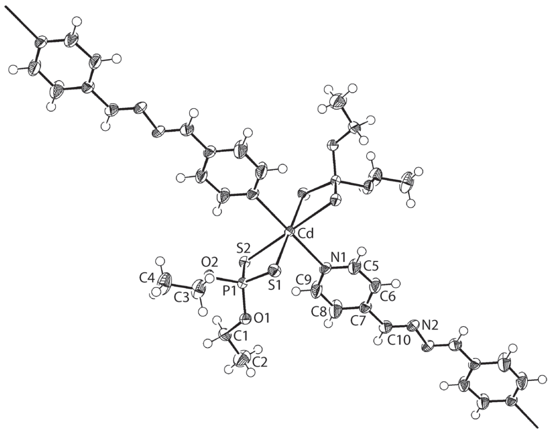
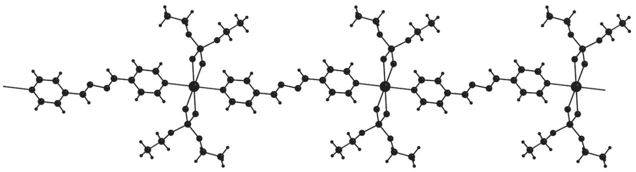
Yee Seng Tan and Edward R.T. Tiekink*

Crystal structure of *catena*-[(bis(*O,O′*-diethyl dithiophosphato-*S,S′*)-μ$_2$-1,2-bis(4-pyridylmethylene)hydrazine-*N,N′*)cadmium(II)], $\{C_{20}H_{30}CdN_4O_4P_2S_4\}_n$





https://doi.org/10.1515/ncrs-2019-0653
Received September 5, 2019; accepted October 21, 2019; available online November 9, 2019

Abstract

$C_{20}H_{30}CdN_4O_4P_2S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.3353(2)$ Å, $b = 9.7725(2)$ Å, $c = 10.6884(2)$ Å, $\alpha = 63.153(2)°$, $\beta = 64.193(2)°$, $\gamma = 62.710(2)°$, $V = 740.43(3)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0171$, $wR_{ref}(F^2) = 0.0465$, $T = 100$ K.

CCDC no.: 1960465

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.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	$0.18 \times 0.11 \times 0.09$ mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	9.84 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω-scans
θ_{max}, completeness:	67°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17287, 2640, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2640
$N(param)_{refined}$:	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 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 $Cd[S_2P(OEt)_2]_2$ (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 $Cd[S_2P(OEt)_2]_2$). **M. pt** (MelTemp Melting Point Apparatus): 437.2–428.2 K. **Elem. Anal.** [Leco TruSpec Micro CHN Elemental Analyser]: Calc. for $C_{20}H_{30}CdN_4O_4P_2S_4$: 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) ν(C—O); 1012(s) ν(P—O); 660(s) ν(P—S); 385(w) ν(Cd—N), 270(m) ν(Cd—S).

Experimental details

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

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. https://orcid.org/0000-0003-1401-1520
Yee Seng Tan: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

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	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-$NC_5H_4C(H){=}N{-}N{=}C(H)C_5H_4N$-4 (hereafter, 4-PyAld), in a cadmium dithiocarbamate compound, namely $Cd[S_2CN(nPr)CH_2CH_2OH]_2$(4-PyAld)$_2$ [5]. Whereas a trans-N_2S_4 donor set for cadmium was noted in this structure, a geometry tending towards square-pyramidal based on a NS_4 donor set was seen in the related zinc(II) structure, $Zn[S_2CN(Me)CH_2CH_2OH]_2$(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. $\{Cd[S_2P(O\text{-}iPr)_2]_2(4\text{-}PyAld)\}_n$ [7]. In continuation of systematic studies in the field [8], the title compound, a one-dimensional coordination polymer, i.e. $\{Cd[S_2P(OEt)_2]_2(4\text{-}PyAld)\}_n$, (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-N_2S_4 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, $\{Cd[S_2P(O\text{-}iPr)_2]_2(4\text{-}PyAld)\}_n$ [7]. By constrast, in the analogous zinc(II) structure to (I), $\{Zn[S_2P(OEt)_2]_2(4\text{-}PyAld)\}_n$, isolated as a di-acetonitrile solvate, a distorted tetrahedal N_2S_2 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$\cdots$O(alkoxide) [C1—H1a$\cdots$O2^{iii}: H1a$\cdots$O2^{iii} = 2.53 Å, C1a$\cdots$O2^{iii} 3.315(3) Å with angle at H1a = 136° for (iii) 2 − x, 1 − y, 1 − z] and pyridyl-C—H$\cdots$S(thiolate) [C10—H10$\cdots$S1^{iv}: H10$\cdots$S1^{iv} = 2.79 Å, C10$\cdots$S1^{iv} = 3.7293(19) Å with angle at H10 = 168° for (iv) x, −1 + y, z].

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCTR-RCCM-001-2019.

References

1. Rigaku Oxford Diffraction: CrysAlis PRO. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Cryst. **45** (2012) 849–854.
5. Broker, G. A.; Tiekink, E. R. T.: Bis[*N*-(2-hydroxyethyl)-*N*-propyldithiocarbamato-κ^2*S,S′*] bis-(4-{[(pyridin-4-ylmethylidene)hydrazinylidene]methyl}pyridine-κ^1*N*)cadmium. Acta Crystallogr. **E67** (2011) m320–m321.

6. Broker, G. A.; Jotani, M. M.; Tiekink, E. R. T.: Bis[*N*-2-hydroxyethyl, *N*-methyldithiocarbamato-κ²*S,S′*)-4-{[(pyridin-4-ylmethylidene)hydrazinylidene}methyl]pyridine-κ*N*¹)zinc(II): crystal structure and Hirshfeld surface analysis. Acta Crystallogr. **E73** (2017) 1458–1464.
7. Lai, C. S.; Tiekink, E. R. T.: Polymeric topologies in cadmium(II) dithiophosphate adducts of the isomeric *n*-pyridinealdazines, $n = 2$, 3 and 4. Z. Kristallogr. C. M. **221** (2006) 288–293.
8. Tiekink, E. R. T.: Perplexing coordination behaviour of potentially bridging bipyridyl-type ligands in the coordination chemistry of zinc and cadmium 1,1-dithiolate compounds. Crystals **8** (2018) Article no. 18.
9. Tan, Y. S.; Tiekink, E. R. T.: Crystal structure of *catena*-{poly[bis(*O*,*O′*-diethyldithiophosphato-*S*)-(μ₂-1,2-bis(4-pyridylmethylene)hydrazine-*N,N′*)-zinc(II)] di-acetonitrile solvate}, $\{C_{20}H_{30}N_4O_4P_2S_4Zn.2C_2H_3N\}_n$. Z. Kristallogr. NCS **234** (2019) 895–897.