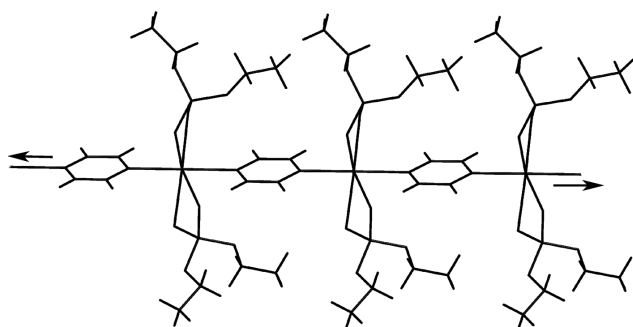
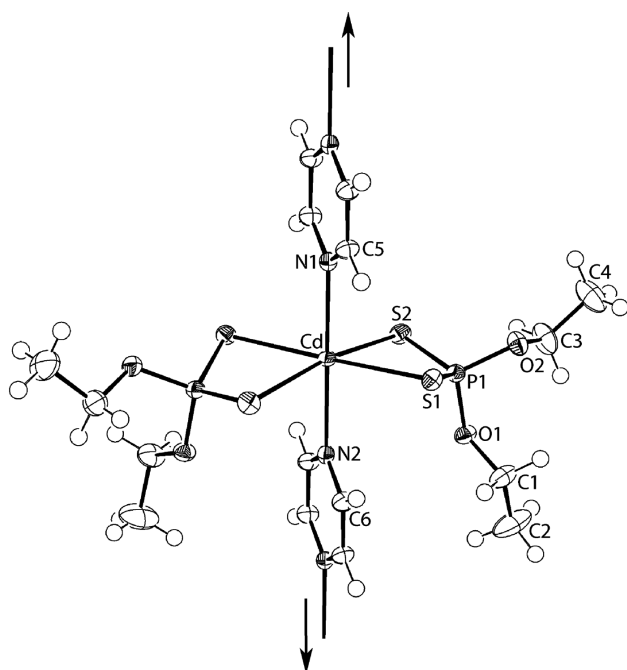


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Crystal structure of *catena*-[(μ_2 -pyrazine- $\kappa^2N:N'$)-bis(*O,O'*-di-ethylthiophosphato- κ^2S,S')cadmium(II)], $\{C_{12}H_{24}CdN_2O_4P_2S_4\}_n$



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Abstract

$C_{12}H_{24}CdN_2O_4P_2S_4$, monoclinic, $P2/n$ (no. 13), $a = 11.7844(2)$ Å, $b = 7.6063(1)$ Å, $c = 13.1965(2)$ Å, $\beta = 111.594(2)^\circ$, $V = 1099.86(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0171$, $wR_{ref}(F^2) = 0.0467$, $T = 100$ K.

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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:	0.21 × 0.11 × 0.08 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	13.1 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	12357, 1960, 0.021
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1949
$N(param)_{refined}$:	117
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The $Cd[S_2P(OEt)_2]_2$ precursor was prepared in high yield from the *in situ* reaction of $Cd(NO_3)_2 \cdot 4 H_2O$ (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 title compound was obtained by mixing a suspension of $Cd[S_2P(OEt)_2]_2$ (0.50 g, 1.04 mmol), pyrazine (Merck, 0.09 g, 1.12 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min. at 373 K. The solution was filtered, the filtrate was dissolved in acetonitrile (Merck; 1 mL) and held in a sample vial. Yellow crystals formed after one day. Yield: 0.15 g, (25.6%, based on $Cd[S_2P(OEt)_2]_2$). **M.pt** (MelTemp Melting Point Apparatus): 430.2–432.2 K. **IR** (Bruker Vertex 70 V equipped

