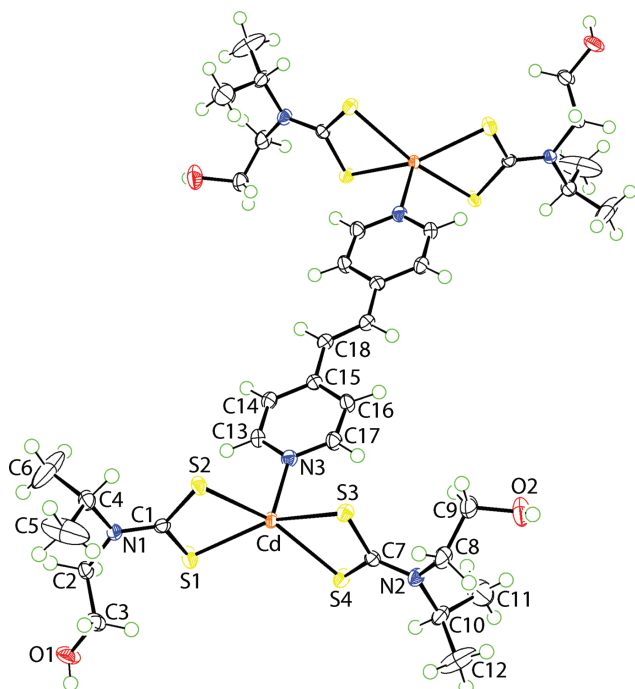


Chien Ing Yeo and Edward R.T. Tiekink\*

# Crystal structure of tetrakis (*N*-(2-hydroxyethyl)-*N*-isopropylcarbamodithioato- $\kappa$ S, $S'$ )-( $\mu_2$ (2-(pyridin-4-yl)vinyl)pyridine- $\kappa$ N, $N'$ ) dicadmium(II), C<sub>36</sub>H<sub>58</sub>Cd<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>8</sub>



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## Abstract

C<sub>36</sub>H<sub>58</sub>Cd<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>8</sub>, monoclinic,  $P2_1/c$  (no. 14),  $a = 7.82927(4)$  Å,  $b = 11.64209(5)$  Å,  $c = 26.2493(1)$  Å,  $\beta = 95.6985(4)^\circ$ ,  $V = 2380.775(18)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0158$ ,  $wR_{\text{ref}}(F^2) = 0.0411$ ,  $T = 100(2)$  K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list

