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μ-1,4-Diazabicyclo[2.2.2]octane-κ^2N:N'-bis[bis(O,O'-diisopropyl dithiophosphato-κ^2S,S')zinc(II)]

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.014 Å
Disorder in main residue
R factor = 0.080
wR factor = 0.175
Data-to-parameter ratio = 14.8

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

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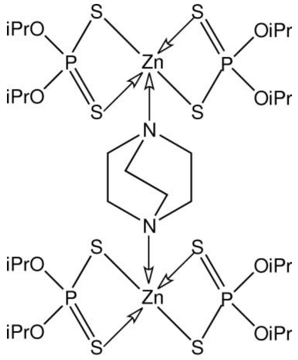
The dinuclear title molecule, $[Zn_2(C_6H_{14}O_2PS_2)_4(C_6H_{12}N_2)]$, is disposed about a centre of inversion and features a heavily distorted coordination geometry, owing to the presence of asymmetrically coordinating dithiophosphate ligands. In the crystal structure, molecules are stacked into layers, with connections between layers provided by C—H···O interactions.

Comment

In connection with ongoing studies of the structural chemistry of Lewis base adducts of zinc and cadmium dithiophosphates $[^{-}S_2P(OR)_2]$, the title compound, (I), was investigated. This research is motivated by the desire to understand the factors that allow for the formation of polymeric structures and the control of their topology once formed (Lai *et al.*, 2004; Lai & Tiekink, 2004, 2006; Chen *et al.*, 2006).



(I)

The structure of (I) (Fig. 1 and Table 1) is similar to that of the recently reported Cd analogue (Ellis & Tiekink, 2006), but with some important differences (see also *Experimental*).

The molecule is disposed about a centre of inversion and features two $Zn[S_2P(O^iPr)_2]_2$ fragments bridged by a 1,4-diazabicyclo[2.2.2]octane (dabco) ligand. A heavily distorted coordination geometry is found for Zn, as both dithiophosphate ligands form asymmetric Zn—S bonds. This asymmetry is reflected in the associated P—S bond distances (Table 1). For the S1,S2-ligand, the asymmetry is less marked than for the S3,S4-ligand. At one extreme, with the S4 atom considered as non-bonding, the Zn atom could be described as being within an NS_3 donor set that defines a tetrahedral geometry. If the Zn—S4 interaction is considered bonding, the coordination geometry would be intermediate between square-pyramidal (SP) and trigonal–pyramdial (TP), as seen in the value of $\tau = 0.57$ (τ = 0.0 and 1.0 are for ideal SP and TP, respectively; Addison *et al.*, 1984).

In contrast with the above description for (I), the Cd analogue is non-centrosymmetric and the coordination geometry is based on a five-coordinate NS_4 donor set (Ellis & Tiekink, 2006). Despite these differences, the crystal packing in both structures is essentially the same. Thus, dimeric molecules of (I) pack into layers that are stacked along [101]. Connections between layers are provided by C—H⋯O interactions, with $C4—H4B\cdots O3^{ii}$ = 2.54 Å, $C4\cdots O3^{ii}$ = 3.453 (16) Å and an angle at H4*B* of 154° [symmetry code: (ii) $-1 + x, y, z$].

Experimental

Compound (I) was prepared by refluxing the parent compound $Zn[S_2P(O^iPr)_2]_2$ with 1,4-diazabicyclo[2.2.2]octane (Aldrich) using a literature procedure (Lai & Tiekink, 2004). Colourless crystals were isolated by the slow evaporation of a propan-2-ol–$CHCl_3$ (1:1 *v*/*v*) solution of the compound (m.p. 470–473 K). IR (KBr disk, cm^{-1}): ν(C—O) 1104 (*w*), ν(P—O) 955 (*s*), $\nu(P—S)_{asymm}$ 664 (*s*), $\nu(P—S)_{sym}$ 545 (*s*).

