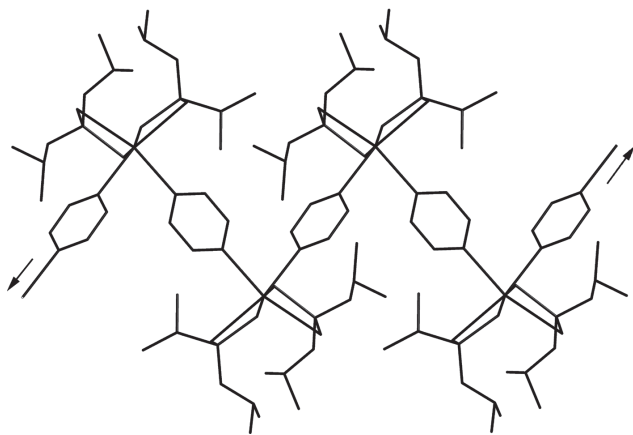
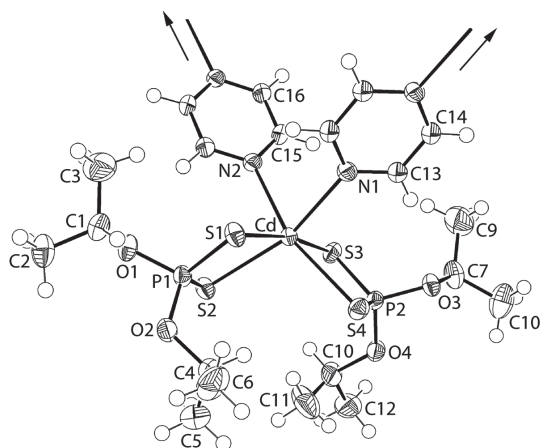


Yee Seng Tan and Edward R.T. Tiekink*

Crystal structure of *catena-poly*[(μ_2 -pyrazine-*N,N'*)-bis(*O,O'*-diisopropylidithiophosphato-*S,S'*)cadmium(II) acetonitrile di-solvate], $[\text{C}_{16}\text{H}_{32}\text{CdN}_2\text{O}_4\text{P}_2\text{S}_4 \cdot 2(\text{C}_2\text{H}_3\text{N})]_n$



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*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

Abstract

$\text{C}_{20}\text{H}_{38}\text{CdN}_4\text{O}_4\text{P}_2\text{S}_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.6352(2)$ Å, $b = 11.3986(2)$ Å, $c = 14.8017(3)$ Å, $\alpha = 85.713(2)^\circ$, $\beta = 89.877(2)^\circ$, $\gamma = 86.048(2)^\circ$, $V = 1617.23(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0285$, $wR_{\text{ref}}(F^2) = 0.0829$, $T = 100$ K.

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A part of the coordination polymer 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:	$0.20 \times 0.16 \times 0.11$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	9.01 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	35021, 5774, 0.026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5699
$N(\text{param})_{\text{refined}}$:	326
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The $\text{Cd}[\text{S}_2\text{P}(\text{OiPr})_2]_2$ 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 Organic; 15.42 g, 0.05 mol), *i*PrOH (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). The anticipated title compound was obtained by mixing a suspension of $\text{Cd}[\text{S}_2\text{P}(\text{OiPr})_2]_2$ (0.50 g, 0.93 mmol) and pyrazine (Merck, 0.08 g, 1.00 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min. at 373 K. The solution was filtered and the filtrate collected in a sample vial containing acetonitrile (Merck; 1 mL). Yellow crystals formed after three days. An isolated crystal was harvested and examined directly by X-ray crystallography without further characterization.

