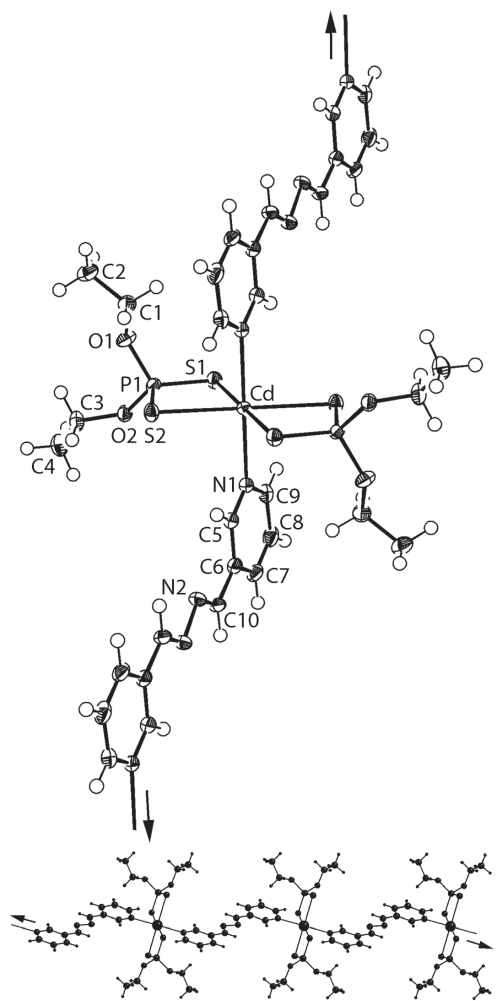


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Crystal structure of *catena*-poly[(bis(*O,O'*-diethyl dithiophosphato- κ^2 S, S')- μ_2 -1,2-bis(3-pyridylmethylene)hydrazine- κ^2 N:N')cadmium(II)], $\{C_{20}H_{30}CdN_4O_4P_2S_4\}_n$



Abstract

$C_{20}H_{30}CdN_4O_4P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.0764(3)$ Å, $b = 9.3969(3)$ Å, $c = 9.6964(3)$ Å, $\alpha = 86.516(3)^\circ$, $\beta = 63.362(3)^\circ$, $\gamma = 75.250(3)^\circ$, $V = 713.50(4)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0166$, $wR_{ref}(F^2) = 0.0462$, $T = 100(2)$ K.

CCDC no.: 1959871

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:	Yellow prism
Size:	0.22 × 0.14 × 0.11 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	10.21 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	15508, 2560, 0.021
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2560
$N(param)_{refined}$:	162
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

Source of material

The $Cd[S_2P(OEt)_2]_2$ precursor was prepared in high yield from the in situ reaction of $Cd(NO_3)_2 \cdot 4H_2O$ (Acros Organic; 15.42 g, 0.05 mol), EtOH (Merck; 12.25 mL, 0.21 mol), P_2S_5 (Sigma-Aldrich; 11.11 g, 0.05 mol) and 50% w/w NaOH solution (Merck; 8.80 mL, 0.11 mol). The 1,2-bis(3-pyridylmethylene)hydrazine ligand was prepared in high yield from the 2:1 reaction (reflux) of 3-picolylamine (Aldrich; 2.03 mL, 0.02 mol) and hydrazinium hydroxide (Merck; 0.49 mL, 0.01 mol) in ethanol solution (Merck; 5 mL). The title compound was obtained by mixing a suspension of $Cd[S_2P(OEt)_2]_2$ (0.50 g, 1.04 mmol) and 1,2-bis(3-pyridylmethylene)hydrazine (0.22 g, 1.05 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min. at 373 K. The solution was filtered and the filtrate collected in a sample vial containing acetonitrile (Merck; 1 mL). Yellow block crystals formed after one day. Yield: 0.39 g, (54.1%, based on $Cd[S_2P(OEt)_2]_2$). **M. pt** (MelTemp Melting Point Apparatus): 426–428 K. **Elem. Anal.** (Leco TruSpec Micro CHN Elemental Analyser): Calc.

