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Crystal structure of *catena-poly*{(μ_2 - N^1,N^2 -bis[(pyridin-4-yl)methyl]ethanediamide- $\kappa^2N:N'$)-bis(O,O' -di-isopropyldithiophosphato- κ^1S)zinc(II)} – acetonitrile (1/1), $C_{26}H_{42}N_4O_6P_2S_4Zn \cdot C_2H_3N$

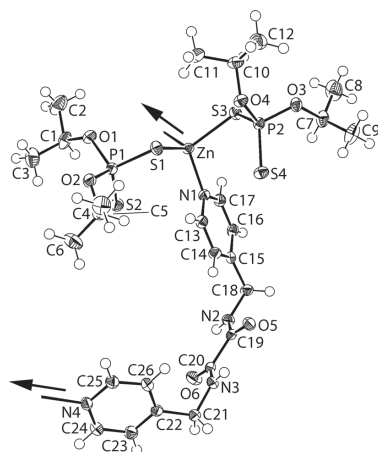


Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.13 × 0.10 × 0.06 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	4.11 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{\max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	42746, 6793, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6561
$N(\text{param})_{\text{refined}}$:	430
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

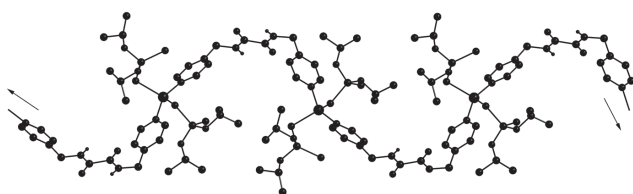


Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn	0.14526(2)	0.27129(2)	0.27222(2)	0.01304(6)
S1	0.38897(4)	0.24625(2)	0.23149(2)	0.01615(8)
S2	0.04782(4)	0.18846(2)	0.13725(2)	0.01786(8)
S3	0.18841(4)	0.32602(2)	0.36011(2)	0.01598(8)
S4	0.30265(4)	0.43011(2)	0.26352(2)	0.01813(8)
P1	0.28829(4)	0.17728(2)	0.17662(2)	0.01424(8)
P2	0.35930(4)	0.39163(2)	0.34014(2)	0.01324(8)
O1	0.31846(13)	0.11522(5)	0.21361(4)	0.0199(2)
O2	0.42539(13)	0.16829(5)	0.13249(4)	0.0177(2)
O3	0.38062(12)	0.43939(4)	0.39351(4)	0.0165(2)
O4	0.55075(12)	0.36273(4)	0.34833(4)	0.0165(2)
O5	-0.15909(13)	0.49101(5)	0.03897(4)	0.0172(2)
O6	-0.45124(14)	0.41764(5)	-0.07211(4)	0.0240(2)
N1	-0.03786(15)	0.31956(5)	0.21747(5)	0.0140(2)
N2	-0.39940(15)	0.43209(5)	0.04544(5)	0.0156(2)
H2N	-0.4874(17)	0.4121(7)	0.0261(7)	0.019*
N3	-0.20479(16)	0.47374(5)	-0.07837(5)	0.0163(2)
H3N	-0.1151(17)	0.4924(7)	-0.0585(7)	0.020*
N4	0.02107(15)	0.30624(5)	-0.20220(5)	0.0147(2)
N5	0.2613(2)	0.36616(7)	0.03191(7)	0.0377(4)
C1	0.2049(2)	0.06063(7)	0.20077(7)	0.0221(3)
H1	0.0797	0.0743	0.1937	0.026*
C2	0.2367(3)	0.02105(8)	0.25512(8)	0.0361(4)
H2A	0.3545	0.0032	0.2594	0.054*
H2B	0.1499	-0.0124	0.2519	0.054*
H2C	0.2265	0.0466	0.2895	0.054*
C3	0.2460(2)	0.02731(8)	0.14717(8)	0.0292(4)
H3A	0.2200	0.0546	0.1130	0.044*

