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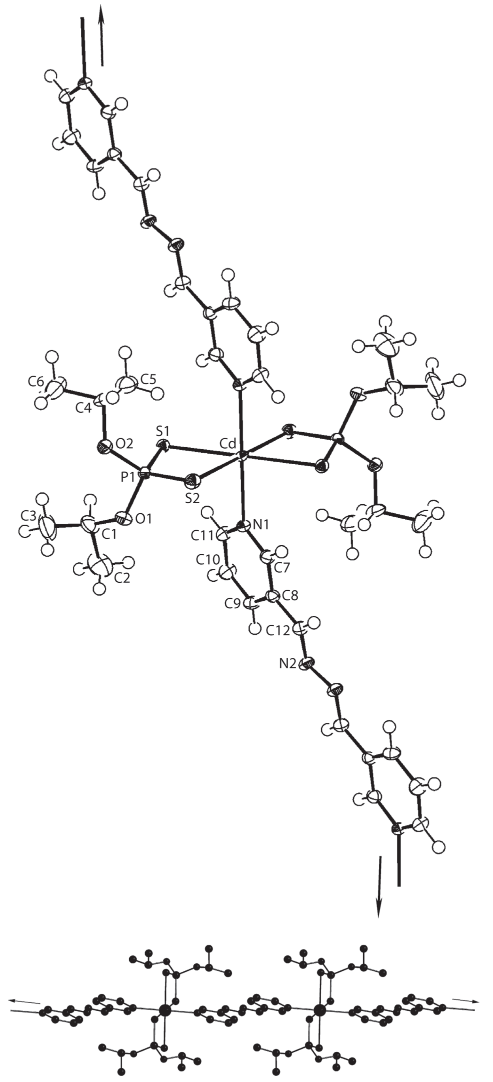
A redetermination of the crystal structure of *catena*-poly[(bis(*O*,*O*′-isopropyl dithiophosphato-κ²*S*,*S*′)-(μ₂-1,2-bis(3-pyridylmethylene) hydrazine-κ²*N*,*N*′)cadmium(II)], $\{C_{24}H_{38}CdN_4O_4P_2S_4\}_n$



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Abstract

$C_{24}H_{38}CdN_4O_4P_2S_4$, monoclinic, $P2_1/n$ (no. 14), $a = 12.2264(1)$ Å, $b = 10.8805(1)$ Å, $c = 12.9590(1)$ Å, $\beta = 108.172(1)°$, $V = 1637.95(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0183$, $wR_{ref}(F^2) = 0.0468$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	$0.13 \times 0.08 \times 0.03$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	8.94 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20310, 2925, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2812
$N(param)_{refined}$:	182
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The $Cd[S_2P(OiPr)_2]_2$ precursor was prepared in high yield from the *in situ* reaction of $Cd(NO_3)_2 \cdot 4\ H_2O$ (Acros Organic; 15.42 g, 0.05 mol), iPrOH (Merck; 16.05 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). 1,2-Bis(3-pyridylmethylene)hydrazine was prepared in high yield from the 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 $Cd[S_2P(OiPr)_2]_2$ (0.50 g, 0.93 mmol) and 1,2-bis(3-pyridylmethylene)hydrazine (0.20 g, 0.95 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 vial containing acetonitrile (Merck; 1 mL). Yellow crystals formed after one day. Yield: 0.50 g, (71.8%, based

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cd	0.500000	0.500000	0.500000	0.01180(6)
S1	0.69732(3)	0.43408(4)	0.46778(3)	0.01209(9)
S2	0.56960(3)	0.71056(4)	0.42854(3)	0.01499(10)
P1	0.69306(3)	0.60475(4)	0.40785(3)	0.01118(10)
O1	0.67671(10)	0.60406(11)	0.28177(9)	0.0159(3)
O2	0.81785(9)	0.66439(11)	0.45351(9)	0.0149(2)
N1	0.39584(11)	0.43433(14)	0.31914(10)	0.0127(3)
N2	0.05064(12)	0.46461(14)	0.01847(11)	0.0141(3)
C1	0.74818(17)	0.5275(2)	0.23550(15)	0.0238(4)
H1	0.785854	0.461264	0.288120	0.029*
C2	0.6692(2)	0.4708(2)	0.13343(18)	0.0369(5)
H2A	0.608986	0.423730	0.150917	0.055*
H2B	0.713476	0.416033	0.101442	0.055*
H2C	0.633747	0.535907	0.081476	0.055*
C3	0.8387(2)	0.6081(3)	0.2140(2)	0.0561(8)
H3A	0.801431	0.674617	0.164499	0.084*
H3B	0.886090	0.559034	0.180837	0.084*
H3C	0.887469	0.643109	0.282563	0.084*
C4	0.88713(14)	0.66523(18)	0.56840(13)	0.0194(4)
H4	0.879395	0.584297	0.602022	0.023*
C5	0.85025(17)	0.7655(2)	0.62818(15)	0.0284(5)
H5A	0.858669	0.844867	0.595719	0.043*
H5B	0.898277	0.764436	0.704478	0.043*
H5C	0.769497	0.753254	0.623740	0.043*
C6	1.01057(16)	0.6814(2)	0.56736(18)	0.0339(5)
H6A	1.031905	0.611637	0.529750	0.051*
H6B	1.062453	0.685079	0.642170	0.051*
H6C	1.016738	0.757740	0.529477	0.051*
C7	0.29587(15)	0.48664(16)	0.26350(13)	0.0137(4)
H7	0.270844	0.556636	0.293778	0.016*
C8	0.22667(13)	0.44330(16)	0.16321(12)	0.0123(3)
C9	0.26435(14)	0.34128(17)	0.11888(13)	0.0157(4)
H9	0.219390	0.309253	0.050633	0.019*
C10	0.36786(15)	0.28734(18)	0.17539(14)	0.0187(4)
H10	0.395498	0.217828	0.146720	0.022*
C11	0.43099(14)	0.33687(17)	0.27531(13)	0.0161(4)
H11	0.502267	0.299663	0.314042	0.019*
C12	0.11717(15)	0.50510(15)	0.10886(14)	0.0140(4)
H12	0.095577	0.575692	0.141063	0.017*

