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Key indicators

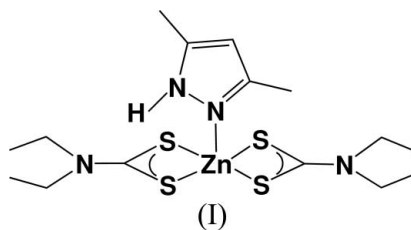
Single-crystal X-ray study
 $T = 193$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.037
 wR factor = 0.079
Data-to-parameter ratio = 17.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis(*N,N*-diethyldithiocarbamato- κ^2S,S')-(3,5-dimethylpyrazolato- κN)zinc(II)

The crystal structure of the title compound, $[Zn(C_5H_{10}NS_2)_2(C_5H_8N_2)]$, an adduct of $Zn(S_2CNEt_2)_2$ and 3,5-dimethylpyrazole (DMPZ), has the Zn atom coordinated by one N atom from one DMPZ ligand and four S atoms of two S_2CNEt_2 ligands in a square-pyramidal geometry; the N atom occupies the apical site.

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Comment

Interest in the zinc dithiocarbamate complexes of nitrogen-containing ligands arises from their interesting structural variations and applications in materials science (Cusack *et al.*, 2004; Barrelet *et al.*, 2003; Yin & Xing, 2004; Yin *et al.*, 2003). Some such complexes are suitable single-source precursors for ZnS nanoparticles (Zhu & Bo, 2003; Guo *et al.*, 2001; Yuan & Zhang, 2001). Among the complexes reported to date (Tang *et al.*, 2006; Li *et al.*, 2005; Chen & Powers, 1995; Hong *et al.*, 2000), a small number have been characterized crystallographically, *e.g.* $[Zn(S_2CNMe_2)_2(C_3H_4N_2)]$ ($C_3H_4N_2$ is imidazole; Chen & Powers, 1995) and $[Zn(SCNMe_2)_2(py)]$ (py is pyridine; Fraser & Harding, 1967). To this number we now add the title zinc diethyldithiocarbamate complex with 3,5-dimethylpyrazole (DMPZ), $[Zn(S_2CNEt_2)_2(DMPZ)]$, (I).



Compound (I) has the Zn centre in a distorted square-pyramidal geometry, as it is coordinated by four S atoms from two S_2CNEt_2 ligands and one N atom from the DMPZ molecule (Fig. 1). The four S atoms, S1–S4, define the square plane with a mean deviation of 0.25 Å, whereas atom N1 occupies the apical position. Chelation by the dithiocarbamate anion is unsymmetrical. The average Zn1–S bond distance [2.468 (9) Å] is longer than that found in $[Zn(S_2CNMe_2)_2(C_3H_4N_2)]$ [2.367 (2) Å; Chen & Powers, 1995] but shorter than that observed in $[Zn(phen)_2WS_4]$ [2.548 (3) Å; Wang *et al.*, 2001]. The Zn1–N3 bond length is close to those found in five-coordinate Zn complexes such as $[Zn(SCNMe_2)_2(py)]$ [2.079 (6) Å; Fraser & Harding, 1967] and $\{Zn[S_2CN(CH_2Ph)_2]_2(4,4'-bipy)\}$ [2.0552 (16) Å; 4,4'-bipy is 4,4'-bipyridine; Yin *et al.*, 2003]. The mean chelate bite angle [73.28 (3)°] is comparable with values found in

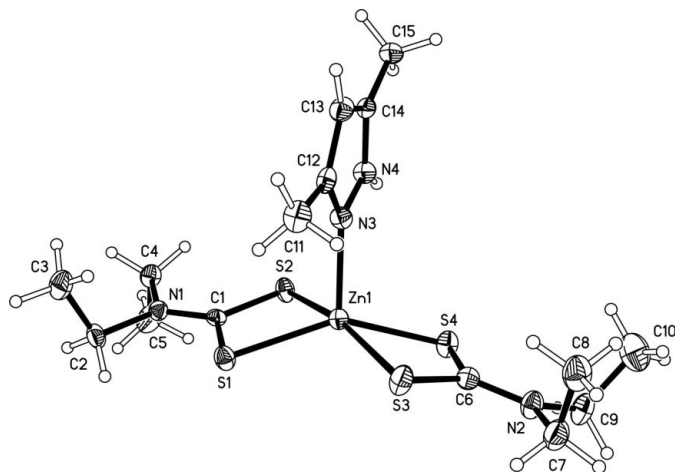


Figure 1
The molecular structure of complex (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

