

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

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Key indicators

Single-crystal X-ray study
 T = 223 K
 Mean $\sigma(C-C)$ = 0.004 Å
 Disorder in main residue
 R factor = 0.057
 wR factor = 0.137
 Data-to-parameter ratio = 24.3

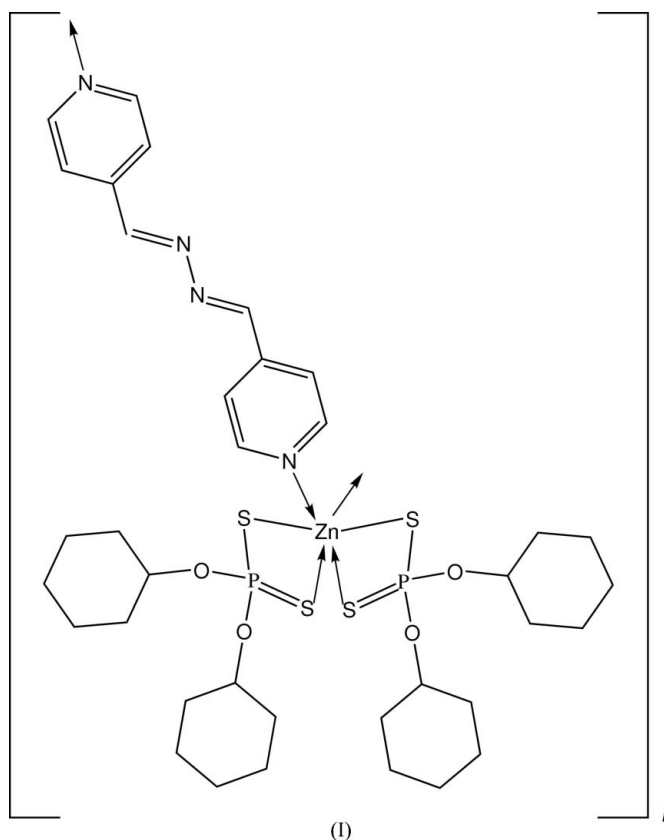
For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

The Zn atom in the polymeric title complex, $[Zn(C_{12}H_{22}O_2PS_2)_2(C_{12}H_{10}N_4)]_n$, lies on a twofold axis and exists in a distorted octahedral geometry defined by a *cis*-N₂O₄ donor set, provided by two *S,S*-chelating dithiophosphate ligands and two N atoms derived from two bridging dipyrindyl-type ligands, each of which is disposed about a centre of inversion. The resultant polymeric structure has a zigzag topology.

Received 14 September 2005
 Accepted 16 September 2005
 Online 21 September 2005

Comment

Interest in crystal structures related to the polymeric title complex, $[Zn\{S_2P(OCy)_2\}_2\{4-NC_5H_4C(H)=NN=C(H)C_5H_4-N-4\}]_n$, (I), arises from the desire to rationalize the formation of polymer topologies based on the steric requirements of the respective ligands, *i.e.* dithiolate-bound *R* groups and/or the dipyrindyl-type ligands themselves (Lai *et al.*, 2002, 2004a; Tiekink, 2003; Lai & Tiekink, 2004).



The immediate coordination geometry about the Zn atom (Fig. 1) is defined by four S atoms, derived from two chelating

