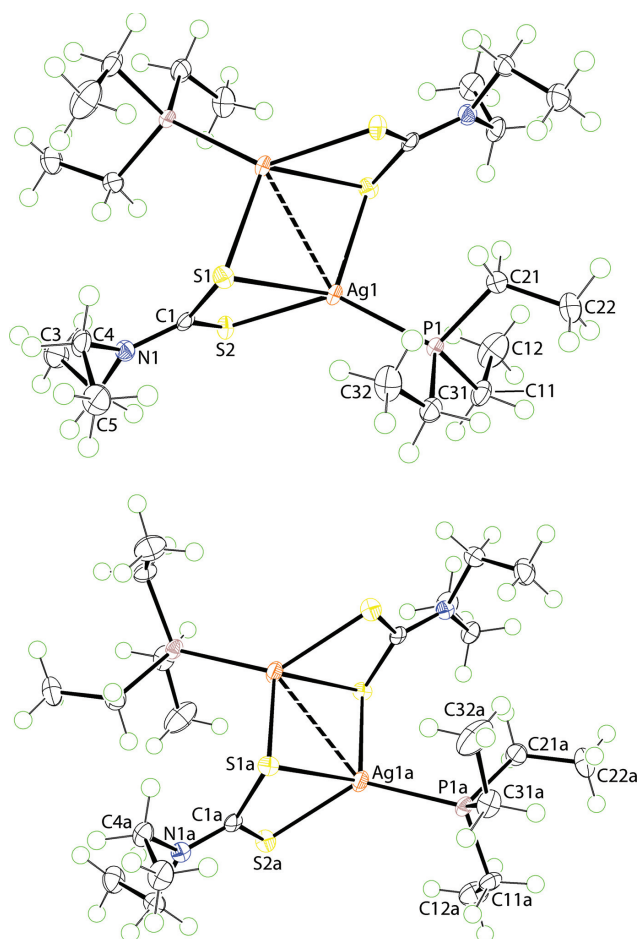


Chien Ing Yeo, Yi Jiun Tan, Aya Shiomitsu, Jacty Chew, Nathan R. Halcovitch and Edward R.T. Tiekink*

Crystal structure of bis[μ_2 -(*N,N*-diethylcarbamo-dithioato- $\kappa S:\kappa S,\kappa S'$)]-bis(triethylphosphine-*P*)-di-silver(I), $C_{22}H_{50}Ag_2N_2P_2S_4$



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*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. <https://orcid.org/0000-0003-1401-1520>

Chien Ing Yeo and Yi Jiun Tan: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Aya Shiomitsu and Jacty Chew: Department of Biological Sciences, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Nathan R. Halcovitch: Department of Chemistry, Lancaster University, Lancaster LA1 4YB, United Kingdom

Abstract

$C_{22}H_{50}Ag_2N_2P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.0672(2)$ Å, $b = 11.2091(3)$ Å, $c = 16.6853(4)$ Å, $\alpha = 91.097(2)^\circ$, $\beta = 90.363(2)^\circ$, $\gamma = 110.989(2)^\circ$, $V = 1582.85(7)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0241$, $wR_{ref}(F^2) = 0.0653$, $T = 100(2)$ 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:	0.25 × 0.18 × 0.08 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	13.4 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	76.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	28526, 6597, 0.031
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 6479
$N(param)_{refined}$:	299
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) taken in acetonitrile (10 mL), followed by the addition of sodium diethyldithiocarbamate (BDH; 0.043 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 3 weeks. Yield: 0.066 g (71%). **M. pt.** (Biobase automatic melting point apparatus MP450): 358–359 K. Elemental Analysis for $C_{22}H_{50}Ag_2N_2P_2S_4$ (Leco TruSpec Micro CHN Elemental Analyser): C, 35.30; H, 6.73; N, 3.74%. Found: C, 35.12; H, 6.96; N, 3.95%. ¹H NMR (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in CDCl₃ solution at 298 K, ppm): δ 3.98 (q, 4H, NCH₂, $J_{HH} = 7.10$ Hz), 1.67 (dq, 6H, PCH₂, $J_{HH} = 7.65$ Hz, $J_{PH} = 7.56$ Hz), 1.31 (t, 6H, NCH₂CH₃, $J_{HH} = 7.10$ Hz), 1.18 (dt, 9H, PCH₂CH₃,

