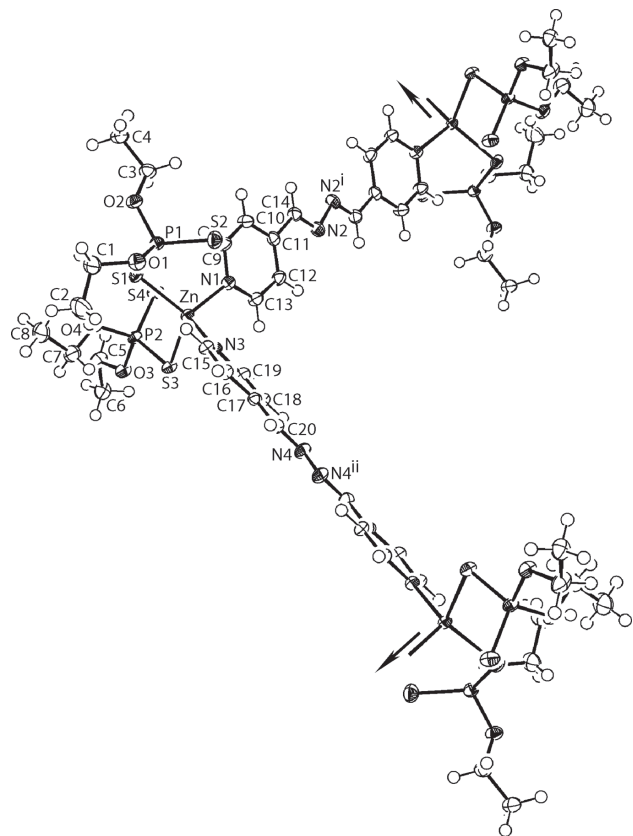


Yee Seng Tan and Edward R.T. Tiekink\*

# Crystal structure of *catena*-{poly[bis(*O,O'*-diethyldithiophosphato-*S*)-(μ<sub>2</sub>-1,2-bis(4-pyridylmethylene)hydrazine-*N,N'*)-zinc(II)] di-acetonitrile solvate}, {C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>Zn · 2 C<sub>2</sub>H<sub>3</sub>N}<sub>n</sub>



**Table 1:** Data collection and handling.

Crystal:	Yellow prism
Size:	0.21 × 0.11 × 0.11 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	4.59 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ <sub>max</sub> , completeness:	67.1°, >99%
<i>N</i> ( <i>hkl</i> ) <sub>measured</sub> , <i>N</i> ( <i>hkl</i> ) <sub>unique</sub> , <i>R</i> <sub>int</sub> :	36948, 5995, 0.024
Criterion for <i>I</i> <sub>obs</sub> , <i>N</i> ( <i>hkl</i> ) <sub>gt</sub> :	<i>I</i> <sub>obs</sub> > 2 σ( <i>I</i> <sub>obs</sub> ), 5730
<i>N</i> ( <i>param</i> ) <sub>refined</sub> :	376
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

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.

## Source of material

The Zn[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub> precursor was prepared in high yield from the *in situ* reaction of Zn(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (Alfa Aesar; 14.87 g, 0.05 mol), EtOH (Merck; 12.25 mL, 0.21 mol), P<sub>2</sub>S<sub>5</sub> (Sigma-Aldrich; 11.11 g, 0.05 mol) and 50° w/w NaOH solution (Merck; 8.80 mL, 0.11 mol). The ligand, 1,2-bis(4-pyridylmethylene)hydrazine, was prepared in high yield from the 2:1 reflux reaction of 4-picolyamine (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 the suspension of Zn[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub> (0.50 g, 1.15 mmol) and 1,2-bis(4-pyridylmethylene)hydrazine (0.25 g, 1.20 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min at 373 K. The solution was filtered and the filtrate was collected in a sample vial containing acetonitrile (Merck; 1 mL). Yellow blocks formed after one day. Yield: 0.55 g, (66%, based on Zn[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub>). M. pt. (Biobase Automatic Melting Apparatus MP45): 387.15–388.95 K. IR (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm<sup>-1</sup>, cm<sup>-1</sup>): 1015(s) ν(C–O), 932(s) ν(P–O), 661(s) ν(P–S)<sub>asym</sub>, 522(m) ν(P–S)<sub>sym</sub>. <sup>1</sup>H NMR (Bruker Ascend 400 MHz, d<sub>6</sub>-DMSO): δ [p.p.m.] 8.75 (dd, 4H, 2-aryl-H, <sup>3</sup>J<sub>HH</sub> = 6.04 Hz, <sup>4</sup>J<sub>HH</sub> = 2.92 Hz), 8.70 (s, 2H, N=CH), 7.83 (dd, 4H, 3-aryl-H, <sup>3</sup>J<sub>HH</sub> = 6.08 Hz, <sup>4</sup>J<sub>HH</sub> = 2.92 Hz), 3.82 (dq, 8H, OCH<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 9.08 Hz, <sup>3</sup>J<sub>HH</sub> = 7.10 Hz), 2.08

