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Crystal structure of *catena*-[(bis(*O,O'*-diethyl dithiophosphato-*S,S'*)- μ_2 -1,2-bis(4-pyridylmethylene)hydrazine-*N,N'*)cadmium(II)], $\{\text{C}_{20}\text{H}_{30}\text{CdN}_4\text{O}_4\text{P}_2\text{S}_4\}_n$

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.18 × 0.11 × 0.09 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	9.84 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
θ_{max} , completeness:	67°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	17287, 2640, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2640
$N(\text{param})_{\text{refined}}$:	162
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

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Abstract

$\text{C}_{20}\text{H}_{30}\text{CdN}_4\text{O}_4\text{P}_2\text{S}_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.3353(2)$ Å, $b = 9.7725(2)$ Å, $c = 10.6884(2)$ Å, $\alpha = 63.153(2)^\circ$, $\beta = 64.193(2)^\circ$, $\gamma = 62.710(2)^\circ$, $V = 740.43(3)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0171$, $wR_{\text{ref}}(F^2) = 0.0465$, $T = 100$ K.

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Parts of the coordination polymer 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.

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Source of material

The $\text{Cd}[\text{S}_2\text{P}(\text{OEt})_2]_2$ precursor was prepared in high yield from the in situ reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Acros Organics; 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(4-pyridylmethylene)hydrazine molecule was prepared in high yield from the 2:1 reaction (reflux) of 4-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 $\text{Cd}[\text{S}_2\text{P}(\text{OEt})_2]_2$ (0.50 g, 1.04 mmol) and 1,2-bis(4-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 transferred to a sample vial containing acetonitrile (Merck; 1 mL). Yellow crystals formed after one day. Yield: 0.55 g, (76.3%, based on $\text{Cd}[\text{S}_2\text{P}(\text{OEt})_2]_2$). **M. pt** (MelTemp Melting Point Apparatus): 437.2–428.2 K. **Elem. Anal.** [Leco TruSpec Micro CHN Elemental Analyser]: Calc. for $\text{C}_{20}\text{H}_{30}\text{CdN}_4\text{O}_4\text{P}_2\text{S}_4$: C, 34.66; H, 4.36; N, 8.09%. Found: C, 34.40; H, 4.37; N, 8.42%. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm⁻¹): 1149(w) $\nu(\text{C}-\text{O})$; 1012(s) $\nu(\text{P}-\text{O})$; 660(s) $\nu(\text{P}-\text{S})$; 385(w) $\nu(\text{Cd}-\text{N})$, 270(m) $\nu(\text{Cd}-\text{S})$.

Experimental details

The C-bound H atoms were geometrically placed ($\text{C}-\text{H} = 0.95\text{--}0.99$ Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Cd	0.500000	0.500000	1.000000	0.01659(6)
S1	0.43784(5)	0.73691(5)	0.75644(4)	0.01992(10)
S2	0.78190(5)	0.40747(5)	0.79299(4)	0.01703(9)
P1	0.66908(5)	0.61525(5)	0.66070(4)	0.01563(10)
O1	0.65337(14)	0.59094(15)	0.53066(13)	0.0214(3)
O2	0.79503(15)	0.71679(14)	0.58518(13)	0.0214(3)
N1	0.37474(18)	0.34397(17)	0.97217(16)	0.0200(3)
N2	0.01926(19)	0.05402(17)	1.01210(16)	0.0211(3)
C1	0.8052(2)	0.5068(2)	0.4358(2)	0.0272(4)
H1A	0.893396	0.438216	0.486862	0.033*
H1B	0.849115	0.586777	0.345291	0.033*
C2	0.7606(3)	0.4041(3)	0.3987(3)	0.0435(6)
H2A	0.859683	0.350611	0.331630	0.065*
H2B	0.670229	0.472448	0.351581	0.065*
H2C	0.722602	0.321908	0.488372	0.065*
C3	0.7498(3)	0.8799(2)	0.4819(2)	0.0328(4)
H3A	0.652187	0.954195	0.533556	0.039*
H3B	0.718928	0.877899	0.405200	0.039*
C4	0.8977(3)	0.9366(2)	0.4146(3)	0.0391(5)
H4A	0.870227	1.045995	0.344756	0.059*
H4B	0.993353	0.862601	0.363273	0.059*
H4C	0.926936	0.938490	0.491230	0.059*
C5	0.2169(3)	0.3459(3)	1.0460(2)	0.0361(5)
H5	0.150836	0.412889	1.107210	0.043*
C6	0.1434(3)	0.2556(3)	1.0385(2)	0.0330(5)
H6	0.030023	0.261564	1.093482	0.040*
C7	0.2358(2)	0.1576(2)	0.95107(19)	0.0206(3)
C8	0.3986(3)	0.1568(3)	0.8726(3)	0.0456(6)
H8	0.466819	0.091970	0.809652	0.055*
C9	0.4625(3)	0.2513(3)	0.8861(3)	0.0394(5)
H9	0.574927	0.249402	0.830795	0.047*
C10	0.1685(2)	0.0547(2)	0.9409(2)	0.0239(4)
H10	0.238062	−0.012362	0.879892	0.029*