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ag1	0.84362(2)	0.50099(2)	0.97038(2)	0.01231(5)
S1	0.96224(7)	0.54872(6)	1.13183(4)	0.01210(12)
S2	0.96253(7)	0.73817(6)	1.00805(3)	0.01206(12)
P1	0.58699(7)	0.33751(6)	0.95088(4)	0.01010(12)
N1	0.9951(2)	0.7907(2)	1.16492(13)	0.0116(4)
C1	0.9763(3)	0.7016(2)	1.10691(15)	0.0101(4)
C2	0.9878(3)	0.9170(2)	1.14852(16)	0.0139(5)
H2A	0.9414	0.9460	1.1951	0.017*
H2B	0.9174	0.9093	1.1016	0.017*
C4	1.0197(3)	0.7674(3)	1.24975(15)	0.0153(5)
H4A	1.0835	0.8493	1.2767	0.018*
H4B	1.0799	0.7093	1.2528	0.018*
C5	0.8647(3)	0.7088(3)	1.29354(16)	0.0196(5)
H5A	0.8052	0.7665	1.2913	0.029*
H5B	0.8865	0.6956	1.3496	0.029*
H5C	0.8025	0.6265	1.2679	0.029*
C3	1.1494(3)	1.0164(3)	1.13205(18)	0.0191(5)
H3A	1.2186	1.0263	1.1790	0.029*
H3B	1.1383	1.0984	1.1210	0.029*
H3C	1.1954	0.9887	1.0856	0.029*
C11	0.4661(3)	0.3552(3)	0.86651(16)	0.0160(5)
H11A	0.3682	0.2787	0.8620	0.019*
H11B	0.4357	0.4306	0.8766	0.019*
C12	0.5563(4)	0.3715(3)	0.78825(17)	0.0273(7)
H12A	0.6542	0.4462	0.7931	0.041*
H12B	0.4909	0.3838	0.7445	0.041*
H12C	0.5817	0.2950	0.7769	0.041*
C21	0.6070(3)	0.1831(2)	0.92865(16)	0.0148(5)
H21A	0.6782	0.1938	0.8824	0.018*
H21B	0.6593	0.1608	0.9752	0.018*
C22	0.4543(3)	0.0703(3)	0.90956(18)	0.0200(6)
H22A	0.3822	0.0577	0.9548	0.030*
H22B	0.4788	-0.0072	0.9003	0.030*
H22C	0.4041	0.0882	0.8614	0.030*
C31	0.4487(3)	0.3064(3)	1.03390(16)	0.0160(5)
H31A	0.4088	0.3777	1.0389	0.019*
H31B	0.3573	0.2273	1.0215	0.019*
C32	0.5221(3)	0.2916(3)	1.11406(17)	0.0210(6)
H32A	0.5558	0.2178	1.1107	0.032*
H32B	0.4439	0.2786	1.1564	0.032*
H32C	0.6137	0.3690	1.1265	0.032*
Ag1A	0.84851(2)	0.00650(2)	0.53744(2)	0.01342(6)
S1A	0.95174(7)	0.23888(6)	0.49669(4)	0.01313(12)
S2A	0.93475(7)	0.03774(6)	0.37322(3)	0.01140(11)
P1A	0.59468(7)	-0.14349(6)	0.57379(4)	0.01113(12)
N1A	0.9867(2)	0.2820(2)	0.34066(13)	0.0114(4)
C1A	0.9621(3)	0.1954(2)	0.39831(15)	0.0102(4)
C2A	0.9942(3)	0.4137(2)	0.35819(16)	0.0149(5)
H2A1	0.9203	0.4123	0.4019	0.018*
H2A2	0.9597	0.4474	0.3100	0.018*
C3A	1.1596(3)	0.5025(3)	0.38274(18)	0.0198(6)
H3A1	1.1911	0.4734	0.4328	0.030*
H3A2	1.1604	0.5896	0.3906	0.030*
H3A3	1.2340	0.5017	0.3406	0.030*
C4A	1.0116(3)	0.2542(3)	0.25615(15)	0.0138(5)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H4A1	1.0574	0.1862	0.2538	0.017*
H4A2	1.0885	0.3317	0.2325	0.017*
C5A	0.8593(3)	0.2115(3)	0.20666(15)	0.0180(5)
H5A1	0.7849	0.1319	0.2279	0.027*
H5A2	0.8824	0.1971	0.1508	0.027*
H5A3	0.8126	0.2779	0.2094	0.027*
C11A	0.4514(3)	-0.0785(3)	0.61497(16)	0.0155(5)
H11C	0.4133	-0.0377	0.5714	0.019*
H11D	0.3595	-0.1498	0.6349	0.019*
C12A	0.5183(4)	0.0188(3)	0.68284(18)	0.0236(6)
H12D	0.5443	-0.0234	0.7289	0.035*
H12E	0.4397	0.0559	0.6986	0.035*
H12F	0.6140	0.0867	0.6649	0.035*
C21A	0.6096(3)	-0.2545(3)	0.65037(16)	0.0157(5)
H21C	0.6852	-0.2940	0.6315	0.019*
H21D	0.6550	-0.2043	0.6999	0.019*
C22A	0.4562(4)	-0.3614(3)	0.67196(18)	0.0217(6)
H22D	0.3804	-0.3242	0.6920	0.033*
H22E	0.4778	-0.4138	0.7135	0.033*
H22F	0.4119	-0.4149	0.6242	0.033*
C31A	0.4816(3)	-0.2495(3)	0.49206(16)	0.0171(5)
H31C	0.3826	-0.3110	0.5135	0.021*
H31D	0.4530	-0.1981	0.4514	0.021*
C32A	0.5755(4)	-0.3224(4)	0.4526(2)	0.0318(7)
H32D	0.6770	-0.2618	0.4347	0.048*
H32E	0.5159	-0.3721	0.4064	0.048*
H32F	0.5943	-0.3803	0.4913	0.048*