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## Abstract

C<sub>24</sub>H<sub>36</sub>N<sub>6</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>Zn, triclinic, *P* $\bar{1}$  (no. 2), *a* = 11.2847(2) Å, *b* = 12.6967(3) Å, *c* = 13.6595(3) Å, α = 64.738(2)°, β = 72.181(2)°, γ = 76.681(2)°, *V* = 1673.68(7) Å<sup>3</sup>, *Z* = 2, *R*<sub>gt</sub>(*F*) = 0.0225, *wR*<sub>ref</sub>(*F*<sup>2</sup>) = 0.0582, *T* = 100(2) K.

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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

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<sup>2</sup>).

Atom	x	y	z	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Zn	0.36954(2)	0.36824(2)	0.39290(2)	0.01202(6)
S1	0.23479(4)	0.25914(3)	0.39044(3)	0.01609(9)
S2	0.44385(4)	0.31226(4)	0.14029(3)	0.02028(9)
S3	0.30974(4)	0.42341(3)	0.54632(3)	0.01496(9)
S4	0.38117(4)	0.13012(3)	0.67850(3)	0.01831(9)
P1	0.27842(4)	0.27156(3)	0.23001(3)	0.01397(9)
P2	0.26007(4)	0.26812(3)	0.66833(3)	0.01314(9)
O1	0.17459(11)	0.36124(10)	0.17050(10)	0.0194(2)
O2	0.24593(10)	0.15270(9)	0.23711(9)	0.0173(2)
O3	0.22195(11)	0.30000(9)	0.77577(9)	0.0170(2)
O4	0.13372(10)	0.24194(9)	0.65770(9)	0.0171(2)
N1	0.54321(12)	0.27137(11)	0.39660(11)	0.0141(3)
N2	0.95302(13)	0.04823(12)	0.48961(12)	0.0184(3)
N3	0.38850(12)	0.53304(11)	0.27162(11)	0.0134(3)
N4	0.49900(13)	0.94340(11)	0.04248(11)	0.0170(3)
N5	0.13990(18)	0.66076(17)	0.96912(18)	0.0445(5)
N6	1.11947(17)	−0.07987(16)	0.07853(17)	0.0408(4)
C1	0.04195(16)	0.34375(16)	0.21888(16)	0.0241(4)
H1A	0.032927	0.273662	0.289388	0.029*
H1B	0.007302	0.331212	0.166792	0.029*
C2	−0.0273(2)	0.44934(18)	0.2404(2)	0.0418(5)
H2A	−0.117089	0.441069	0.267596	0.063*
H2B	−0.013376	0.519058	0.171264	0.063*
H2C	0.002783	0.457531	0.296666	0.063*
C3	0.33081(16)	0.04584(14)	0.26961(14)	0.0189(3)
H3A	0.344472	0.027818	0.343627	0.023*
H3B	0.412775	0.054799	0.214865	0.023*
C4	0.27153(17)	−0.05114(15)	0.27361(15)	0.0235(4)
H4A	0.326712	−0.124904	0.295402	0.035*
H4B	0.258642	−0.032382	0.199909	0.035*
H4C	0.190628	−0.059253	0.328134	0.035*
C5	0.17875(19)	0.20868(16)	0.88552(14)	0.0248(4)
H5A	0.229800	0.132644	0.890510	0.030*
H5B	0.090138	0.199753	0.896697	0.030*
C6	0.19155(17)	0.24412(16)	0.97293(14)	0.0228(4)
H6A	0.162991	0.184123	1.046802	0.034*
H6B	0.140450	0.319232	0.967611	0.034*
H6C	0.279576	0.252198	0.961565	0.034*
C7	0.02414(17)	0.32960(16)	0.64874(17)	0.0266(4)
H7A	0.048823	0.406397	0.591597	0.032*
H7B	−0.013492	0.338386	0.720901	0.032*
C8	−0.06881(17)	0.29051(18)	0.61691(17)	0.0293(4)
H8A	−0.140728	0.351011	0.605847	0.044*
H8B	−0.097240	0.217280	0.676360	0.044*
H8C	−0.029327	0.277624	0.547664	0.044*
C9	0.56162(16)	0.16826(14)	0.38555(14)	0.0176(3)
H9	0.498765	0.148442	0.365428	0.021*
C10	0.66789(16)	0.08988(14)	0.40218(14)	0.0181(3)
H10	0.677403	0.017762	0.393576	0.022*
C11	0.76067(15)	0.11732(14)	0.43154(13)	0.0149(3)
C12	0.74283(15)	0.22512(14)	0.44183(14)	0.0171(3)
H12	0.805142	0.247775	0.460179	0.021*
C13	0.63360(15)	0.29795(14)	0.42496(14)	0.0166(3)
H13	0.621354	0.370306	0.433719	0.020*
C14	0.87041(15)	0.03032(14)	0.45404(13)	0.0167(3)