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 $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. Owing to poor agreement, three reflections,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cd	0.24881(2)	0.01263(2)	0.30020(2)	0.01594(8)
S1	0.20107(8)	0.24528(7)	0.28202(6)	0.02164(18)
S2	0.44987(8)	0.08041(7)	0.18577(5)	0.02047(17)
S3	0.30923(8)	−0.21808(7)	0.29062(6)	0.02071(17)
S4	0.04659(8)	−0.04897(7)	0.19308(6)	0.02090(17)
P1	0.13777(8)	−0.21045(7)	0.21454(5)	0.01741(17)
P2	0.36493(8)	0.24181(7)	0.19914(6)	0.01782(17)
O1	0.4831(2)	0.3179(2)	0.23202(17)	0.0221(5)
O2	0.3252(2)	0.3087(2)	0.10350(16)	0.0237(5)
O3	0.0227(2)	−0.2885(2)	0.25895(16)	0.0209(5)
O4	0.1688(2)	−0.2733(2)	0.12354(16)	0.0232(5)
N1	0.0902(3)	0.0030(2)	0.42669(18)	0.0184(6)
N2	0.4108(3)	0.0061(2)	0.42553(18)	0.0180(6)
N3	0.6923(5)	0.7159(4)	0.4335(3)	0.0584(11)
N4	0.8120(5)	0.2285(5)	0.3963(3)	0.0743(17)
C1	0.4530(4)	0.4409(3)	0.2569(3)	0.0233(7)
H1	0.3547	0.4674	0.2402	0.028*
C2	0.5500(4)	0.5153(3)	0.2020(3)	0.0322(9)
H2A	0.6464	0.4865	0.2155	0.048*
H2B	0.5354	0.5974	0.2172	0.048*
H2C	0.5313	0.5105	0.1373	0.048*
C3	0.4715(5)	0.4427(4)	0.3571(3)	0.0420(10)
H3A	0.4036	0.3940	0.3884	0.063*
H3B	0.4571	0.5239	0.3744	0.063*
H3C	0.5658	0.4113	0.3741	0.063*
C4	0.2183(4)	0.2609(3)	0.0481(2)	0.0277(8)
H4	0.1800	0.1916	0.0825	0.033*
C5	0.2872(5)	0.2217(4)	−0.0371(3)	0.0447(11)
H5A	0.3220	0.2900	−0.0719	0.067*
H5B	0.2194	0.1856	−0.0737	0.067*
H5C	0.3649	0.1639	−0.0211	0.067*
C6	0.1039(5)	0.3572(4)	0.0312(3)	0.0450(11)
H6A	0.0647	0.3791	0.0892	0.068*
H6B	0.0307	0.3289	−0.0058	0.068*
H6C	0.1419	0.4262	−0.0008	0.068*
C7	0.0543(4)	−0.4154(3)	0.2875(3)	0.0272(8)
H7	0.1431	−0.4443	0.2590	0.033*
C8	−0.0643(5)	−0.4782(4)	0.2530(3)	0.0418(11)
H8A	−0.1504	−0.4523	0.2832	0.063*
H8B	−0.0458	−0.5634	0.2657	0.063*
H8C	−0.0741	−0.4598	0.1875	0.063*
C9	0.0687(5)	−0.4289(4)	0.3893(3)	0.0451(11)
H9A	0.1419	−0.3802	0.4081	0.068*
H9B	0.0934	−0.5117	0.4088	0.068*
H9C	−0.0197	−0.4034	0.4170	0.068*
C10	0.2906(4)	−0.2496(4)	0.0664(3)	0.0353(10)
H10	0.3737	−0.2450	0.1060	0.042*
C11	0.2644(6)	−0.1347(4)	0.0106(3)	0.0527(13)
H11A	0.1777	−0.1359	−0.0237	0.079*
H11B	0.3418	−0.1234	−0.0315	0.079*
H11C	0.2567	−0.0699	0.0506	0.079*
C12	0.3134(4)	−0.3540(4)	0.0101(3)	0.0359(9)
H12A	0.3236	−0.4266	0.0501	0.054*
H12B	0.3979	−0.3461	−0.0261	0.054*
H12C	0.2335	−0.3574	−0.0302	0.054*
C13	0.0030(3)	−0.0832(3)	0.4409(2)	0.0204(7)
H13	0.0028	−0.1437	0.4001	0.025*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C14	0.0868(3)	0.0856(3)	0.4857(2)	0.0208(7)
H14	0.1475	0.1478	0.4774	0.025*
C15	0.4142(3)	−0.0842(3)	0.4887(2)	0.0205(7)
H15	0.3540	−0.1458	0.4826	0.025*
C16	0.4973(3)	0.0906(3)	0.4372(2)	0.0207(7)
H16	0.4981	0.1563	0.3939	0.025*
C17	0.6917(4)	0.7703(4)	0.3664(3)	0.0351(9)
C18	0.6907(4)	0.8379(4)	0.2804(3)	0.0455(11)
H18A	0.7792	0.8218	0.2494	0.068*
H18B	0.6782	0.9221	0.2900	0.068*
H18C	0.6140	0.8158	0.2432	0.068*
C19	0.8125(4)	0.2179(4)	0.3205(4)	0.0476(13)
C20	0.8130(4)	0.2061(4)	0.2239(3)	0.0412(10)
H20A	0.7463	0.2656	0.1943	0.062*
H20B	0.7867	0.1272	0.2120	0.062*
H20C	0.9064	0.2177	0.2000	0.062*

i.e. (1 − 5 2), (0 5 4) and (3 − 5 5), were omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 1.27 and 0.55 eÅ^{−3}, respectively, were located 0.91 and 0.83 Å from the S3 and Cd atoms, respectively.