on $Cd[S_2P(OiPr)_2]_2$). **M. pt.** (Stuart SMP 30 Melting point apparatus): 453.5–454.9 K. **Elem. Anal.** [Leco TruSpec Micro CHN Elemental Analyser]: Calc. for $C_{24}H_{38}CdN_4O_4P_2S_4$: C, 38.47; H, 5.11; N, 7.48%. Found: C, 38.87; H, 5.47; N, 7.77%. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm^{-1}): 1178(w) ν(C—O); 968(s) ν(P—O); 657(s) ν(P—S); 384(w) ν(Cd—N); 278(m) ν(Cd—S).

Experimental details

The H atoms were geometrically placed (C—H = 0.95–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Comment

A recent review describes the diverse structural chemistry of the zinc-triad 1,1-dithiolates with bipyridyl-type molecules [5]. Early systematic studies of the zinc(II) [6, 7] and cadmium(II) [8] dithiophosphates [$^-S_2P(OR)_2$] were motivated by evaluating the control of coordination polymer formation and, when one-dimensional coordination polymers did form, the topology of the resulting chain. This is nicely illustrated in the 1:1 adducts formed between $Cd[S_2P(OR)_2]_2$ and *trans*-1,2-bis(4-pyridyl)propane (bpp). When R = iPr, a linear one-dimensional chain was characterized in the solid-state, i.e. $\{Cd[S_2P(O\text{-}iPr)_2]_2(bpp)\}_n$, but when the steric bulk of R is increased to cyclohexyl (Cy), only binuclear species could be isolated, i.e. $\{Cd[S_2P(OCy)_2]_2(bpp)\}_2$ with bpp coordinating in a bidentate, bridging mode [8]. It was in this context the title compound, $\{Cd[S_2P(O\text{-}iPr)_2]_2(3\text{-}PyAld)\}_n$ (I) was originally characterized by crystallographic methods [9]; 3-PyAld is 3-pyridylaldazine, i.e. 3-$NC_5H_4C(H)$=N—N=$C(H)C_5H_4N$-3. While the original connectivity was determined unambiguously as a one-dimensional coordination polymer with a step-ladder topology, disorder was noted in the structure. Herein, a low temperature (100 K) redetermination of (I) is described in which the disorder is no longer apparent and, with the aid of Cu Kα radiation, a better resolution data set was achieved with the result that significantly improved standard uncertainty values are evident. The new data will enable a better comparison of geometric parameters with related structures in the literature.

The asymmetric unit of (I) comprises half a $Cd[S_2P(O\text{-}iPr)_2]_2$ entity as, the cadmium atom lies on a centre of inversion, and half a 3-PyAld molecule, being disposed about a centre of inversion, as indicated in the figure (70% probability displacement ellipsoids; the unlabelled atoms of "$Cd[S_2P(O\text{-}iPr)_2]_2$" are related by the symmetry operation (i) $1 - x$, $1 - y$, $1 - z$, and those for the 3-PyAld molecule are related by (ii) $-x$, $1 - y$, $-z$). The cadmium(II) atom is octahedrally coordinated within a *trans*-N_2S_4 donor set defined by two chelating dithiophosphate ligands and two nitrogen atoms derived from symmetry related pyridyl-nitrogen atoms. The Cd—S1 [2.6715(4) Å] and Cd—S2 [2.7059(4) Å] bond lengths differ by less that 0.04 Å, a result consistent with a symmetric mode of coordination of the dithiophosphato ligand. The small disparity in the P1—S1 [2.0073(6) Å] and P1—S2 [1.9820(6) Å] bond lengths also reflects this observation. Nevertheless, the longer P1—S1 bond involves the more tighly bound S1 atom. The Cd—N1 bond length is 2.4008(13) Å. The greatest distortion from the regular octahedral geometry is manifested in the acute S1—P1—S2 chelate angle of 77.18(1)°.

The lower view of the figure highlights the resultant coordination polymer after the application of translational symmetry. The topology of the linear chain is that of a step-ladder, as noted for the $\{Zn[S_2P(O\text{-}iPr)_2]_2(3\text{-}PyAld)\}_n$ analogue [10], indeed, the structures are isostructural. A step-ladder topology was also found in $\{Cd[S_2P(OCy)_2]_2(3\text{-}PyAld)\}_n$, isolated as a chloroform solvate [11], but in the recently determined $\{Zn[S_2P(OEt)_2]_2(3\text{-}PyAld)\}_n$ derivative, a twisted topology was noted [12].

In the crystal, the chain is aligned along the [1 0 1] direction. The only directional links between chains are of the type pyridyl-C—H···S [C9—H9···S1^{iii}: H9···S1^{iii} = 2.84 Å, C9···S1^{iii} = 3.5329(18) Å with angle at H9 = 131° for (iii) $-1/2+x$, $1/2-y$, $-1/2+z$] and as these occur laterally, the result is a supramolecular layer. Layers stack without directional interactions between them.

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