**Table 2** (continued)

Atom	x	y	z	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
H14	0.879863	−0.039831	0.441983	0.020*
C15	0.32950(15)	0.58031(13)	0.18764(13)	0.0150(3)
H15	0.278337	0.534234	0.182018	0.018*
C16	0.34066(15)	0.69352(14)	0.10925(13)	0.0156(3)
H16	0.297096	0.724345	0.051494	0.019*
C17	0.41625(15)	0.76200(13)	0.11561(13)	0.0139(3)
C18	0.47594(15)	0.71347(14)	0.20364(13)	0.0152(3)
H18	0.527312	0.757754	0.211425	0.018*
C19	0.45930(15)	0.60071(14)	0.27886(13)	0.0151(3)
H19	0.499589	0.568848	0.338864	0.018*
C20	0.43083(15)	0.88201(14)	0.03285(13)	0.0155(3)
H20	0.390281	0.913673	−0.026980	0.019*
C21	0.21585(19)	0.59990(17)	0.93470(17)	0.0291(4)
C22	0.31250(18)	0.52305(17)	0.89175(16)	0.0300(4)
H22A	0.339860	0.456145	0.953821	0.045*
H22B	0.383920	0.566160	0.842211	0.045*
H22C	0.279202	0.494782	0.850125	0.045*
C23	1.0354(2)	−0.02649(18)	0.11918(17)	0.0332(5)
C24	0.9283(2)	0.04170(19)	0.16674(18)	0.0394(5)
H24A	0.861349	−0.008259	0.213589	0.059*
H24B	0.897335	0.108283	0.106446	0.059*
H24C	0.954489	0.070652	0.211969	0.059*

(s, 6H, CH<sub>3</sub>CN), 1.14 (t, 12H, CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 7.08 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (Bruker Ascend 400 MHz, d<sub>6</sub>-DMSO): δ [p.p.m.] 159.6 (C= N), 150.5 (2-C<sub>5</sub>H<sub>4</sub>N), 140.6 (1-C<sub>5</sub>H<sub>4</sub>N), 122.2 (3-C<sub>5</sub>H<sub>4</sub>N), 118.1 (CH<sub>3</sub>CN), 60.0 (d, OCH<sub>2</sub>, <sup>2</sup>*J*<sub>PC</sub> = 6.69 Hz), 16.1 (d, CH<sub>3</sub>, <sup>3</sup>*J*<sub>PC</sub> = 8.75 Hz), 1.2 (CH<sub>3</sub>CN). <sup>31</sup>P{<sup>1</sup>H} NMR (Bruker Ascend 400 MHz, d<sub>6</sub>-DMSO): δ [p.p.m.] 112.2.

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with *U*<sub>iso</sub>(H) = 1.2–1.5*U*<sub>eq</sub>(C). Analysis of the residual electron density revealed that one of the two acetonitrile molecules (C23, C24, N6) is disordered over two positions with occupancy factors of 0.9 and 0.1. Refinement of a heavily restrained/constrained disordered model was unsatisfactory and was not included in the final refinement.