**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.09 × 0.07 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
$\mu$ :	10.8 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\text{max}}$ , completeness:	67.0°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	54794, 4261, 0.035
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4150
$N(\text{param})_{\text{refined}}$ :	263
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd	0.71091(2)	0.62352(2)	0.37053(2)	0.01250(4)
S1	0.93273(5)	0.46304(3)	0.36641(2)	0.01989(9)
S2	0.66387(5)	0.51256(3)	0.28132(2)	0.01588(8)
S3	0.59248(5)	0.82372(3)	0.34060(2)	0.01447(8)
S4	0.83252(5)	0.78543(3)	0.43382(2)	0.01618(8)
O1	1.38063(14)	0.32142(10)	0.30949(5)	0.0246(3)
H10	1.463(2)	0.3618(17)	0.3023(9)	0.037*
O2	0.39500(17)	1.18190(11)	0.39613(5)	0.0288(3)
H20	0.387(3)	1.2296(17)	0.3722(7)	0.043*
N1	0.91388(16)	0.35621(11)	0.27654(5)	0.0129(2)
N2	0.72959(16)	0.99297(11)	0.39879(5)	0.0148(3)
N3	0.49446(16)	0.56317(11)	0.41659(5)	0.0141(3)
C1	0.84387(18)	0.43496(12)	0.30488(5)	0.0122(3)
C2	1.07853(19)	0.30102(13)	0.29495(6)	0.0146(3)
H2A	1.092294	0.229538	0.275341	0.018*
H2B	1.077394	0.280154	0.331474	0.018*
C3	1.2294(2)	0.38057(13)	0.28892(6)	0.0184(3)
H3A	1.236134	0.398740	0.252325	0.022*
H3B	1.216146	0.453264	0.307692	0.022*
C4	0.8292(2)	0.31936(14)	0.22592(6)	0.0188(3)
H4	0.720516	0.364455	0.219564	0.023*
C5	0.9371(3)	0.3474(3)	0.18334(8)	0.0648(9)
H5A	0.966824	0.429224	0.184699	0.097*
H5B	0.872450	0.330009	0.150343	0.097*
H5C	1.042384	0.301402	0.187192	0.097*
C6	0.7792(4)	0.19359(18)	0.22774(10)	0.0610(8)
H6A	0.883024	0.146345	0.233226	0.091*
H6B	0.714490	0.171961	0.195282	0.091*
H6C	0.707881	0.181253	0.255881	0.091*
C7	0.71972(19)	0.87986(12)	0.39222(6)	0.0122(3)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
C8	0.6260(2)	1.06950(13)	0.36309(6)	0.0190(3)
H8A	0.633780	1.042043	0.327697	0.023*
H8B	0.676229	1.147570	0.365770	0.023*
C9	0.4359(2)	1.07717(14)	0.37244(7)	0.0228(3)
H9A	0.364495	1.069806	0.339305	0.027*
H9B	0.407500	1.012232	0.394437	0.027*
C10	0.8360(2)	1.04509(13)	0.44299(6)	0.0181(3)
H10	0.910508	0.982526	0.459073	0.022*
C11	0.7238(3)	1.0859(2)	0.48308(7)	0.0358(5)
H11A	0.647280	1.146812	0.468641	0.054*
H11B	0.796295	1.115835	0.512705	0.054*
H11C	0.655231	1.021539	0.493863	0.054*
C12	0.9551(3)	1.1375(2)	0.42606(8)	0.0454(6)
H12A	1.013971	1.108793	0.397360	0.068*
H12B	1.040098	1.157349	0.454640	0.068*
H12C	0.888032	1.205840	0.415244	0.068*
C13	0.4663(2)	0.45336(13)	0.42853(6)	0.0147(3)
H13	0.544779	0.396618	0.419317	0.018*
C14	0.3275(2)	0.41893(13)	0.45375(6)	0.0149(3)
H14	0.312198	0.340184	0.461621	0.018*
C15	0.21064(18)	0.50104(13)	0.46745(5)	0.0121(3)
C16	0.2430(2)	0.61562(13)	0.45590(6)	0.0154(3)
H16	0.168084	0.674494	0.465227	0.019*
C17	0.3841(2)	0.64267(13)	0.43092(6)	0.0163(3)
H17	0.404434	0.721045	0.423460	0.020*
C18	0.05861(19)	0.46486(13)	0.49150(5)	0.0130(3)
H18	0.041645	0.384654	0.495370	0.016*

of the atoms including atomic coordinates and displacement parameters.

### Source of material

Cd[S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH]<sub>2</sub> [5] (0.235 g, 0.5 mmol) in acetonitrile (3 mL) and 1,2-di(4-pyridyl)ethylene (Sigma Aldrich; 0.091 g, 0.5 mmol) in acetonitrile (3 mL) were added to a wide neck 10 mL vial equipped with a magnetic stirring bar, and subject to microwave heating on an Anton Paar Monowave 450 with the following parameters: spinning rate = 1000 rpm, ramp from room temperature to 70 °C in 30 mins, holding for 2 h, followed by cooling to 60 °C and left for slow evaporation at room temperature; crystals formed after 3 weeks.

