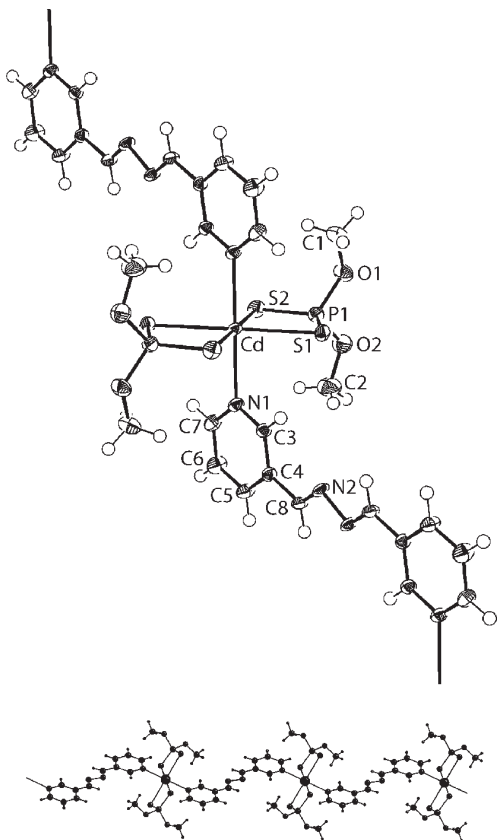


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# Crystal structure of *catena*-poly[( $\mu_2$ -1,2-bis(3-pyridylmethylene)hydrazine- $\kappa^2N:N'$ )-bis(*O,O'*-dimethyl dithiophosphato- $\kappa^2-S,S'$ )cadmium(II)], { $C_{16}H_{22}CdN_4O_4P_2S_4$ }<sub>n</sub>



## Abstract

$C_{16}H_{22}CdN_4O_4P_2S_4$ , orthorhombic, *Pbca* (no. 61),  $a = 12.66410(10)$  Å,  $b = 13.00140(10)$  Å,  $c = 15.30720(10)$  Å,  $V = 2520.35(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.0186$ ,  $wR_{ref}(F^2) = 0.0503$ ,  $T = 100(2)$  K.

CCDC no.: 1959862

The crystal structure is 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:	Yellow prism
Size:	0.11 × 0.11 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
$\mu$ :	11.51 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$ -scans
$\theta_{max}$ , completeness:	67°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	15972, 2247, 0.026
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2 \sigma(I_{obs})$ , 2144
$N(param)_{refined}$ :	144
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX and ORTEP [4]

## Source of material

The  $Cd[S_2P(OMe)_2]_2$  precursor was prepared in high yield from the *in situ* reaction of  $Cd(NO_3)_2 \cdot 4H_2O$  (Acro Organic; 15.42 g, 0.05 mol), MeOH (Merck; 8.90 mL, 0.22 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). 1,2-Bis(3-pyridylmethylene)hydrazine was prepared in high yield from the 2:1 reaction (reflux) of 3-picolyamine (Aldrich; 2.04 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  $Cd[S_2P(OMe)_2]_2$  (0.50 g, 1.17 mmol) and 1,2-bis(3-pyridylmethylene)hydrazine (0.25 g, 1.19 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min. at 373 K. The solution was filtered and the collected filtrate transferred to a sample vial containing acetonitrile (Merck; 1 mL). Yellow blocks formed after one day. Yield: 0.33 g, (44.3%, based on  $Cd[S_2P(OMe)_2]_2$ ). **M. pt** (MelTemp Melting Point Apparatus): 431.2–433.2 K. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm<sup>-1</sup>):

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**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	0.500000	0.01276(8)
S1	0.50422(3)	0.39582(3)	0.65173(3)	0.01638(11)
S2	0.33651(3)	0.58052(3)	0.58891(2)	0.01796(10)
P1	0.38285(3)	0.48585(3)	0.68372(3)	0.01570(11)
O1	0.40685(9)	0.54459(9)	0.77269(7)	0.0217(3)
O2	0.28538(10)	0.42263(9)	0.72038(8)	0.0252(3)
N1	0.40015(10)	0.36017(10)	0.44326(8)	0.0142(3)
N2	0.49313(11)	0.05353(14)	0.49356(9)	0.0162(4)
C1	0.50294(13)	0.60421(15)	0.78070(13)	0.0255(4)
H1A	0.507665	0.632915	0.839765	0.038*
H1B	0.502156	0.660303	0.737940	0.038*
H1C	0.564029	0.559750	0.769809	0.038*
C2	0.22779(17)	0.35511(16)	0.66230(13)	0.0347(5)
H2A	0.166223	0.327039	0.692903	0.052*
H2B	0.273833	0.298631	0.643690	0.052*
H2C	0.204290	0.393915	0.610977	0.052*
C3	0.42940(12)	0.26373(12)	0.46251(9)	0.0137(3)
H3	0.493338	0.253436	0.493771	0.016*
C4	0.37027(13)	0.17807(12)	0.43873(9)	0.0136(3)
C5	0.27606(13)	0.19419(12)	0.39422(11)	0.0183(3)
H5	0.232323	0.137669	0.378782	0.022*
C6	0.24663(13)	0.29370(13)	0.37259(11)	0.0220(4)
H6	0.183340	0.306358	0.341064	0.026*
C7	0.31101(13)	0.37392(12)	0.39774(10)	0.0170(3)
H7	0.291233	0.441953	0.382081	0.020*
C8	0.40368(12)	0.07275(12)	0.45912(10)	0.0146(3)
H8	0.357338	0.017321	0.446280	0.017*