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Cd	0.250000	0.26705(2)	0.250000	0.01170(7)
S1	0.13015(4)	0.26199(5)	0.03434(4)	0.01404(11)
S2	0.43145(4)	0.29672(6)	0.17353(4)	0.01542(11)
P1	0.29145(4)	0.34260(6)	0.03540(3)	0.01227(11)
O1	0.29205(11)	0.54937(16)	0.01490(10)	0.0155(3)
O2	0.30864(13)	0.25480(16)	-0.06730(12)	0.0171(3)
N1	0.250000	-0.0465(3)	0.250000	0.0126(4)
N2	0.250000	0.5876(3)	0.250000	0.0125(4)
C1	0.19491(18)	0.6268(3)	-0.07831(16)	0.0233(4)
H1A	0.116764	0.624213	-0.066364	0.028*
H1B	0.184606	0.559572	-0.145355	0.028*
C2	0.2302(2)	0.8126(3)	-0.0898(2)	0.0410(6)
H2A	0.164203	0.870026	-0.149096	0.062*
H2B	0.304792	0.813320	-0.106268	0.062*
H2C	0.244762	0.876071	-0.021527	0.062*
C3	0.4168(2)	0.3048(3)	-0.09081(18)	0.0272(5)
H3A	0.489242	0.309613	-0.022284	0.033*
H3B	0.404677	0.422576	-0.125074	0.033*
C4	0.4361(2)	0.1723(3)	-0.1658(2)	0.0351(5)
H4A	0.508071	0.204600	-0.182105	0.053*
H4B	0.364245	0.168743	-0.233558	0.053*
H4C	0.448756	0.056297	-0.131073	0.053*
C5	0.15206(16)	-0.1384(2)	0.18873(14)	0.0148(4)
H5	0.081034	-0.077428	0.143738	0.018*
C6	0.15177(16)	0.6792(2)	0.18933(14)	0.0150(4)
H6	0.080141	0.618175	0.145637	0.018*

with Platinum ATR): 1160(w) ν (C—O); 1009(s) ν (P—O); 665(m) ν (P—S).

Experimental details

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

Comment

A recent review of the structural chemistry of the zinc-triad 1,1-dithiolates [e.g. dithiocarbamate ($^-S_2CNR_2$), xanthates (^-S_2COR) and dithiophosphates ($^-S_2P(OR)_2$)] with bipyridyl-type ligands, revealed relatively few examples of structures featuring the simplest of all potentially bridging ligands of this class of molecule, namely pyrazine (pyr) [5]. For dithiocarbamates, two examples are known, i.e. binuclear $\{Zn[S_2CN(CH_2CH_2OH)_2]_2\}_2(\text{pyr})$, isolated in solvent-free form and as a dioxane solvate [6]. A sole example of a zinc(II) xanthate adduct is known, i.e. a linear coordination polymer $[Zn(S_2COEt)_2(\text{pyr})]_n$ [7]. Similarly, there is only one dithiophosphate example, again with zinc(II), namely $\{Zn[S_2P(O-iPr)_2]_2(\text{pyr})\}_n$, i.e. binuclear [8]. In the absence of structural data for cadmium analogues, herein the crystal and molecular structures of $\{Cd[S_2P(OEt)_2]_2(\text{pyr})\}_n$, (I), are

described in continuation of long-held interest in this area [5, 9].

The immediate coordination geometry about the cadmium atom is illustrated in the figure (70% probability displacement ellipsoids). The cadmium(II) lies on a crystallographic 2-fold axis with the second dithiophosphate ligand related by the symmetry operation (i) $1/2 - x, y, 1/2 - z$. The 2-fold axis bisects the pyrazine molecule with the N1 and N2 atoms lying on the axis (the remaining atoms for each residue shown in the figure are generated by translation, i.e. for the N1-pyrazine molecule, (ii) $x, 1 + y, z$ and for the N2-pyrazine, (iii) $x, -1 + y, z$). The cadmium(II) centre is octahedrally coordinated within a *trans*- N_2S_4 donor set defined by two chelating dithiophosphate ligands and two pyrazine-nitrogen atoms. The Cd—S1 [2.6715(5) \AA] and Cd—S2 [2.6889(4) \AA] bond lengths differ by only 0.017 \AA and this symmetric mode of coordination is reflected in the near equivalence of the P1—S1 [1.9924(6) \AA] and P1—S2 [1.9881(6)] bond lengths. There are two independent Cd—N bond lengths, i.e. Cd—N1 [2.385(2) \AA] and Cd—N2 [2.438(2) \AA], and these are experimentally distinct. A noteworthy feature of the structure is the relative disposition of the dithiophosphate ligands. Often, these are co-planar in bipyridyl-type adducts of cadmium dithiophosphates [5]. However, in the present case, these are twisted as seen in the dihedral angle between the two CdS₂ residues of 10.366(17) $^\circ$.

The lower view of the figure highlights the extended one-dimensional coordination polymer which, from symmetry, is strictly linear and aligned along the *b*-axis direction. A linear coordination polymer was also noted in $[Zn(S_2COEt)_2(\text{pyr})]_n$ [7]. The common feature of both the preceding structures is a *trans*- N_2S_4 donor set about the central metal atom. However, in an accompanying report [10], a *cis*- N_2S_4 donor set is found in the crystal of $\{Cd[S_2P(O-iPr)_2]_2(\text{pyr})\}_n$, isolated as a diacetonitrile solvate, with the result that the one-dimensional coordination polymer formed has a zig-zag topology [10].

In the crystal, the chains pack without directional interactions between them based on the criteria assumed in PLATON [11].

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