Yield: 0.171 g (61%, based on Cd). **M. pt** (Stuart melting point apparatus SMP30): 466–467 K. **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in CDCl<sub>3</sub> solution at 298 K, ppm): δ 8.70 (dd, 4H, aryl-NCH, <sup>2</sup>*J*<sub>HH</sub> = 6.20 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.00 Hz), 7.44 (dd, 4H, aryl-CCH, <sup>2</sup>*J*<sub>HH</sub> = 6.24 Hz, <sup>4</sup>*J*<sub>HH</sub> = 3.04 Hz), 7.24 (s, 2H, =CH), 8.70 (sept, 4H, NCH, *J*<sub>HH</sub> = 6.20 Hz), 4.02–3.95 (m, br, 16H, CH<sub>2</sub>), 2.44 (s, br, 4H, OH), 1.28 (d, 24H, CH<sub>3</sub>, *J*<sub>HH</sub> = 6.70 Hz). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): δ 204.9 (S<sub>2</sub>C),

150.4 (aryl-Cq), 143.7 (aryl-CNC), 130.7 (=CH), 121.4 (aryl-CCC), 60.9 (OCH<sub>2</sub>), 58.0 (NCH<sub>2</sub>), 51.0 (NCH), 20.3 (CH<sub>3</sub>).

### Experimental details

The carbon-bound H-atoms were placed in calculated positions (C–H = 0.95–1.00 Å) and were included in the refinement in the riding model approximation, with *U*<sub>iso</sub>(H) set to 1.2–1.5*U*<sub>eq</sub>(C). The O-bound H atoms were refined with O–H = 0.84 ± 0.01 Å and with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

### Comment

In common with most cadmium dithiocarbamate, Cd(S<sub>2</sub>CNRR')<sub>2</sub>, structures [6], the species with R = isopropyl and R' = CH<sub>2</sub>CH<sub>2</sub>OH is known to associate into a dimer formulated as [Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub> as a result of equal numbers of tridentate-μ<sub>2</sub>- and chelating-dithiocarbamate ligands leading to five-coordinate Cd centres [5, 7]. However, a kinetic form has also been characterised for this compound [5, 7] which is a rare example of a one-dimensional coordination polymer for cadmium dithiocarbamates [5–8]. Experiments show the polymers to convert to the dimeric form with the egress of time. It is now well established [9] that the addition of potentially bridging bi-pyridyl type molecules (NN) will disrupt the above self-association to form one-dimensional coordination polymers in the case of 1:1 adducts, i.e. {Cd(S<sub>2</sub>CNRR')<sub>2</sub>(NN)}<sub>n</sub> or zero-dimensional adducts when 2:1 species are formed, i.e. {Cd(S<sub>2</sub>CNRR')<sub>2</sub>]<sub>2</sub>(NN); NN is μ<sub>2</sub>-bridging in each case. However, when NN is added to [Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub>, unpredictable crystallisation outcomes occur, possibly owing to the intervention of hydrogen bonding. Thus, for example, with the classic example of NN, namely 4,4'-bipyridyl, a [Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub>(4,4'-bipyridyl). (4,4'-bipyridyl) species is isolated, i.e. with monodentate and non-coordinating 4,4'-bipyridyl [10]. Monodentate coordination is also found for NN in {[Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(3-pyridinealdazine)<sub>2</sub> where the dimeric core of {[Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub> is retained but, capped by two NN molecules [11]. In a structure closely related to the title compound, formulated as {[Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>[1,2-di(4-pyridyl)ethylene]<sub>3</sub>, one of the NN ligands is bidentate bridging while the others are terminal, monodentate [12]. In continuation of these studies, the crystal structure determination of the title compound, {[Cd(S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>[1,2-di(4-pyridyl)ethylene], (I), is described which was isolated from the 1:1 reaction of Cd[S<sub>2</sub>CN(iPr)CH<sub>2</sub>CH<sub>2</sub>OH]<sub>2</sub> and 1,2-di(4-pyridyl)ethylene.

The crystallographic asymmetric unit of (I) contains half a molecule as the binuclear molecule/complex is located around a centre of inversion. As shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) –*x*, 1 – *y*, 1 – *z*], the Cd atom is