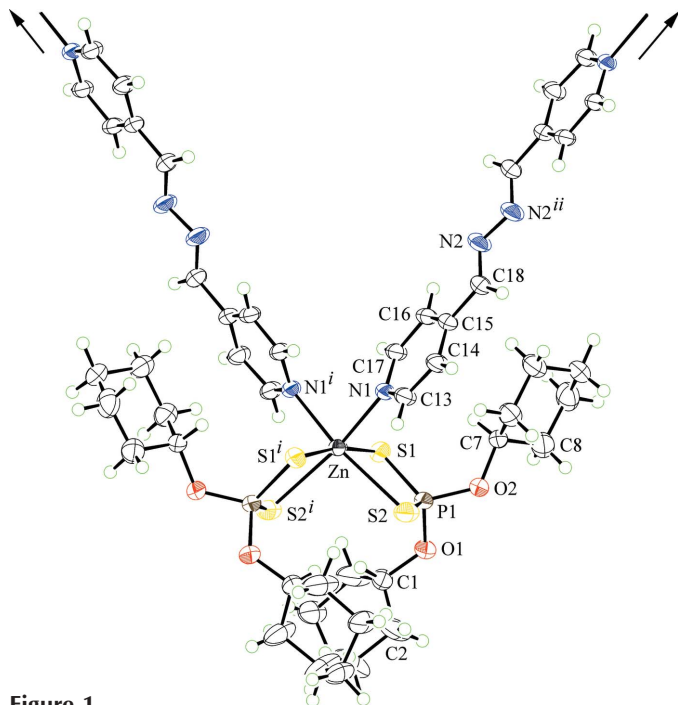


Figure 1

The octahedral coordination geometry for zinc in (I), showing the crystallographic numbering scheme; partially labelled rings have their atoms numbered sequentially. Displacement ellipsoids are shown at the 50% probability level. Only one position for each of the disordered C5 and C6 atoms is shown. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, 2 - y, 1 - z$.]

dithiophosphate ligands, and two N atoms, derived from two μ_2 -bridging dipyrindyl-type ligands. There is crystallographic symmetry in the structure so that the Zn atom is located on a twofold axis and each dipyrindyl-type ligand is disposed about a centre of inversion. The *cis*-N₂S₄ donor set defines an octahedral geometry with the major distortion being due to the restricted bite distance of the dithiophosphate ligand; the S1—Zn—S2 chelate angle is 79.17 (2)°. Other geometric parameters are as expected (Table 1).

The *cis* disposition of the N-donor atoms gives rise to a polymer with a zigzag topology (Fig. 2). The polymer is aligned along the *c* axis and a small twist in the dipyrindyl-type ligand is noted, as seen in the N2—C18—C15—C16 torsion angle of 19.8 (4)°. It is noteworthy that, in the absence of any obvious steric hindrance in the structure of (I), a zigzag polymer is found, an observation consistent with the majority of structures of the general formula $[\text{Zn}\{\text{S}_2\text{P}(\text{OR})_2\}_2(\text{bridging dipyrindyl-type ligand})]_n$. Thus, for each of the $[\text{Zn}\{\text{S}_2\text{P}(\text{OR})_2\}_2(4\text{-NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N-4})]_n$, for $R = \text{Et}$ (Zhu *et al.*, 1996) and $R = \text{Pr}$ (Glinskaya *et al.*, 2000), and $[\text{Zn}\{\text{S}_2\text{P}(\text{OR})_2\}_2(4\text{-NC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N-4})]_n$, $R = \text{Pr}$ and Cy (Lai *et al.*, 2004a) structures, a zigzag topology is found. By contrast, in the two cases where steric influences become a factor in polymer formation, a linear chain is formed, *viz.* $[\text{Zn}\{\text{S}_2\text{P}(\text{OCy})_2\}_2(4\text{-NC}_5\text{H}_4\text{C}(\text{H})=\text{C}(\text{H})\text{C}_5\text{H}_4\text{N-4})]_n$ (Lai *et al.*, 2004a) and $[\text{Zn}\{\text{S}_2\text{P}(\text{O}^i\text{Bu})_2\}_2(4\text{-NC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N-4})]_n$ (Lai *et al.*, 2004b).

Experimental

The title compound was prepared by refluxing the parent zinc dithiophosphate with 4-pyrindinealdazine (Aldrich) using a literature procedure (Lai *et al.*, 2004a). Colourless crystals were isolated in 65% yield by slow evaporation of a chloroform–acetonitrile (3:1 (*v/v*)) solution of the compound (m.p. 377–379 K). Analysis found: C 50.38, H 6.34%; $\text{C}_{36}\text{H}_{54}\text{N}_4\text{O}_4\text{P}_2\text{S}_4\text{Zn}$ requires: C 50.14, H 6.31%. IR (KBr disk): $\nu(\text{C—O})$ 1153 (*m*), $\nu(\text{P—O})$ 968 (*s*), $\nu(\text{P—S})_{\text{asymm}}$ 658 (*m*), $\nu(\text{P—S})_{\text{symm}}$ 523 (*m*) cm^{-1} .