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Abstract

$C_{28}H_{45}N_5O_6P_2S_4Zn$, monoclinic, $P2_1/c$ (no. 14), $a = 7.73670(10)$ Å, $b = 21.56370(10)$ Å, $c = 23.1184(2)$ Å, $\beta = 99.121(1)^\circ$, $V = 3808.12(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0210$, $wR_{\text{ref}}(F^2) = 0.0580$, $T = 100(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H3B	0.1744	−0.0103	0.1406	0.044*
H3C	0.3702	0.0160	0.1531	0.044*
C4	0.4273(2)	0.21403(7)	0.08568(6)	0.0200(3)
H4	0.3571	0.2511	0.0936	0.024*
C5	0.6156(2)	0.23289(8)	0.08609(8)	0.0281(4)
H5A	0.6638	0.2498	0.1246	0.042*
H5B	0.6211	0.2645	0.0560	0.042*
H5C	0.6840	0.1966	0.0779	0.042*
C6	0.3458(2)	0.18447(9)	0.02869(7)	0.0296(4)
H6A	0.4131	0.1476	0.0214	0.044*
H6B	0.3463	0.2142	−0.0034	0.044*
H6C	0.2249	0.1725	0.0311	0.044*
C7	0.23637(19)	0.48154(7)	0.40048(7)	0.0207(3)
H7	0.1301	0.4697	0.3721	0.025*
C8	0.1990(2)	0.47379(9)	0.46193(8)	0.0346(4)
H8A	0.1604	0.4312	0.4674	0.052*
H8B	0.1066	0.5028	0.4687	0.052*
H8C	0.3055	0.4824	0.4898	0.052*
C9	0.2907(2)	0.54666(7)	0.38731(9)	0.0330(4)
H9A	0.3959	0.5581	0.4147	0.049*
H9B	0.1958	0.5755	0.3916	0.049*
H9C	0.3158	0.5486	0.3471	0.049*
C10	0.61769(19)	0.32944(7)	0.40286(6)	0.0195(3)
H10	0.5234	0.3273	0.4278	0.023*
C11	0.6630(2)	0.26454(8)	0.38597(8)	0.0310(4)
H11A	0.5651	0.2472	0.3587	0.047*
H11B	0.6854	0.2386	0.4211	0.047*
H11C	0.7678	0.2657	0.3671	0.047*
C12	0.7703(2)	0.36561(8)	0.43494(7)	0.0280(3)
H12A	0.8631	0.3680	0.4107	0.042*
H12B	0.8153	0.3447	0.4719	0.042*
H12C	0.7318	0.4076	0.4431	0.042*
C13	0.00384(18)	0.34232(6)	0.16738(6)	0.0153(3)
H13	0.1141	0.3319	0.1569	0.018*
C14	−0.10758(18)	0.38026(6)	0.13071(6)	0.0155(3)
H14	−0.0737	0.3958	0.0957	0.019*
C15	−0.27014(18)	0.39560(6)	0.14527(6)	0.0137(3)
C16	−0.31376(18)	0.37144(6)	0.19675(6)	0.0154(3)
H16	−0.4244	0.3802	0.2078	0.018*
C17	−0.19424(19)	0.33453(6)	0.23167(6)	0.0162(3)
H17	−0.2239	0.3190	0.2673	0.019*
C18	−0.39457(18)	0.43947(7)	0.10838(6)	0.0165(3)
H18A	−0.5139	0.4329	0.1176	0.020*
H18B	−0.3600	0.4826	0.1194	0.020*
C19	−0.28532(18)	0.45962(6)	0.01659(6)	0.0146(3)
C20	−0.32338(19)	0.44770(6)	−0.05001(6)	0.0161(3)
C21	−0.2181(2)	0.46908(7)	−0.14173(6)	0.0190(3)
H21A	−0.1605	0.5056	−0.1563	0.023*
H21B	−0.3432	0.4701	−0.1595	0.023*
C22	−0.13580(18)	0.41080(6)	−0.16179(6)	0.0151(3)
C23	−0.21693(19)	0.37857(7)	−0.21067(6)	0.0177(3)
H23	−0.3274	0.3917	−0.2309	0.021*
C24	−0.13473(18)	0.32710(7)	−0.22954(6)	0.0170(3)
H24	−0.1906	0.3055	−0.2632	0.020*
C25	0.09867(19)	0.33775(7)	−0.15481(6)	0.0178(3)
H25	0.2087	0.3235	−0.1351	0.021*
C26	0.02608(19)	0.38958(7)	−0.13356(6)	0.0181(3)
H26	0.0855	0.4106	−0.1001	0.022*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C27	0.1434(2)	0.33521(8)	0.01795(7)	0.0266(3)
C28	−0.0085(2)	0.29544(9)	0.00094(8)	0.0355(4)
H28A	−0.0245	0.2686	0.0339	0.053*
H28B	0.0099	0.2698	−0.0326	0.053*
H28C	−0.1130	0.3212	−0.0100	0.053*