Comment

In a recent report, the first example of a cadmium(II) 1,1-dithiolate compound complexed with pyrazine (pyr) was described, namely, {Cd[S₂P(OEt)₂]₂(pyr)}_n, (I) [5]. In its crystal, this is a one-dimensional coordination polymer with a linear topology, analogous to that found in the zinc xanthate analogue [Zn(S₂COEt)₂(pyr)]_n [6]. The only other related examples were found to be binuclear, i.e. {Zn[S₂CN(CH₂CH₂OH)₂]₂(pyr)}, isolated in solvent-free form and as a dioxane solvate [7], and {Zn[S₂P(O-*i*Pr)₂]₂(pyr)} [8]. In continuation of systematic studies in this area [7–10], herein, the crystal and molecular structures of {Cd[S₂P(O-*i*Pr)₂]₂(pyr)}_n, (II), i.e. the isopropyl analogue of (I), isolated as a di-acetonitrile solvate, are described.

The immediate coordination environment for the cadmium atom in (II) is shown in the figure (70% probability displacement ellipsoids; solvent molecules are omitted). The cadmium atom and dithiophosphate ligands lie in general positions whereas each of the independent pyr molecules is disposed about a centre of inversion (referring to the figure, the complete N1-pyr molecule is completed by the application of symmetry operation (i) −*x*, −*y*, 1 − *z* while (ii) 1 − *x*, −*y*, 1 − *z* is required to generate the full N2-pyr molecule). The cadmium atom is octahedrally coordinated within a cis-N₂S₄ donor set defined by two chelating dithiophosphate ligands and two pyr-nitrogen atoms. The dithiophosphate ligands are chelating in a symmetric mode [Cd–S1,

$S2 = 2.6537(8)$ and $2.6861(8)$ Å; $Cd-S3$, $S4 = 2.6681(8)$ and $2.6780(8)$ Å]. The differences between $Cd-S(\text{long})$ and $Cd-S(\text{short}) = \Delta(Cd-S)$ are quite small, i.e. values of 0.03 and 0.01 Å are noted for the $S1$ - and $S3$ -dithiophosphate ligands, respectively. The difference in $\Delta(Cd-S)$ is also reflected in the $P-S$ bond lengths. Thus, $\Delta(P-S)$ is greater, i.e. 0.013 Å for the $S1$ -dithiophosphate ($P1-S1$, $S2 = 1.9974(12)$ and $1.9849(12)$ Å] than 0.007 for the $S3$ -dithiophosphate ligand [$P2-S3$, $S4 = 1.9946(11)$ and $1.9879(12)$ Å]. The $Cd-N$ bond lengths are experimentally equivalent [$Cd-N1$, $N2 = 2.416(3)$ and $2.420(3)$ Å]. In the N_2S_4 octahedron, the more tightly bound $S1$ and $S3$ atoms occupy mutually *trans*-positions [$170.78(3)^\circ$] and the pyrazine-nitrogen atoms are each *trans* to a less-tightly bound $S2$ or $S4$ atom [$N1-Cd-S2 = 162.22(7)^\circ$ and $N2-Cd-S4 = 160.15(7)^\circ$]. The maximum distortion in terms of *cis*-angles is seen in $S2-Cd-S4$ angle of $104.75(3)^\circ$.

As shown in the lower view of the figure, the resultant one-dimensional coordination polymer in the crystal of (II) is a zigzag chain. This contrasts the linear chain noted in the crystal of (I) [5]. An obvious difference between the molecular structures of (II) and (I) relates to the relative positions of the nitrogen atoms within the N_2S_4 donor set, i.e. *cis*- and *trans*-, respectively. As to why one disposition occurs preferentially in (I) and (II) is not yet clear.

In the packing, each of the acetonitrile molecules is loosely associated with the one-dimensional chain, i.e. *via* pyrazinyl- $C-H \cdots N(\text{acetonitrile})$ [$C15-H15 \cdots N4^{ii}$: $H15 \cdots N4^{ii} = 2.57$ Å, $C15 \cdots N4^{ii} = 3.227(6)$ Å with angle at $H15 = 127^\circ$] and methyl- $C-H \cdots O(\text{alkoxy})$ interactions [$C18-H18a \cdots O3^{iii}$: $H18a \cdots O3^{iii} = 2.58$ Å, $C18 \cdots O3^{iii} = 3.441(4)$ Å with angle at $H18a = 146^\circ$ for (iii) $1 + x, 1 + y, z$]. The resultant aggregates pack without directional interactions between them.

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