Crystal data

$[\text{Zn}(\text{C}_{12}\text{H}_{22}\text{O}_2\text{PS}_2)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]$
 $M_r = 862.38$
 Orthorhombic, *Pbcn*
 $a = 18.3340$ (8) Å
 $b = 12.0404$ (5) Å
 $c = 19.1304$ (8) Å
 $V = 4223.0$ (3) Å³
 $Z = 4$
 $D_x = 1.356$ Mg m⁻³

Mo K α radiation
 Cell parameters from 6234 reflections
 $\theta = 2.4\text{--}25.8^\circ$
 $\mu = 0.90$ mm⁻¹
 $T = 223$ (2) K
 Block, yellow
 $0.52 \times 0.36 \times 0.26$ mm

Data collection

Bruker SMART area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS, Bruker, 2000)
 $T_{\text{min}} = 0.565$, $T_{\text{max}} = 0.792$
 39717 measured reflections

6155 independent reflections
 4886 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -25 \rightarrow 25$
 $k = -14 \rightarrow 16$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.137$
 $S = 1.10$
 6155 reflections
 253 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 1.9949P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.92$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn—S1	2.4880 (7)	P1—O2	1.5849 (18)
Zn—S2	2.6600 (7)	N1—C13	1.328 (3)
Zn—N1	2.1850 (18)	N1—C17	1.344 (3)
P1—S1	1.9946 (9)	N2—N2 ⁱ	1.410 (4)
P1—S2	1.9716 (10)	N2—C18	1.270 (3)
P1—O1	1.5876 (18)		
S1—Zn—S2	79.17 (2)	N1 ⁱⁱ —Zn—N1	87.09 (10)
S1—Zn—N1	95.15 (5)	Zn—S1—P1	86.63 (3)
S1—Zn—S1 ⁱⁱ	170.66 (3)	Zn—S2—P1	82.46 (3)
S1—Zn—S2 ⁱⁱ	94.60 (2)	S1—P1—S2	111.74 (4)
S1—Zn—N1 ⁱⁱ	91.62 (5)	Zn—N1—C13	121.33 (15)
S2—Zn—N1	88.57 (5)	Zn—N1—C17	120.79 (15)
S2—Zn—S2 ⁱⁱ	97.27 (3)	C13—N1—C17	117.79 (19)
S2—Zn—N1 ⁱⁱ	169.43 (5)	C18—N2—N2 ⁱ	111.4 (3)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, y, -z + \frac{3}{2}$.

H atoms were included in the riding-model approximation, with aromatic C—H = 0.94 Å, methine C—H = 0.99 Å and methylene C—H = 0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The C1—C6 cyclohexyl group is disordered and two sites were discerned for atoms C5 and C6. As the occupancy for each site refined to nearly 50%, the occupancies of the disordered atoms were fixed at 50%.

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Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE* and *SHELXTL* (Bruker, 2000); 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) and *DIAMOND* (Crystal Impact, 2002); software used to prepare material for publication: *SHELXL97*.

The National University of Singapore (R-143-000-213-112) is thanked for support. Cheminova is also thanked for the gift of the dithiophosphate ligand used in this study.

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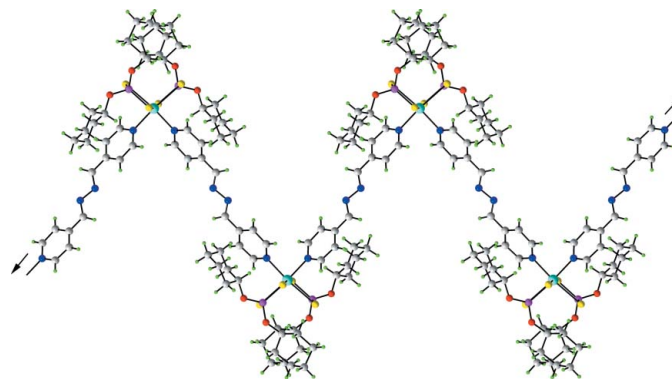


Figure 2

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

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