

catena-Poly[[bis(*O,O'*-diisobutyldithio-phosphato- κ^2S,S')zinc(II)]- μ -1,2-bis(4-pyridyl)-ethane- $\kappa^2N:N'$]

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Key indicators

Single-crystal X-ray study

$T = 223$ K

Mean $\sigma(C-C) = 0.003$ Å

R factor = 0.036

wR factor = 0.093

Data-to-parameter ratio = 27.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The polymeric title compound, $[Zn(C_8H_{18}O_2PS_2)_2(C_{12}H_{12}N_2)]_n$ or $[Zn\{S_2P(OBu^i)_2\}_2(NC_5H_4CH_2CH_2C_5H_4N)]_n$, has the Zn atom located on a centre of inversion and the bridging bipyridine ligand situated around another centre of inversion. The Zn atom exists in a distorted octahedral, N_2S_4 , geometry and the overall topology of the polymer is a straight chain.

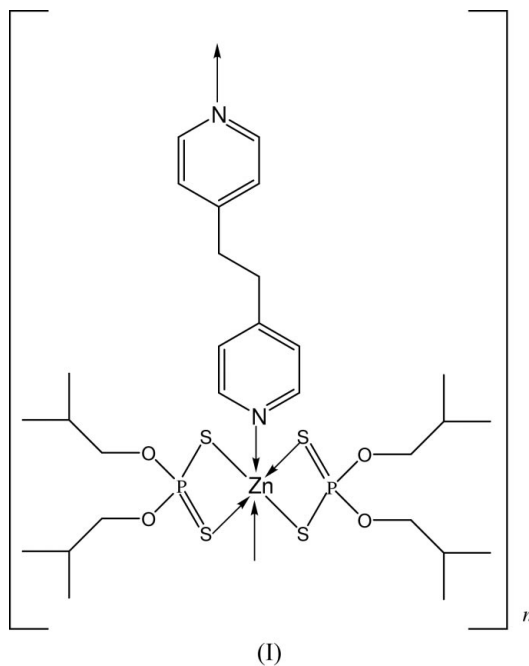
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Comment

In a recent contribution, it was demonstrated that the topology of polymeric chains of the general formula $[Zn(S_2P(OR)_2)_2(\text{bridging bipyridine})]_n$, *i.e.* straight or zigzag, could be controlled by judicious choice of the the R substituent of the dithiophosphate ligand for species with $R = Pr^i$ and Cy (Lai *et al.*, 2004). During the course of this study, the structure of the title compound, (I), was determined.



The Zn atom is located on a centre of inversion and the bridging 1,2-bis(4-pyridyl)ethane ligand is disposed about a different centre. The coordination geometry about the Zn atom (Fig. 1 and Table 1) is distorted octahedral, defined by two chelating dithiophosphate ligands and two N atoms. The independent dithiophosphate ligand forms slightly asymmetric bond distances of 2.5448 (4) and 2.6218 (4) Å for Zn–S1 and Zn–S2, respectively. Other geometric parameters are as expected. The most interesting feature of the structure is the adoption of the straight chain, as shown in

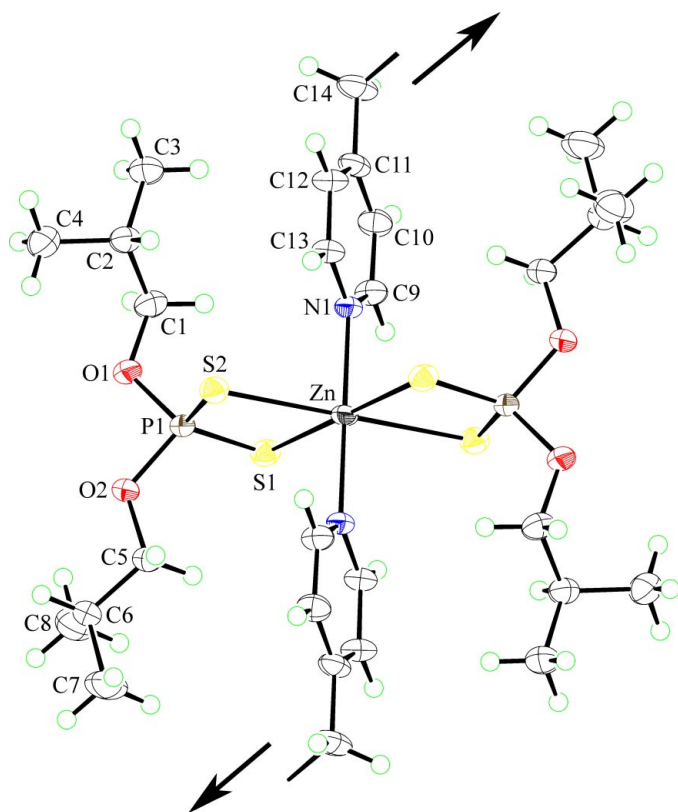


Figure 1
The molecular structure and crystallographic numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level (Johnson, 1976).

Fig. 2; the base vector for the polymer is $[1\bar{1}0]$. A similar straight-chain topology was found in the structure of $[\text{Zn}\{\text{S}_2\text{P}(\text{OCy})_2\}_2(\text{NC}_5\text{H}_4-\text{CH}=\text{CH}-\text{C}_5\text{H}_4\text{N})]_n$ (Lai *et al.*, 2004), but a zigzag topology was found in each of $[\text{Zn}\{\text{S}_2\text{P}(\text{OR})_2\}_2(\text{NC}_5\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_5\text{H}_4\text{N})]_n$ ($R = \text{Pr}^i$ and Cy ; Lai *et al.*, 2004) and $[\text{Zn}\{\text{S}_2\text{P}(\text{OR})_2\}_2(\text{NC}_5\text{H}_4-\text{C}_5\text{H}_4\text{N})]_n$ [$R = \text{Et}$ (Zhu *et al.*, 1996) and $R = \text{Pr}^i$ (Glinskaya *et al.*, 2000)].