chelated by two dithiocarbamate ligands with the fifth position in the five-coordinate geometry completed by a N atom [ $Cd-N3 = 2.2879(13)$  Å] of the  $\mu_2$ -bridging 1,2-di(4-pyridyl) ethylene ligand. The dithiocarbamate ligands are coordinating in a symmetric mode [ $Cd-S1, S2 = 2.5603(4), 2.6676(4)$  Å and  $Cd-S3, S4 = 2.6009(4), 2.6280(4)$  Å] with the differences in the Cd–S bond lengths being small at 0.11 and 0.02 Å, respectively. This equivalence is reflected in the very narrow range in the associated  $C1-S1, S2$  [ $1.7252(14), 1.7354(15)$  Å] and  $C7-S3, S4$  [ $1.7284(15), 1.7291(15)$  Å] bond lengths. The angles subtended at the Cd atom range from a narrow  $69.150(11)^\circ$  for the  $S3-Cd-S4$  chelate angle to a wide  $155.796(12)^\circ$  for  $S2-Cd-S4$ , i.e. subtended by the S atoms forming the weaker of the Cd–S bonds for each ligand. A measure of a five-coordination geometry is the value of  $\tau$  [13], which has values of 0.0 and 1.0 for ideal square-pyramidal and trigonal-pyramidal geometries, respectively. In (I),  $\tau = 0.10$ , being indicative of a square-pyramidal geometry. In this description, the Cd atom lies  $0.5982(2)$  Å out of the  $S1-S4$  plane [r.m.s. deviation =  $0.0610$  Å] in the direction of the  $N3$  atom.

The crystal of (I) features conventional hydroxyl- $O-H \cdots O$  (hydroxyl) hydrogen bonding [ $O2-H2o \cdots O1^{ii}$ :  $H2o \cdots O1^{ii} = 1.959(19)$  Å,  $O2 \cdots O1^{ii} = 2.7879(18)$  Å with angle at  $H2o = 170.9(18)^\circ$  for (ii)  $-1+x, 1+y, z$ ] as well as hydroxyl- $O-H \cdots S$  (thiolate) hydrogen bonds [ $O1-H1o \cdots S2^{iii}$ :  $H1o \cdots S2^{iii} = 2.455(18)$  Å,  $O1 \cdots S2^{iii} = 3.2775(12)$  Å with angle at  $H1o = 168.5(17)^\circ$  for (iii)  $1+x, 1+y, z$ ], consistent with the notion that  $O-H \cdots O$  hydrogen bonding is not all-pervasive and can be readily subjugated in hydroxyethyl-substituted dithiocarbamates [14]. In the present case, the aforementioned hydrogen bonding gives rise to a supramolecular layer in the *ab*-plane. The isopropyl substituents project to either side of the layers which stack along the *c*-axis direction. The directional interactions between layers appear to be methine- $C-H \cdots S$  (thiolate) [ $C4-H4 \cdots S3^{iv}$ :  $H4 \cdots S3^{iv} = 2.82$  Å,  $C4 \cdots S3^{iv} = 3.5786(16)$  Å, with angle at  $H4 = 133^\circ$  for (iv)  $1-x, -1/2+y, 1/2-z$ ] and methyl- $C-H \cdots \pi$  (chelate ring) [ $C5-H5c \cdots Cg(Cd, S3, S4, C7)^v$ :  $H5c \cdots Cg(Cd, S3, S4, C7)^v = 2.82$  Å with angle at  $H5c = 127^\circ$  for (v)  $2-x, -1/2+y, 1/2-z$ ] interactions, the latter increasingly being recognised as important in the supramolecular chemistry of metal dithiocarbamates [15].

Finally, the Hirshfeld surfaces and two-dimensional fingerprint plots were calculated for (I) employing Crystal Explorer 17 [16] and literature methods [17]. The most prominent feature of the fingerprint plot is the appearance of sharp spikes ascribed to the  $O-H \cdots O$  hydrogen bonding. Nevertheless, the total contribution to the overall Hirshfeld surface from  $H \cdots O/O \cdots H$  contacts is only 5.9%. Reflecting the significant role of  $S \cdots H$  contacts in the molecular packing, in both the intra- and inter-layer regions,  $H \cdots S/S \cdots H$  contacts

amount to nearly a quarter of all contacts, i.e. 22.1%. The most significant contribution to the surface is due to  $H \cdots H$  contacts, at 53.6%, with other notable contributions from  $H \cdots C/C \cdots C$  [8.5%] and  $S \cdots C/C \cdots S$  [3.5%] contacts.

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