Discussion

Previously, an interesting monodentate coordination mode was observed for the potentially bridging 4-pyridylaldazine molecule, i.e. 4-NC₅H₄C(H)=N=N=C(H)C₅H₄N-4 (hereafter, 4-PyAld), in a cadmium dithiocarbamate compound, namely Cd[S₂CN(nPr)CH₂CH₂OH]₂(4-PyAld)₂ [5]. Whereas a trans-N₂S₄ donor set for cadmium was noted in this structure, a geometry tending towards square-pyramidal based on a NS₄ donor set was seen in the related zinc(II) structure, Zn[S₂CN(Me)CH₂CH₂OH]₂(4-PyAld), i.e. with one terminally bound 4-PyAld ligand [6]. In the only other cadmium(II) 1,1-dithiolate structure with 4-PyAld, a conventional bidentate bridging mode of coordination was observed, i.e. {Cd[S₂P(O-iPr)₂]₂(4-PyAld)}_n [7]. In continuation of systematic studies in the field [8], the title compound, a one-dimensional coordination polymer, i.e. {Cd[S₂P(OEt)₂]₂(4-PyAld)}_n, (I), was investigated by X-ray crystallography.

The extended coordination geometry for the cadmium(II) atom in (I) is shown in the figure (70% probability displacement ellipsoids). The cadmium centre is located on a centre of inversion and the second dithiophosphate ligand is related by the symmetry operation (i) 1 − x, 1 − y, 2 − z. The 4-PyAld ligand is also disposed about a centre of inversion with the unlabelled atoms of the molecule related by (ii) −x, −y, 2 − z. The cadmium(II) atom is octahedrally coordinated within a trans-N₂S₄ donor set defined by two chelating dithiophosphate ligands and two 4-PyAld-nitrogen atoms. The Cd—S1 [2.6671(4) Å] and Cd—S2 [2.6822(4) Å] bond lengths differ by only 0.015 Å, consistent with a symmetric mode of coordination. Reflecting this, the P1—S1 [1.9856(6) Å] and P1—S2 [1.9934(6) Å] bond lengths differ by only 0.008 Å. The independent Cd—N1 bond length is 2.4755(13) Å. The greatest deviation from the ideal octahedral geometry is manifested in the S1—Cd—S2 chelate angle of 77.898(12)°.

From symmetry, the topology of the resultant one-dimensional coordination polymer is linear, as shown in the lower view of the figure, and resembles the literature precedent, {Cd[S₂P(O-iPr)₂]₂(4-PyAld)}_n [7]. By contrast, in the analogous zinc(II) structure to (I), {Zn[S₂P(OEt)₂]₂(4-PyAld)}_n, isolated as a di-acetonitrile solvate, a distorted tetrahedral N₂S₂ donor set is observed and the resulting coordination polymer has a zigzag topology [9].

The chains are parallel to the [1 1 0] direction. The atom-to-atom connections between chains in the crystal of (I), leading to a three-dimensional architecture, are of the type methylene-C—H...O(alkoxide) [C1—H1a...O2ⁱⁱⁱ: H1a...O2ⁱⁱⁱ = 2.53 Å, C1a...O2ⁱⁱⁱ 3.315(3) Å with angle at H1a = 136° for (iii) 2 − x, 1 − y, 1 − z] and pyridyl-C—H...S(thiolate) [C10—H10...S1^{iv}: H10...S1^{iv} = 2.79 Å, C10...S1^{iv} = 3.7293(19) Å with angle at H10 = 168° for (iv) x, −1 + y, z].

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