Crystal data

$[Zn_2(C_6H_{14}O_2PS_2)_4(C_6H_{12}N_2)]$
M_r = 1095.96
Monoclinic, $P2_1/n$
a = 7.9456 (18) Å
b = 18.831 (4) Å
c = 17.570 (4) Å
β = 93.624 (5)°
V = 2623.7 (11) $Å^3$
Z = 2
D_x = 1.387 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.40 mm^{-1}
T = 150 (2) K
Block, pale-yellow
0.35 × 0.15 × 0.10 mm

Data collection

Rigaku AFC-12 κ/SATURN724 diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995) T_{min} = 0.702, T_{max} = 1 (expected range = 0.611–0.870)
54647 measured reflections
4529 independent reflections
4403 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.080
$wR(F^2)$ = 0.175
S = 1.23
4529 reflections
306 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0128P)^2 + 24.4666P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.81 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.97 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Zn—S1	2.327 (2)	S1—P1	2.013 (3)
Zn—S2	2.621 (2)	S2—P1	1.969 (3)
Zn—S3	2.3041 (19)	S3—P2	2.013 (3)
Zn—S4	2.914 (2)	S4—P2	1.962 (2)
Zn—N1	2.097 (6)		
S1—Zn—S2	82.86 (7)	S2—Zn—S4	163.76 (7)
S1—Zn—S3	129.54 (8)	S2—Zn—N1	100.06 (17)
S1—Zn—S4	89.34 (7)	S3—Zn—S4	77.88 (6)
S1—Zn—N1	116.23 (15)	S3—Zn—N1	113.60 (15)
S2—Zn—S3	96.14 (7)	S4—Zn—N1	96.16 (17)

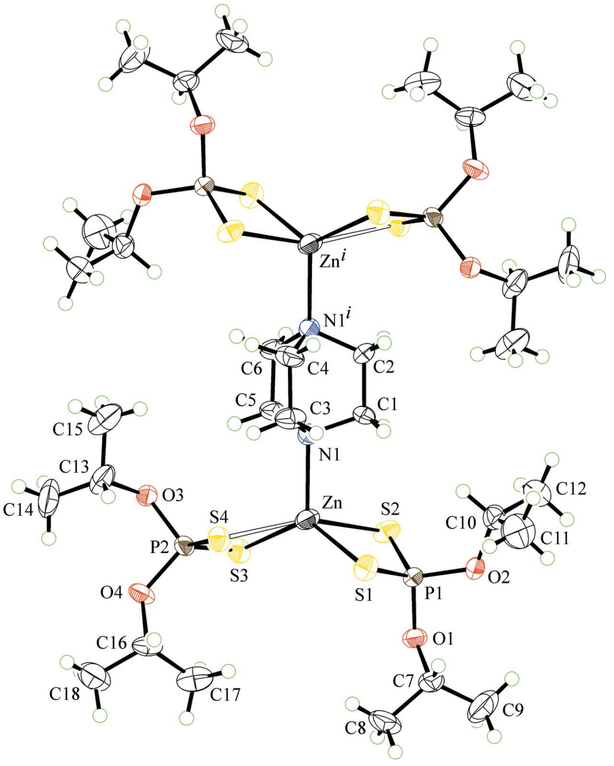


Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The minor disorder components have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

Although the Cd analogue (Ellis & Tiekink, 2006) of (I) was solved and refined in the space group $P2_1$ with Z = 2 and very similar cell parameters to (I), the *n*-glide systematic absences in the data for (I) are clearly absent and the space group $P2_1/n$ was assigned. Refinements of (I) in the alternative space groups $P2_1$ and Pn led to structure models giving lower values for the $R_{observed}$ parameter but did not give any significant increase in the precision of the geometric parameters, and hence the centrosymmetric structure model was selected.

H atoms were included in the riding-model approximation, with C—H = 0.98–1.00 Å, and with $U_{iso}(H) = 1.2U_{eq}$(methylene C) or $1.5U_{eq}$(methyl C). The C atoms of the bridging dabco ligand are disordered over a centre of inversion. Six C atoms were assigned site occupancies of 0.5. Distance restraints [N—C = 1.45 (1) and C—C = 1.50 (1) Å] were imposed. In addition, one isopropyl group of each dithiophosphate ligand was disordered. The C—C distances were restrained to 1.54 (1) Å and the 1,3-related distance restrained to 2.51 (1) Å. The displacement parameters for these groups were restrained to be approximately isotropic. The occupancy factors refined to 0.91 (4):0.09 (4) for C10–C12 and 0.58 (2):0.42 (2) for C16–C18.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Acta Cryst. (2007). E**63**, m108–m110 Ellis *et al.* • $[Zn_2(C_6H_{14}O_2PS_2)_4(C_6H_{12}N_2)]$ **m109**

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