Source of material

The Zn[S₂P(O-iPr)₂]₂ precursor was prepared in high yield from the *in situ* reaction of Zn(NO₃)₂·6 H₂O (Alfa Aesar; 14.87 g, 0.05 mol), iPrOH (Merck; 16.05 mL, 0.21 mol), P₂S₅ (Sigma-Aldrich; 11.11 g, 0.05 mol) and 50% w/w NaOH solution (Merck; 8.80 mL, 0.11 mol). *N,N*-Bis(pyridin-4-ylmethyl)ethanediamide (⁴LH₂) was prepared in high yield from the 2:1 reaction (reflux) of 4-picolyamine (Aldrich; 2.03 mL, 0.02 mol) and diethyl oxalate (Aldrich; 1.36 mL, 0.01 mol) in ethanol solution (Merck; 5 mL). The title compound was obtained by mixing a suspension of Zn[S₂P(O-iPr)₂]₂ (0.50 g, 1.02 mmol) and *N,N*-bis(pyridin-4-ylmethyl)ethanediamide (0.28 g, 1.04 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min at 373 K. The solution was filtered, the filtrate taken in acetonitrile (Merck; 1 mL) and transferred to a vial for crystallisation. Yellow crystals formed after one day. Yield: 0.5432 g, (69.9%, based on Zn[S₂P(O-iPr)₂]₂). **M. pt** (Stuart SMP 30 Melting point apparatus): 380.0–381.1 K. **IR** (Bruker Vertex 70 V equipped with a Platinum ATR from 400 to 80 cm^{−1}): 1177(w) ν(C–O); 1029(w) ν(P–O); 665(s) ν(P–S)_{asym}; 530(m) ν(P–S)_{sym}.

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 N-bound H atoms were refined with N–H = 0.88 ± 0.01 Å, and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Comment

The bis[(pyridin-*n*-yl)methyl]ethanediamides, i.e. molecules of the general formula (n-C₅H₄N)CH₂N(H)C(=O)C(=O)N(H)CH₂(C₅H₄N-*n*), for the *n* = 2, 3 and 4 isomers, abbreviated as ^{*n*}LH₂, attract attention for their diverse structural chemistry as co-crystals, salts and metal complexes [5]. As part of on-going studies of the ability of these molecules to coordinate zinc-triad elements, the presence of two pyridyl residues suggests an ability to bridge metal atoms [5, 6]. Further, the central di-amide group leads to the possibility of forming strong hydrogen bonding interactions to facilitate supramolecular assemblies. In the context of the zinc-triad elements, ⁴LH₂ has been shown to

coordinate a zinc dithiocarbamate ($^-S_2CNR_2$), as in binuclear $[Zn(S_2CNEt_2)_2]_2(^4LH_2)$ [7], and zinc xanthates (^-S_2COR) [8]. For the latter, depending on the bulk of the R group, different aggregation patterns could be observed mirroring the analogous chemistry with 1,2-bis(4-pyridyl)ethylene [9]. Thus, when $R = Et$, a twisted chain, i.e. $[Zn(S_2COEt)_2(^4LH_2)]_n$, was seen in the crystal. However, when the steric bulk of R was increased to cyclohexyl (Cy), only a binuclear aggregate could be isolated, i.e. $[Zn(S_2COCy)_2(^4LH_2)]_n$ [8]. Herein, in continuation of studies in this area, the crystal and molecular structures of a zinc(II) dithiophosphate ($^-S_2P(OR)_2$) derivative, namely $\{Zn[S_2P(O-iPr)_2]_2(^4LH_2)\}_n$, (I) is described.

