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Crystal structure of *catena*-poly[(μ_2 -4,4'-bipyridyl- $\kappa N, N'$)-bis(*O, O'*-dimethyldithiophosphato- κS)-zinc(II)], $\{C_{14}H_{20}N_2O_4P_2S_4Zn\}_n$

Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	0.13 × 0.12 × 0.08 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	6.54 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
$\theta_{\max}$, completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	21867, 4014, 0.023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3854
$N(\text{param})_{\text{refined}}$:	248
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The $Zn[S_2P(OMe)_2]_2$ precursor was prepared in high yield from an in-situ reaction of $Zn(NO_3)_2 \cdot 4H_2O$ (Alfa Aesar; 7.18 g, 0.05 mol), MeOH (Merck; 8.52 mL, 0.21 mol), P_2S_5 (Sigma-Aldrich; 11.71 g, 0.05 mol) and 50% w/w NaOH solution (Merck; 8.43 mL, 0.11 mol). The title compound was obtained by mixing the suspension of this precursor (0.50 g, 1.32 mmol) and 4,4'-bipyridine (Merck; 0.21 g, 1.34 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 mins at 373 K. The solution was filtered and the filtrate was collected in a sample vial containing acetonitrile (Merck; 1 mL). Colorless blocks formed after one day. Yield: 0.38 g, (54%, based on $Zn[S_2P(OMe)_2]_2$). M. pt (Biobase Automatic Melting Apparatus MP45): 418.85–420.95 K. IR (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm⁻¹, cm⁻¹): 1172 (s) $\nu(C-O)$; 1008(s) $\nu(P-O)$; 664 (s) $\nu(P-S)_{\text{asym}}$; 526 (m) $\nu(P-S)_{\text{sym}}$.

Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.95-0.98$ Å) and refined as riding with $U_{\text{iso}}(H) = 1.2-1.5U_{\text{eq}}(C)$. Owing to relatively high motion, the anisotropic displacement parameters for the C5–C9 atoms were constrained to be nearly isotropic.

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Abstract

$C_{14}H_{20}N_2O_4P_2S_4Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 8.0014(2)$ Å, $b = 10.3376(2)$ Å, $c = 14.2488(3)$ Å, $\alpha = 84.676(2)^\circ$, $\beta = 76.042(2)^\circ$, $\gamma = 79.752(2)^\circ$, $V = 1124.01(4)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0265$, $wR_{\text{ref}}(F^2) = 0.0655$, $T = 100(2)$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Zn	0.46343(3)	0.27283(2)	0.73472(2)	0.01664(8)
P1	0.38164(7)	0.59038(5)	0.79734(4)	0.01873(12)
P2	0.82244(7)	0.05797(5)	0.70454(4)	0.01998(12)
S1	0.56722(6)	0.43041(5)	0.79876(3)	0.01991(11)
S2	0.14367(7)	0.57448(5)	0.86223(5)	0.03204(14)
S3	0.65819(7)	0.14158(6)	0.61888(4)	0.02815(13)
S4	0.73109(7)	0.07731(7)	0.84130(4)	0.03506(15)
O1	0.4511(2)	0.70523(14)	0.83702(11)	0.0267(3)
O2	0.4066(2)	0.63970(15)	0.68607(10)	0.0267(3)
O3	1.0025(2)	0.11140(15)	0.66932(11)	0.0266(3)
O4	0.88684(19)	−0.09007(14)	0.67307(12)	0.0272(3)
N1	0.3015(2)	0.17093(16)	0.83413(11)	0.0173(3)
N2	0.2890(2)	0.35794(15)	0.64923(11)	0.0162(3)
C1	0.4552(4)	0.7019(3)	0.93833(18)	0.0393(6)
H1A	0.484272	0.785001	0.952654	0.059*
H1B	0.543463	0.628765	0.952308	0.059*
H1C	0.340489	0.689712	0.978553	0.059*
C2	0.2830(4)	0.7433(3)	0.65822(18)	0.0397(6)
H2A	0.292596	0.743187	0.588344	0.059*
H2B	0.306003	0.827759	0.674027	0.059*
H2C	0.165078	0.730507	0.693050	0.059*
C3	1.0985(3)	0.1029(2)	0.56954(17)	0.0334(5)
H3A	1.205302	0.140999	0.560794	0.050*
H3B	1.026177	0.151565	0.527190	0.050*
H3C	1.129009	0.010406	0.553021	0.050*
C4	0.7687(4)	−0.1842(3)	0.7003(2)	0.0497(7)
H4A	0.831707	−0.272114	0.682763	0.075*
H4B	0.673889	−0.160255	0.666194	0.075*
H4C	0.719966	−0.184385	0.770301	0.075*
C5	0.2111(3)	0.2216(2)	0.91792(16)	0.0275(5)
H5	0.228056	0.305721	0.932074	0.033*
C6	0.0946(3)	0.1569(2)	0.98448(16)	0.0278(5)
H6	0.034425	0.195988	1.043573	0.033*
C7	0.0649(2)	0.03512(19)	0.96561(14)	0.0167(4)
C8	0.1618(3)	−0.0178(2)	0.88001(17)	0.0280(5)
H8	0.148929	−0.102423	0.864601	0.034*
C9	0.2772(3)	0.0519(2)	0.81694(17)	0.0275(5)
H9	0.342525	0.013325	0.758506	0.033*
C10	0.3489(3)	0.39310(19)	0.55554(14)	0.0187(4)
H10	0.471460	0.378964	0.529788	0.022*
C11	0.2420(3)	0.4485(2)	0.49494(14)	0.0186(4)
H11	0.290662	0.471350	0.429110	0.022*
C12	0.0607(2)	0.47097(18)	0.53119(14)	0.0151(4)
C13	−0.0003(3)	0.43506(19)	0.62835(14)	0.0187(4)
H13	−0.122104	0.448758	0.656302	0.022*
C14	0.1156(3)	0.37956(19)	0.68428(14)	0.0188(4)
H14	0.070656	0.355666	0.750386	0.023*

