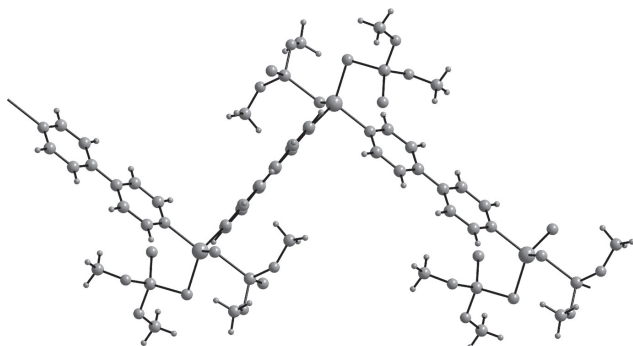
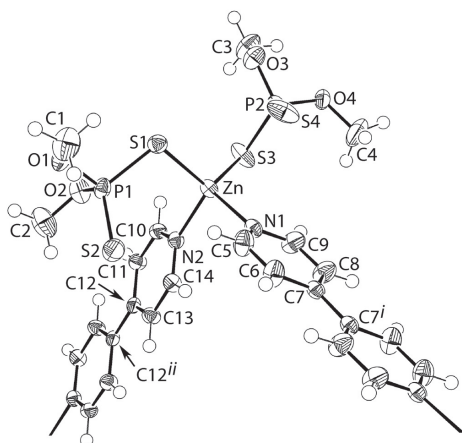


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Crystal structure of *catena*-poly[(μ_2 -4,4'-bipyridyl- $\kappa N, N'$)-bis(*O, O'*-dimethyldithiophosphato- κS)-zinc(II)], $\{C_{14}H_{20}N_2O_4P_2S_4Zn\}_n$



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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, $Z = 2$, $R_{gt}(F) = 0.0265$, $wR_{ref}(F^2) = 0.0655$, $T = 100(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	$0.13 \times 0.12 \times 0.08$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	6.54 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
θ_{\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.

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

Atom	x	y	z	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 $Zn \cdots S2, S4$ 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 $97.79(5)^\circ$, for $N2-Zn-S3$, to $118.10(2)^\circ$, 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 $[0\ 1\ \bar{2}]$. 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 $\cdots S$ [$C6-H6 \cdots S2^{iii} = 2.82$ Å, $C6 \cdots S2^{iii} = 3.654(2)$ Å with angle at $H6 = 148^\circ$ and $C13-H13 \cdots S1^{iv} = 2.83$ Å, $C13 \cdots S1^{iv} = 3.723(2)$ Å with angle at $H13 = 157^\circ$ for symmetry operations iii: $-x, 1-y, 2-z$ and iv: $-1+x, y, z$] and methyl-C–H $\cdots \pi$ (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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