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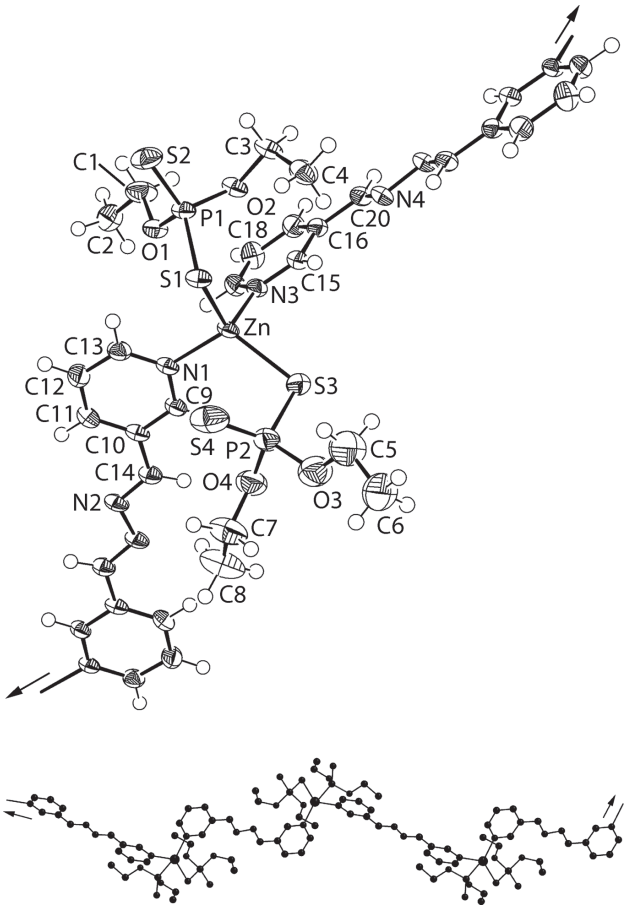
Crystal structure of *catena*-[(bis(*O*,*O*′-diethyl dithiophosphato-*S*,*S*′)-μ_2-1,2-bis(3-pyridylmethylene)hydrazine-*N*,*N*′)zinc(II)], $\{C_{20}H_{30}N_4O_4P_2S_4Zn\}_n$



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Abstract

$C_{20}H_{30}N_4O_4P_2S_4Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 8.01840(1)$ Å, $b = 8.4326(1)$ Å, $c = 23.5086(2)$ Å, $\alpha = 80.478(1)°$, $\beta = 80.679(1)°$, $\gamma = 76.112(1)°$, $V = 1509.37(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0449$, $wR_{ref}(F^2) = 0.1182$, $T = 100(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.16 × 0.12 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	4.99 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	32995, 5385, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5075
$N(param)_{refined}$:	320
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Part of the polymeric structure 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 $Zn[S_2P(OEt)_2]_2$ precursor was prepared in high yield from the *in situ* reaction of $Zn(NO_3)_2 \cdot 6\,H_2O$ (Alfa Aesar; 14.87 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). 1,2-Bis(3-pyridylmethylene)aldazine was prepared in high yield from reaction of 3-picolylamine (Sigma-Aldrich; 2.03 mL, 0.02 mol) and hydrazinium hydroxide (Merck; 0.49 mL, 0.01 mol) in ratio 2:1 in ethanol solution (Merck; 5 mL) under reflux for 1 h. The title compound was obtained by mixing a suspension of $Zn[S_2P(OEt)_2]_2$ (0.50 g, 1.15 mmol) and 1,2-bis(3-pyridylmethylene)hydrazine (0.25 g, 1.19 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). Colourless prisms formed after one day. Yield: 0.49 g, (66.0%, based on $Zn[S_2P(OEt)_2]_2$). **M.pt** (Stuart SMP 30 Melting point apparatus): 387.6–388.6 K. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm^{-1}): 1059(w) ν(C—O); 1015(s) ν(P—O); 651(s) ν(P—S)asym; 522(w) ν(P—S)sym, 287(m) ν(Zn—S); 379(w) ν(Zn—N).