The asymmetric unit of I excluding the acetonitrile molecule of crystallization, is illustrated in the figure (70% probability displacement ellipsoids). The zinc(II) atom is tetrahedrally coordinated by two sulphur atoms, derived from two monodentate dithiophosphate ligands, and two pyridyl-nitrogen atoms, derived from symmetry related 4LH_2 ligands. The Zn–S1 bond length of 2.3014(4) Å is shorter than the Zn–S3 bond of 2.3275(4) Å. Both dithiophosphate ligands are orientated with the thione-S2 and S4 atoms oriented towards the zinc(II) atom, rather than the alkoxide atom(s) as is sometimes seen in related systems [10]. However, the Zn···S2 and Zn···S4 separations of 3.5706(6) and 3.6510(6) Å, respectively are not indicative of significant bonding interactions. This conclusion is substantiated by the disparity in the P–S bond lengths. Thus, the P1–S1 [2.0282(5) Å] and P2–S3 [2.0386(5) Å] bond lengths involving the coordinating sulphur atoms are considerably longer than the P1–S2 [1.9522(5) Å] and P2–S4 [1.9420(5) Å] bond lengths involving the thione-sulphur atoms. Just as there is a difference in the Zn–S bond lengths, the Zn–N bonds are also different, i.e. Zn–N1, $N4^i = 2.0309(11)$ and $2.0611(12)$ Å, respectively; symmetry operation (i) $x, 1/2 - y, 1/2 + z$. The N_2S_2 donor set is based on a tetrahedron with the tetrahedral angles spanning a relatively narrow range, i.e. ranging from a narrow $99.78(3)^\circ$, for S3–Zn– $N4^i$, to a wide $117.56(1)^\circ$ for S1–Zn–S3. The central $C_2N_2O_2$ residue is planar exhibiting a r.m.s. deviation of 0.016 Å. The dihedral angles between this unit and the N1- and $N4$ -pyridyl rings are $64.56(3)$ and $76.03(3)^\circ$, respectively. The dihedral angle between the two pyridyl rings is $68.76(4)^\circ$ and as they lie to the same side of the central plane, the conformation may be described as U-shaped; the conformational flexibility of 4LH_2 molecules has been commented upon [5]. The central C19–C20 bond is relatively long at 1.5428(18) Å, but this phenomenon is well-known and is due to the presence of the electronegative substituents [5].

The lower view of the figure shows the one-dimensional coordination polymer which is propagated by glide symmetry along the c -axis. The topology of the chain is zigzag

with pairs of successive zinc(II) atoms connected by the curved 4LH_2 molecules with alternating orientations. In the crystal, the key connection between the coordination polymer and the solvent acetonitrile molecule is an amide-N–H···N(acetonitrile) hydrogen bond $[N2-H2n \cdots N5^{ii}: H2n \cdots N5^{ii} = 2.205(14)$ Å, $N2 \cdots N5^{ii} = 2.9580(19)$ Å with angle at $H2n = 145(1)^\circ$ for (ii) $-1 + x, y, z]$. The second amide-N–H forms a hydrogen bond to a carbonyl atom $[N3-H3n \cdots O5^{iii}: H3n \cdots O5^{iii} = 2.128(14)$ Å, $N3 \cdots O5^{iii} = 2.9189(16)$ Å with angle at $H3n = 151(1)^\circ$ for (iii) $-x, 1 - y, -z]$. The latter weakly connects centrosymmetrically related chains into a double-chain *via* eight-membered $\{\cdots HNCO\}_2$ synthons. Further aggregation between chains is precluded owing to the interaction of the acetonitrile with the amide residue. The double-chains assemble in the crystal without directional interactions between them.

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