$J_{\text{HH}} = 7.65$ Hz, $J_{\text{PH}} = 18.01$ Hz). ¹³C{¹H} NMR {as for ¹H NMR}: 209.0 (Cq), 49.3 (NCH₂), 179 (d, PCH₂, $J_{\text{CP}} = 18.51$ Hz), 12.2 (NCH₂CH₃), 9.5 (d, PCH₂CH₃, $J_{\text{CP}} = 4.77$ Hz). ³¹P{¹H} NMR (as for ¹H NMR but with chemical shift referenced to 85% aqueous H₃PO₄ as the external reference): δ 11.0.

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 $U_{\text{iso}}(\text{H})$ set to 1.2–1.5 $U_{\text{eq}}(\text{C})$. Owing to poor agreement, two reflections, i.e. (3 –2 3) and (5 –4 16), were omitted from the final cycles of refinement.

Comment

In response to the exciting anti-bacterial activity, usually against Gram-positive bacteria, exhibited by phosphane-gold(I) dithiocarbamate compounds, R₃PAu(S₂CNR'R'') [5], attention turned to related copper(I) and silver(I) species [6, 7] of which compounds of the general Cy₃PAg(S₂CNR'R'') proved

most promising [7]. Complementing biological studies, are structural investigations which reveal the monomer formulation to be an over-simplification. In the case of $Ph_2(Me)PAu(S_2CNEt_2)$, the dithiocarbamate ligand is tridentate, μ_2 -bridging leading to a one-dimensional coordination polymer [8]. However, in all the other known structures, the tridentate mode of coordination of the dithiocarbamate ligand leads to a binuclear molecule rather than a polymer. Two distinct conformations are noted in the dimers, namely where the molecule has the dithiocarbamate ligands lying to either side of the Ag_2S_2 core, the anti-conformation, or, more rarely a boat form where the dithiocarbamate ligands lie to the same side of the central core, the syn-form. This diversity is evident in the aforementioned $Cy_3PAu(S_2CNR'R'')$ compounds whereby the anti-conformation is formed in the structures with $R' = R'' = Et$ and CH_2CH_2OH , and $R' = Me$, $R'' = CH_2CH_2OH$ but, when $NR'R'' = N(CH_2)_4$, the syn conformation is observed [7]. For the general formula, $R_3PAg(S_2CNR'R'')$, in instances when $R' = R'' = Et$ and $R = Ph$ and *m*-tolyl [8], and $R_3P = Ph_2(2\text{-pyridyl})P$ [8] and $Ph_2(C_5H_3CN)Fe(C_5H_4)P$ [9], the anti-form is observed. Similarly, the anti-conformation is noted in the $R = Ph$ structures with $R' = R'' = (3\text{-pyridyl})$ [10], and $R' = CH_2Ph$, $R'' = (3\text{-pyridyl})$ [10], $R' = Me$, $R'' = CH_2(C_5H_3)Fe(C_5H_4)$ [11] and $NR'R'' = N(CH_2CH_2)C(H)Me$ [12]. Finally, in accompanying structural reports, the $\{Et_3PAg(S_2CNRR')\}_2$ structures with $NR'R'' = N(CH_2)_4$ [13] and $R' = Me$, $R'' = CH_2CH_2OH$ [14] adopt the anti-form in the solid-state. Herein, the crystal and molecular structures of $\{Et_3PAg(S_2CNEt_2)\}_2$, (I), are described. A preliminary evaluation of anti-bacterial activity of (I), employing the protocols outlined in a previous study [7], showed (I) did not display promising potential against the tested pathogens.