Experimental details

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

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn	0.45517(5)	0.43245(5)	0.76591(2)	0.01869(13)
S1	0.21866(9)	0.60295(10)	0.80904(3)	0.02139(18)
S2	0.15525(12)	0.85492(11)	0.90853(4)	0.0330(2)
S3	0.43677(12)	0.18276(10)	0.74057(4)	0.0306(2)
S4	0.14699(14)	0.48242(14)	0.67405(5)	0.0457(3)
P1	0.31649(10)	0.68021(10)	0.87091(3)	0.02081(18)
P2	0.29908(13)	0.26753(12)	0.67376(4)	0.0332(2)
O1	0.4922(3)	0.7231(3)	0.83743(9)	0.0231(5)
O2	0.3956(3)	0.5288(3)	0.91661(9)	0.0239(5)
O3	0.2174(4)	0.1195(4)	0.66502(13)	0.0475(7)
O4	0.4450(4)	0.2507(3)	0.61834(11)	0.0403(6)
N1	0.5757(3)	0.5677(3)	0.69818(11)	0.0197(5)
N2	0.9449(3)	0.5566(3)	0.51762(11)	0.0230(6)
N3	0.6471(3)	0.3375(3)	0.81908(11)	0.0197(5)
N4	0.5137(4)	0.0488(3)	0.97312(11)	0.0236(6)
C1	0.6088(5)	0.7746(5)	0.86863(16)	0.0350(8)
H1A	0.6611	0.6810	0.8963	0.042*
H1B	0.5437	0.8648	0.8910	0.042*
C2	0.7471(5)	0.8323(4)	0.82569(17)	0.0312(8)
H2A	0.8065	0.7446	0.8022	0.047*
H2B	0.8306	0.8604	0.8463	0.047*
H2C	0.6951	0.9299	0.8003	0.047*
C3	0.2988(5)	0.4738(5)	0.97098(14)	0.0292(7)
H3A	0.2357	0.5708	0.9903	0.035*
H3B	0.3807	0.4036	0.9970	0.035*
C4	0.1716(5)	0.3781(5)	0.96204(15)	0.0309(8)
H4A	0.0837	0.4503	0.9394	0.046*
H4B	0.1156	0.3363	0.9999	0.046*
H4C	0.2326	0.2854	0.9410	0.046*
C5	0.0770(6)	0.0743(7)	0.7055(2)	0.0529(12)
H5A	−0.0086	0.1746	0.7157	0.064*
H5B	0.1211	0.0120	0.7415	0.064*
C6	−0.0068(7)	−0.0289(7)	0.6788(2)	0.0572(13)
H6A	−0.0333	0.0259	0.6402	0.086*
H6B	−0.1142	−0.0442	0.7034	0.086*
H6C	0.0718	−0.1364	0.6752	0.086*
C7	0.3937(6)	0.2962(7)	0.56081(18)	0.0513(11)
H7A	0.3406	0.4154	0.5545	0.062*
H7B	0.3076	0.2342	0.5561	0.062*
C8	0.5521(7)	0.2564(8)	0.5179(2)	0.0666(15)
H8A	0.5214	0.2909	0.4783	0.100*
H8B	0.6003	0.1373	0.5232	0.100*
H8C	0.6383	0.3147	0.5240	0.100*
C9	0.6851(4)	0.4912(4)	0.65626(13)	0.0205(6)
H9	0.7067	0.3745	0.6594	0.025*
C10	0.7670(4)	0.5761(4)	0.60876(13)	0.0206(6)
C11	0.7338(4)	0.7471(4)	0.60405(14)	0.0257(7)
H11	0.7875	0.8089	0.5718	0.031*
C12	0.6212(5)	0.8258(4)	0.64713(15)	0.0282(7)
H12	0.5967	0.9425	0.6449	0.034*
C13	0.5449(4)	0.7323(4)	0.69354(14)	0.0237(7)
H13	0.4681	0.7867	0.7231	0.028*
C14	0.8853(4)	0.4823(4)	0.56571(13)	0.0224(7)
H14	0.9179	0.3656	0.5736	0.027*
C15	0.6071(4)	0.2397(4)	0.86746(13)	0.0203(6)
H15	0.4985	0.2090	0.8732	0.024*
C16	0.7173(4)	0.1802(4)	0.91003(13)	0.0211(6)
C17	0.8778(4)	0.2221(4)	0.90024(15)	0.0257(7)
H17	0.9567	0.1840	0.9282	0.031*
C18	0.9216(4)	0.3202(4)	0.84916(16)	0.0288(7)
H18	1.0317	0.3482	0.8413	0.035*
C19	0.8039(4)	0.3761(4)	0.81013(14)	0.0240(7)
H19	0.8339	0.4445	0.7755	0.029*
C20	0.6654(4)	0.0785(4)	0.96354(14)	0.0228(7)
H20	0.7445	0.0345	0.9912	0.027*

density peaks of 1.63 and 1.24 eÅ^{-3}, respectively, were located 1.15 and 0.75 Å from the H5a and S4 atoms, respectively, belonging to one of the two symmetry-independent diethyl dithiophosphate anions. There is some evidence of disorder in this ligand, which could not be modelled satisfactorily.