### Comment

Four-coordinate ZnS<sub>4</sub> geometries and supramolecular association leading to dimers and chains characterize the structural chemistry of the homoleptic zinc dithiophosphates, {Zn[S<sub>2</sub>P(OR)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> [5]. The addition of potentially bridging bipyridyl donors might be expected to increase the dimensionality of the resultant species; however, four-coordination prevails, leading to binuclear species or polymeric chains only [6]. The adoption of zero- or one-dimensional species is regulated by steric effects associated

with the span of the bridge provided by the bipyridyl donor and/or the steric bulk of the remote *R* group in the dithiophosphate ligand [6–8]. A key example of this phenomenon is found when *R* = cyclohexyl in  $Zn[S_2P(OR)_2]_2$ . Thus, when the bipyridyl donor is 4,4'-bipyridine, only the binuclear structure, *i.e.*  $\{Zn[S_2P(OCy)_2]_2(4,4'\text{-bipyridine})\}_n$ , could be isolated despite the stoichiometry of the respective reagents employed in the reaction [8]. When the bridging ligand was 1,2-bis(4-pyridylmethylene)hydrazine, *i.e.* with a significantly greater distance between the bridging nitrogen atoms, a zigzag chain for  $\{Zn[S_2P(OCy)_2]_2(1,2\text{-bis(4-pyridylmethylene)hydrazine})\}_n$  ensued [9]. In continuation of systematic studies in this area [7–10], herein the crystal and molecular structures of polymeric  $\{Zn[S_2P(OEt)_2]_2(1,2\text{-bis(4-pyridylmethylene)hydrazine})\}_n$ , isolated with two molecules of acetonitrile per repeat unit, are described.

The asymmetric unit is shown in the figure (70% displacement ellipsoids; symmetry operations i:  $2 - x, -y, 1 - z$  and ii:  $1 - x, 2 - y, -z$ ) and has been extended to show the full bridging 1,2-bis(4-pyridylmethylene)hydrazine molecules (each disposed about a centre of inversion) and to highlight the zigzag topology of the chain thus formed. The zinc(II) centre is coordinated by two monodentate dithiophosphate ligands [ $Zn-S1, S3 = 2.2964(4)$  and  $2.3468(4)$  Å] and two nitrogen atoms derived from two bridging 1,2-bis(4-pyridylmethylene)hydrazine ligands [ $Zn-N1, N3 = 2.0624(13)$  and  $2.0493(13)$  Å]. As noted earlier [10], the disparity in the P–S bond lengths [ $P1-S1, S2 = 2.0372(6)$  and  $1.9385(6)$  Å;  $P2-S3, S4 = 2.0278(5)$  and  $1.9396(6)$  Å], with the short P–S bonds associated with the non-coordinating sulfur atoms, is as expected. The relatively narrow range of angles subtended at the zinc atom,  $S3-Zn-N3$  [ $97.00(4)^\circ$ ] to  $S1-Zn-N3$  [ $118.58(4)^\circ$ ] indicated minor deviations from a tetrahedral geometry for the  $N_2S_2$  donor set.

In the crystal, the chains are approximately orientated along  $[1 \bar{2} 1]$ . These are connected into a three-dimensional architecture by pyridyl-C–H...S [ $C10-H10 \cdots S4^i: H10 \cdots S4^i = 2.73$  Å,  $C10 \cdots S4^i = 3.6106(19)$  Å with angle at  $H10 = 154^\circ$  for symmetry operation i:  $1 - x, -y, 1 - z$ ], methyl-C–H...N(hydrazine) [ $C4-H4c \cdots N2^i: H4c \cdots N2^i = 2.56$  Å,  $C4 \cdots N2^i = 3.453(2)$  Å, angle =  $151^\circ$ ] and acetonitrile-C–H...S [ $C22-H22a \cdots S2^{ii}: H22a \cdots S2^{ii} = 2.84$  Å,  $C22 \cdots S2^{ii} = 3.792(2)$  Å and angle =  $164^\circ$  and  $C22-H22b \cdots S2^{iii}: H22b \cdots S2^{iii} = 2.86$  Å,  $C22 \cdots S2^{iii} = 3.641(2)$  Å and angle =  $137^\circ$  for ii:  $x, y, 1 + z$  and iii:  $1 - x, 1 - y,$

$1 - z$ ] interactions. The latter contacts prove the crucial role of the N5-acetonitrile solvent molecule in assembling the chains and lead to the formation of centrosymmetric eight-membered  $\{\cdots S \cdots HCH\}_2$  synthons. However, no specific role is noted for the second independent N6-acetonitrile molecule thus also explaining why this molecule is disordered in the crystal.

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