As discussed recently, based on qualitative arguments, the combination of the requirements of the bridging bipyridine ligand and the steric bulk of the R groups of the dithiophosphate ligand controls the topology of the resultant polymer (Lai *et al.*, 2004). In the present case, it is the bulky isobutyl groups of the dithiophosphate ligand that preclude the adoption of the zigzag topology.

Experimental

The title compound was prepared by refluxing zinc dithiophosphate with 1,2-bis(4-pyridyl)ethane (Aldrich) using a literature procedure (Lai *et al.*, 2004). Colourless crystals were isolated by the slow evaporation of a chloroform/acetonitrile (4:1) solution of the compound (m.p. 420–422 K). Elemental analysis found: C 46.24, H 6.62%; $\text{C}_{28}\text{H}_{48}\text{N}_2\text{O}_4\text{P}_2\text{S}_4\text{Zn}$ requires: C 45.93, H 6.61%. ^1H NMR (CDCl_3): δ 0.95 (CH_3), 2.00 (CH), 3.03 (CH_2CH_2), 3.87 (OCH_2), 7.23 (N-CH) and 8.73 (CH-C). ^{13}C NMR (CDCl_3): δ 18.85 (CH_3), 28.68 (CH), 35.40 (CH_2CH_2), 73.45 (OCH_2), 124.33 (CH-C_q), 149.39 (N-CH), 151.54 (C_q). ^{31}P (CDCl_3): δ 101.0. IR (KBr disk): $\nu(\text{C-O})$ 1165, $\nu(\text{P-O})$ 948, $\nu(\text{P-S})_{\text{asym}}$ 676, $\nu(\text{P-S})_{\text{sym}}$ 548 cm^{-1} .

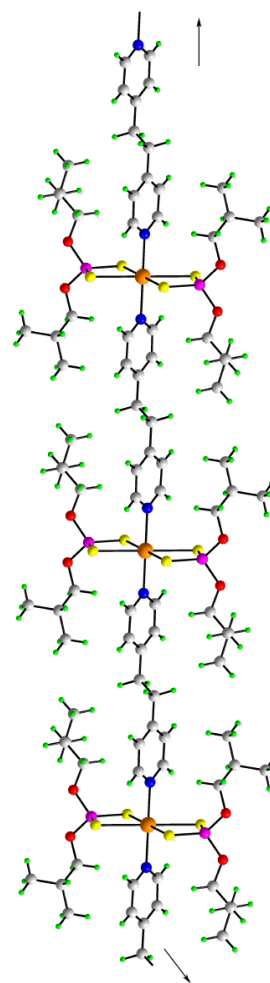


Figure 2
A portion of the straight chain polymer (*DIAMOND*; Crystal Impact, 2002). Colour code: Zn (orange), S (yellow), P (pink), O (red), N (blue), C (grey) and H (green).

Crystal data

$[\text{Zn}(\text{C}_8\text{H}_{18}\text{O}_2\text{PS}_2)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)]$
 $M_r = 732.23$
 Monoclinic, $P2_1/c$
 $a = 9.5874$ (5) Å
 $b = 9.4468$ (5) Å
 $c = 19.4080$ (11) Å
 $\beta = 94.293$ (1)°
 $V = 1752.86$ (16) Å³
 $Z = 2$

$D_x = 1.387$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4606 reflections
 $\theta = 2.4\text{--}29.2^\circ$
 $\mu = 1.06$ mm⁻¹
 $T = 223$ (2) K
 Block, colourless
 $0.47 \times 0.23 \times 0.23$ mm

Data collection

Bruker SMART CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
 $T_{\text{min}} = 0.637$, $T_{\text{max}} = 0.783$
 14428 measured reflections

5114 independent reflections
 4182 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -12 \rightarrow 13$
 $k = -9 \rightarrow 13$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.093$
 $S = 1.03$
 5114 reflections
 187 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.78$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn—S1	2.5448 (4)	P1—O1	1.5833 (12)
Zn—S2	2.6218 (4)	P1—O2	1.5855 (12)
Zn—N1	2.1301 (12)	O1—C1	1.446 (2)
S1—P1	1.9847 (6)	O2—C5	1.436 (2)
S2—P1	1.9840 (6)	C14—C14 ⁱ	1.493 (4)
S1—Zn—S2	79.353 (14)	S1—P1—S2	112.46 (3)
S1—Zn—S2 ⁱⁱ	100.647 (14)	S1—P1—O1	112.61 (6)
S1—Zn—N1	89.71 (4)	S1—P1—O2	111.64 (5)
S1—Zn—N1 ⁱⁱ	90.29 (4)	S2—P1—O1	112.55 (5)
S2—Zn—N1	89.99 (4)	S2—P1—O2	111.51 (6)
S2—Zn—N1 ⁱⁱ	90.01 (4)	O1—P1—O2	94.88 (6)
Zn—S1—P1	85.114 (19)	P1—O1—C1	122.46 (11)
Zn—S2—P1	83.070 (19)	P1—O2—C5	120.79 (11)

Symmetry codes: (i) $-1-x, 1-y, -z$; (ii) $-x, -y, -z$.

The C-bound H atoms were included in the riding-model approximation, with C—H distances of 0.94 (for phenyl), 0.99 (methine), 0.98 (methylene) and 0.97 Å (methyl groups), and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH and CH}_2)$ and $U_{\text{iso}}(\text{methyl-H}) = 1.5U_{\text{eq}}(\text{CH}_3)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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