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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}
Cd	0.500000	0.500000	1.000000	0.01167(6)
S1	0.62710(5)	0.21727(4)	0.89421(5)	0.01518(9)
S2	0.82782(5)	0.48870(4)	0.80199(5)	0.01587(9)
P1	0.84648(5)	0.27358(4)	0.78453(5)	0.01265(10)
O1	0.98987(15)	0.17908(13)	0.82879(14)	0.0187(2)
O2	0.92541(14)	0.21281(13)	0.61007(13)	0.0154(2)
N1	0.41685(17)	0.56317(15)	0.79881(15)	0.0140(3)
N2	0.49294(19)	0.93956(16)	0.54745(17)	0.0203(3)
C1	1.0169(2)	0.2188(2)	0.9563(2)	0.0202(4)
H1A	0.927426	0.198654	1.055805	0.024*
H1B	1.012810	0.324990	0.957880	0.024*
C2	1.1894(2)	0.1272(2)	0.9325(2)	0.0236(4)
H2A	1.216210	0.157193	1.011919	0.035*
H2B	1.275656	0.141812	0.830011	0.035*
H2C	1.188779	0.022857	0.940202	0.035*
C3	1.0940(2)	0.2290(2)	0.4983(2)	0.0199(4)
H3A	1.179689	0.184106	0.535561	0.024*
H3B	1.091571	0.334694	0.484423	0.024*
C4	1.1388(2)	0.1523(2)	0.3478(2)	0.0220(4)
H4A	1.255519	0.152879	0.273481	0.033*
H4B	1.059711	0.203682	0.306990	0.033*
H4C	1.130265	0.050186	0.365003	0.033*
C5	0.4415(2)	0.68340(18)	0.72021(19)	0.0151(3)
H5	0.500008	0.743068	0.741411	0.018*
C6	0.3846(2)	0.72530(19)	0.60771(19)	0.0174(3)
C7	0.2985(2)	0.6367(2)	0.5781(2)	0.0206(4)
H7	0.258755	0.661239	0.502101	0.025*
C8	0.2717(2)	0.5126(2)	0.6608(2)	0.0209(4)
H8	0.212395	0.451349	0.643116	0.025*
C9	0.3327(2)	0.47946(19)	0.76937(19)	0.0170(3)
H9	0.314491	0.394049	0.825640	0.020*
C10	0.4139(2)	0.8573(2)	0.5218(2)	0.0203(4)
H10A	0.373770	0.882130	0.446030	0.024*

for C₂₀H₃₀CdN₄O₄P₂S₄: C, 34.66; H, 4.36; N, 8.09%. Found: C, 34.51; H, 4.08; N, 8.31%. IR (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm⁻¹): 1192(w) ν(C–O); 1012(s) ν(P–O); 661(s) ν(P–S); 379(w) ν(Cd–N); 287(m) ν(Zn–S).

Experimental details

H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C).

Discussion

The potentially bidentate, bridging ligands, *n*-pyridylaldazines (*n*-PyAld), i.e. *n*-NC₅H₄C(H)=N–N=C(H)C₅H₄N-*n*, for *n* = 3 and 4, form one-dimensional coordination polymers in their 1:1 adducts with zinc(II) and cadmium(II) dithiophosphates [–S₂P(OR)₂] [5]. However, very different coordination geometries and topologies of the chains are found in these structures. Thus, for {Zn[S₂P(OR)₂]₂(*n*-PyAld)}₂, a distorted tetrahedral N₂S₂ coordination geometry and a twisted chain is found when *n* = 3