1173(w)  $\nu$ (C—O); 1000(m)  $\nu$ (P—O); 650 (s)  $\nu$ (P—S); 392(m)  $\nu$ (Cd—N); 263(w)  $\nu$ (Cd—S).

### Experimental details

H atoms were geometrically placed (C—H = 0.95–0.98  $\text{\AA}$ ) and refined as riding with  $U_{iso}(H) = 1.2\text{--}1.5U_{eq}(C)$ .

### Discussion

It is well-documented that very different structures/supramolecular architectures can be observed for the zinc-triad 1,1-dithiolates [5] and their adducts with bipyridyl-type ligands [6] when only small changes in the nature of a remote group are made. This has been very recently highlighted in the structures of  $\{Cd[S_2P(OR)_2]_2(\text{pyrazine})\}_n$ . Thus, in the case of  $R = Et$ , an octahedral *trans*- $N_2S_4$  donor set is found for cadmium(II) within a linear, one-dimensional coordination polymer [7]. By contrast, a *cis*- $N_2S_4$  donor set is found in the  $R = isopropyl$  derivative, characterized as an acetonitrile solvate [8]. While the donor set still defines an octahedral geometry, the *cis*-disposition of the nitrogen donors gives rise to a one-dimensional coordination polymer with a zigzag topology [8]. Such intriguing results

vindicate systematic studies in the field. In keeping with this, herein, the crystal and molecular structures of a new coordination polymer,  $\{Cd[S_2P(OEt)_2]_2(3\text{-PyAld})\}_n$ , (I), are described; where 3-PyAld is 3-pyridylaldazine molecule, i.e. 3- $NC_5H_4C(H)=N-N=C(H)C_5H_4N-3$ .

The asymmetric unit of (I) comprises half a  $Cd[S_2P(OEt)_2]_2$  entity as the cadmium(II) centre is located on a centre of inversion as well as half a 3-PyAld molecule as this is disposed about another centre of inversion. Referring to the upper view of the figure (70% probability displacement ellipsoids), the symmetry related dithiophosphate ligand is generated by the symmetry operation (i)  $1 - x, 1 - y, 1 - z$ , and the other half of the 3-PyAld ligand is related by (ii)  $1 - x, -y, 1 - z$ . A *trans*- $N_2S_4$  donor set is evident for the cadmium(II) atom as the dithiophosphate ligands are symmetrically chelating within a plane defined by the four S atoms. The Cd—S1, S2 = 2.6892(4) and 2.6897(4)  $\text{\AA}$  bond lengths are experimentally equivalent. The equivalence of the Cd—S bonds is reflected in the experimental equivalence of the associated P1—S1, S2 bond lengths [i.e. 1.9930(6) and 1.9915(6)  $\text{\AA}$ ]. The Cd—N1 bond length is 2.3788(13)  $\text{\AA}$ . The coordination geometry is based on an octahedron with the maximum deviation traced to the relatively acute S1—Cd—S2 chelate angle of 76.958(11) $^\circ$ .

As seen in the lower view of the figure, the resultant one-dimensional coordination polymer is linear. This resembles the situation observed for the  $R = ethyl$  [9] and the  $R = isopropyl$  [10] derivatives. Thus, the four structures of the general formula  $\{Cd[S_2P(OEt)_2]_2(3\text{-PyAld})\}_n$ ,  $R = methyl$  (I), ethyl [9], isopropyl [10, 11] and cyclohexyl [12] adopt the same structural motif in the solid-state.

In the crystal, the chains are aligned along [0 1 0]. Connections between chains are of the type pyridyl-C—H $\cdots$ O(alkoxy) [C6—H6 $\cdots$ O1<sup>iii</sup>: H6 $\cdots$ O1<sup>iii</sup> = 2.48  $\text{\AA}$ , C6 $\cdots$ O1<sup>iii</sup> = 3.246(2)  $\text{\AA}$  with angle at H6 = 138 $^\circ$  for (iii)  $1/2 - x, 1 - y, -1/2 + z$ ]. These give rise to a three-dimensional architecture with rather large voids. The voids are occupied by a second three-dimensional architecture so that the structure is 3D-3D doubly interpenetrated.

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