Comment

The isomeric, potentially bridging molecules, 1,2-bis(*n*-pyridylmethylene)hydrazine, n-$NC_5H_4C(H)$=N—N=$C(H)C_5H_4$N-n, often referred to as the *n*-pyridylaldazines (n-PyAld), have revealed interesting monodentate modes of coordination in their adducts with zinc-triad 1,1-dithiolates [5]. For example, when the metal node is zinc complexed to dithiocarbamate ($^-S_2CN(R)R'$) and the ligand is 4-PyAld, monodentate coordination of 4-PyAld is observed in mononuclear $Zn[S_2CN(iPr)CH_2CH_2OH]_2$(4-PyAld) with five-coordinate zinc(II) [6]; the non-coordinating pyridyl-nitrogen atom engages in hydroxy-O—H···N(pyridyl) hydrogen bonding. When 3-PyAld is employed and the 1,1-dithiolate ligand is dithiophosphate [$^-S_2P(OR)_2$], bidentate bridging is found in $\{Zn[S_2P(O\text{-}iPr)_2]_2(3\text{-PyAld})\}_n$, (I), which is a one-dimensional coordination polymer with a step-ladder topology [7]. In the present report, the crystal and molecular structures of the ethyl analogue of the latter is described as it is well documented in the structural chemistry of the zinc-triad 1,1-dithiolates that changes in R groups can have profound implications on the ultimate structural motif adopted in the solid-state [5, 8].

The asymmetric unit of (I) comprises $Zn[S_2P(OEt)_2]_2$ and two-half 3-PyAld molecules as each is disposed about a centre of inversion, as indicated in the figure (70% probability displacement ellipsoids; the unlabelled atoms of the N1-3-PyAld molecule are related by the symmetry operation (i) $2-x, 1-y, 1-z$ and those of the N3-3-PyAld molecule by (ii) $1-x, -y, 2-z$). The zinc(II) centre is tetrahedrally coordinated by two sulphur atoms derived from two monodentate dithiophosphate anions as well as two nitrogen atoms derived from two different 3-PyAld molecules. The

dithiophosphate ligands have different modes of coordination. The S1-dithiophosphate coordinates *via* the S1 atom [Zn—S1 = 2.2896(8) Å] and is orientated so the O1 atom [Zn···O1 = 3.286(2) Å], rather than the S2 atom, is directed towards the zinc atom. By contrast, the S3-dithiophosphate ligand coordinates *via* the S3 atom [Zn—S3 = 2.3243(9) Å] with the S4 atom [Zn···S4 = 3.4460(10) Å] directed towards the zinc atom. As anticipated, the P—S bond lengths reflect the different environments of the S1–S4 atoms in that the P1—S1 [2.0208(11) Å] and P2—S3 [2.0021(13) Å] bond lengths, involving the coordinating sulphur atoms are longer than those not involved in coordination [P1—S2 = 1.9418(11) Å and P2—S4 = 1.9265(14) Å]. The Zn—N1 [2.050(3) Å] and Zn—N3 [2.067(3) Å] bond lengths are experimentally equivalent. The range of tetrahedral angles subtended by the N_2S_2 donor set is a narrow 96.82(8)°, for S3—Zn—N3, to a wide 121.49(4)°, for S1—Zn—S3. Small twists are noted in the 3-PyAld bridges as seen in the C9—C10—C14—N2 [170.5(3)°] and C17—C16—C20—N4 [176.2(3)°] torsion angles.

As seen from the lower view of the figure, the application of symmetry gives rise to a coordination polymer. The topology of the chain is twisted which contrasts the step-ladder topology noted for the R = i-Pr analogue [7]. The chain is aligned along [1 1 −1]. The atom-to-atom connections between chains that sustain the three-dimensional architecture are methylene-C—H···N(aldazine) [C1—H1b···N4^{iii}: H1b···N4^{iii} = 2.62 Å, C1···N4^{iii} = 3.520(5) Å with angle at H1b = 151° for (iii) x, $1+y$, z] and pyridyl-C—H···S(thiolate) [C18—H18···S1^{iv}: H18···S1^{iv} = 2.84 Å, C18···S1^{iv} = 3.675(3) Å with angle at H18 = 147° for (iv) $1+x$, y, z] interactions.

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