and R = Et [6]. By contrast, when *n* = 3 and R = isopropyl (iPr), a linear chain with a step-ladder topology and an octahedral *trans*-N₂S₄ donor set is found [7]. In the case when *n* = 4, and R = Et [8] and cyclohexyl (Cy) [9], zigzag coordination polymers are found but with tetrahedral N₂S₂ and octahedral *cis*-N₂S₄ donor sets, respectively. A greater homogeneity in the coordination polymers formed by cadmium(II) is noted in that *trans*-N₂S₄ donor sets are found. Thus, for {Cd[S₂P(OR)₂]₂(*n*-PyAld)}₂, when *n* = 3 and R = Me [10], iPr [11, 12] and Cy [13], linear coordination polymers, with a step-ladder topology, are found. When *n* = 4, and R = Et [14] and iPr [11], linear coordination polymers are found. However, it should be noted that zero-dimensional species are sometimes isolated when polymeric species might otherwise be anticipated. An example is seen in the structure of binuclear {Zn[S₂P(O-iPr)₂]₂(4-PyAld)} [15]. More intriguing are monodentate (terminal) modes of coordination of the 4-PyAld ligand have been noted in some dithiocarbamate (–S₂CNR₂) derivatives, namely Zn[S₂CN(Me)CH₂CH₂OH]₂(4-PyAld), with a square-pyramidal geometry based on a NS₄ donor set [16] and Cd[S₂CN(*n*Pr)CH₂CH₂OH]₂(4-PyAld)₂ [*n*-propyl = *n*Pr], with a *trans*-N₂S₄ donor set [17]. In continuation of systematic studies in this area, herein, the crystal and molecular structures of {Cd[S₂P(OEt)₂]₂(3-PyAld)}_n, (I), are described.

The cadmium(II) atom in (I) lies on a centre of inversion (the symmetry related dithiophosphate ligand is generated by the symmetry operation (i) 1 – *x*, 1 – *y*, 2 – *z*) and the 3-PyAld molecule is disposed about a centre of inversion (the other half of the 3-PyAld ligand is related by (ii) 1 – *x*, 2 – *y*, 1 – *z*). A view of the coordination geometry is shown in the figure (70% probability displacement ellipsoids) which highlights the *trans*-N₂S₄ donor set. While to a first approximation, the dithiophosphate ligands are symmetrically chelating to define a plane defined by four S atoms, there is a disparity of 0.026 Å in the Cd–S1 [2.6741(4) Å] and Cd–S2 [2.7003(4) Å] bond lengths. Nevertheless, the P1–S1, S2 [1.9862(6) and 1.9963(6) Å] differ by only 0.01 Å. Significantly, more symmetric coordination modes are noted in the R = Me [10] and iPr [12] analogues but, the situation in (I) matches that seen in the R = Cy structure [13] where the difference in the Cd–S bond lengths amounts to 0.021 Å. The Cd–N bond length is 2.3830(13) Å. The lack of systematic trends in the Zn, Cd–S, N bond lengths is well-known for these systems, even if control of polymer formation and topology was achieved [18–20]. The coordination geometry in (I) is defined by the *trans*-N₂S₄ donor set and is based on an octahedron with the maximum deviation from the ideal *cis* angle manifested in the acute S1–Cd–S2 chelate angle of 77.236(12)°.

The linear chain in (I), with a step-ladder topology, is parallel to [0 1 –1]. Chains are connected into a two-dimensional array by π ··· π stacking between pyridyl rings

[inter-centroid separation for $Cg(N1,C5-C9)\cdots Cg(N1,C5-C9)^{iii} = 3.6794(10)$ Å for (iii) $1 - x, 1 - y, 1 - z$] and pyridyl-C-H \cdots O(alkoxy) [C7-H7 \cdots O2ⁱⁱⁱ: H7 \cdots O2ⁱⁱⁱ = 2.42 Å, C7 \cdots O2ⁱⁱⁱ = 3.318(2) Å with angle at H7 = 158°] interactions. Layers stack along $[-2\ 2\ 1]$ and inter-digitate with successive layers but there are no directional interactions between them.

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