Discussion

Through the agency of sulphur bridging, homoleptic zinc dithiophosphates, $Zn[S_2P(OR)_2]_2$, are associated in the solid-state [5]. This mode of association invariably breaks down when potentially bidentate bridging molecules, e.g.

4,4'-bipyridine, are complexed with these species [6], forming Zn–N bonds instead. Systematic evaluations of co-crystallisation outcomes when $Zn[S_2P(OR)_2]_2$ and bidentate donors have been conducted [7, 8]. These studies showed that steric influences were important in determining the ultimate structure, for example when R = bulky cyclohexyl, only binuclear species could be isolated when the bridging ligand was 4,4'-bipyridine, regardless of the stoichiometry of the reagents [8]. Even more striking was the observation of monodentate coordination when the potentially bridging ligand was 1,2-bis(2-pyridyl)ethene [7]. In the present study the crystal and molecular structures of $\{Zn[S_2P(OMe)_2]_2(4,4'-bipyridine)\}_n$ are described, where R is a relatively small methyl group.

The asymmetric unit of the title structure, extended to show the full 4,4'-bipyridine molecules (each is disposed about a centre of inversion) is shown in the upper view of the Figure (70% displacement ellipsoids; symmetry operations i: $-x, -y, 2-z$ and ii: $-x, 1-y, 1-z$). The zinc(II) centre is coordinated by two monodentate dithiophosphate ligands [Zn–S1, S3 = 2.3019(5) and 2.3273(6) Å] and two nitrogen atoms derived from two bridging 4,4'-bipyridine ligands [Zn–N1, N2 = 2.0295(17) and 2.0951(16) Å]. The non-coordinating Zn···S2, S4 separations [3.9422(6) and 3.2307(7) Å] are too long to be considered bonding interactions. The distortions from a regular tetrahedral geometry for the resultant N_2S_2 donor set are relatively small with the angles ranging from 97.79(5)°, for N2–Zn–S3, to 118.10(2)°, for S1–Zn–S3. The monodentate mode of coordination of the dithiophosphate ligands is reflected in the significant disparity in the associated P–S bond lengths. Thus, the P–S bonds formed with the non-coordinating S2 and S4 atoms are significantly shorter than the bonds involving the coordinating S1 and S3 atoms [P1–S1, S2 = 2.0185(7) and 1.9342(7) Å; P2–S3, S4 = 2.0341(7) and 1.9248(7) Å].

As seen in the lower view of the Figure, the resulting one-dimensional coordination polymer has a zig-zag topology and is aligned along [0 1 2]. Besides the binuclear species mentioned above, there are two literature precedents for comparison. Thus, for each of $\{Zn[S_2P(OR)_2]_2(4,4'-bipyridine)\}_n$, i.e. R = Et [9] and R = iPr [10], zig-zag chains are observed as for the title structure. To a first approximation the pitch of each polymer is about the same, being 16.8 Å in the structure reported here, 16.4–17.5 Å for the R = Et species (for which there are two independent zinc atoms) and 15.9–16.1 Å for the R = iPr species (three independent zinc atoms).

In the crystal, pyridyl-C–H···S [C6–H6···S2ⁱⁱⁱ = 2.82 Å, C6···S2ⁱⁱⁱ = 3.654(2) Å with angle at H6 = 148° and C13–H13···S1^{iv} = 2.83 Å, C13···S1^{iv} = 3.723(2) Å with angle at H13 = 157° for symmetry operations iii: $-x, 1-y, 2-z$ and iv: $-1+x, y, z$] and methyl-C–H··· π (pyridyl)

$[C3-H3a \cdots Cg(N2, C10-C14)^v] = 2.85 \text{ \AA}$, $C3 \cdots Cg(N2, C10-C14)^v = 3.436(2) \text{ \AA}$ with angle at H3a = 119° for symmetry operation $v: 1+x, y, z$] interactions link the chains into a three-dimensional architecture.

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