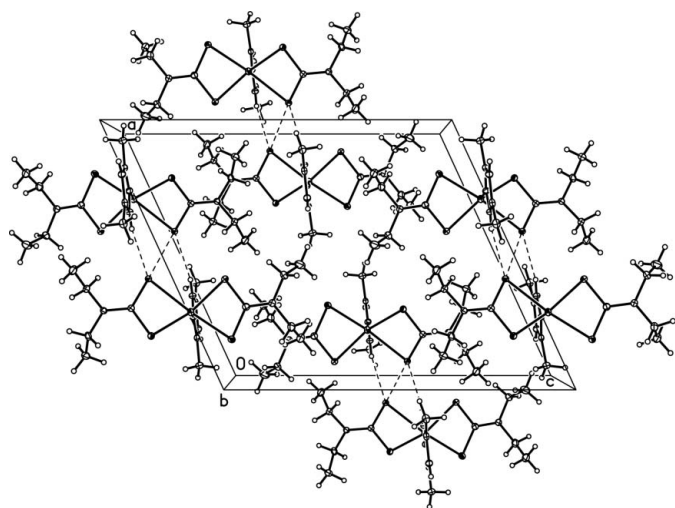


Figure 2
A packing diagram for (I), viewed down the *b* axis. Dashed lines represent the S...S secondary interactions and the N—H...S hydrogen-bonding interactions.

$[\text{Zn}[\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2]_2(4,4'\text{-bipy})]$ [73.032°; Yin *et al.*, 2003] and $\text{Zn}(\text{S}_2\text{CNMe}_2)_2(\text{C}_3\text{H}_4\text{N}_2)$ [73.31°; Chen & Powers, 1995], but is smaller than that observed in $[\text{Zn}(\text{S}_2\text{CC}_4\text{H}_4\text{N})_2]$ [75.2 (3)°; Yin & Xing, 2004].

Through a weak interaction between atom S2 and the symmetry-related atom S2 at $(2-x, 1-y, 1-z)$ [3.274 Å], two molecules of (I) form a dimeric structure that lies on a centre of inversion (Fig. 2). In addition, atom S2 also interacts with the H atom of the DMPZ ligand of a neighbouring molecule [$\text{N4}\cdots\text{S2} = 3.448$ (3) Å; symmetry code: $2-x, 1-y, 1-z$].

Experimental

To a 50 ml flask containing a suspension of anhydrous $\text{Zn}(\text{S}_2\text{CNET}_2)_2$ (0.1805 g, 0.499 mmol) in MeCN (15 ml) was added DMPZ (0.0961 g, 1.0 mmol). After the solid $\text{Zn}(\text{S}_2\text{CNET}_2)_2$ had dissolved, the colour-

less solution was stirred for 2 h and then filtered. Slow evaporation of the solvent from the filtrate afforded crystals after two weeks, which were collected by filtration, washed with Et_2O and dried in air (yield 0.208 g, 91%). Analysis, found: C 39.14, H 5.96, N 11.83%; calculated for $\text{C}_{15}\text{H}_{28}\text{N}_4\text{S}_4\text{Zn}$: C 39.33, H 6.16, N 12.43%.

Crystal data

$[\text{Zn}(\text{C}_5\text{H}_{10}\text{NS}_2)_2(\text{C}_5\text{H}_8\text{N}_2)]$
 $M_r = 458.08$
 Monoclinic, $P2_1/n$
 $a = 14.724$ (3) Å
 $b = 8.8631$ (18) Å
 $c = 17.464$ (4) Å
 $\beta = 114.71$ (3)°
 $V = 2070.4$ (9) Å³

$Z = 4$
 $D_x = 1.469$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.60$ mm⁻¹
 $T = 193$ (2) K
 Block, colourless
 $0.30 \times 0.20 \times 0.09$ mm

Data collection

Rigaku Mercury diffractometer
 ω scans
 Absorption correction: multi-scan
 (Jacobson, 1998)
 $T_{\min} = 0.616$, $T_{\max} = 0.866$

19685 measured reflections
 3789 independent reflections
 3428 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 25.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.079$
 $S = 1.08$
 3789 reflections
 223 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 2.0654P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.36$ e Å⁻³
 $\Delta\rho_{\min} = -0.32$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—N3	2.047 (2)	Zn1—S3	2.4996 (9)
Zn1—S1	2.3570 (10)	Zn1—S2	2.6384 (9)
Zn1—S4	2.3693 (12)		
N3—Zn1—S1	109.05 (7)	S4—Zn1—S3	74.38 (3)
N3—Zn1—S4	106.18 (6)	N3—Zn1—S2	92.58 (6)
S1—Zn1—S4	143.81 (3)	S1—Zn1—S2	72.19 (3)
N3—Zn1—S3	101.66 (6)	S4—Zn1—S2	98.43 (3)
S1—Zn1—S3	105.85 (3)	S3—Zn1—S2	165.33 (3)

The H atom of the pyrazoyl group was located in a difference map, and this atom was allowed to ride on its parent atom with the N—H distance fixed at 0.86 Å. All other H atoms were placed in geometrically idealized positions, with C—H = 0.96 for methyl groups, 0.97 for methylene groups and 0.93 Å for ring CH groups, and constrained to ride on their parent atoms; $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97* and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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