The crystallographic asymmetric unit of (I) comprises two half molecules, each disposed about a centre of inversion to generate the binuclear molecules 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) $2 - x$, $1 - y$, $2 - z$ and (ii) $2 - x$, $-y$, $1 - z$, respectively). The S1-dithiocarbamate ligand chelates the Ag1 atom in an asymmetric mode, forming disparate Ag1–S1, S2 bond lengths of 2.8629(6) and 2.5494(6) Å, respectively, and at the same time bridges to the centrosymmetrically related Agⁱ atom, via a S1–Agⁱ bond intermediate in length, i.e. 2.6498(6) Å, compared to the chelating Ag–S bonds. The distorted PS_3 coordination geometry is completed by the phosphane-P1 ligand, Ag1–P1 = 2.4065(6) Å. The chemically equivalent bond lengths for the second independent molecule, i.e. with the Ag1a atom, follow the same general trends [Ag1a–S1a, S2a, S1aⁱⁱ & P1a = 2.5402(6), 2.8478(6), 2.6494(6) & 2.4034(6) Å, respectively. The major deviations

from the regular tetrahedral geometry defined by the PS_3 donor set are seen in the acute S1–Ag1–S2 chelate angle of 66.773(18)° and in the wide P1–Ag1–S2 angle of 138.73(2)° [for the Ag1a molecule, the range of angles is S1a–Ag1a–S2a = 67.048(18)° to P1a–Ag1a–S1a = 134.78(2)°]. Globally, the conformation of each molecule is anti, as the chelating ligands lie above and below the plane of the central core. An intramolecular Ag1···Ag1ⁱ contact of 3.0051(3) Å is noted; the equivalent separation for the Ag1a molecule is 3.0745(3) Å.

An analysis of the molecular packing indicates the crystal (I) is devoid of significant intermolecular atom-to-atom contacts. Accordingly, the Hirshfeld surfaces and two-dimensional fingerprint plots were calculated for each of the independent binuclear molecules, using Crystal Explorer 17 [15] and standard procedures [16]. Reflecting the lack of directional interactions in the crystal, H···H contacts account for 78.4% of all surface contacts for the Ag1-molecule with the only other significant contribution arising from H···S/S···H contacts [12.5%] but, at separations greater than the sum of the van der Waals radii. For the Ag1a-molecule, H···H [81.2%] and H···S/S···H contacts [14.4%] make similar but greater contributions.

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