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Key indicators

Single-crystal X-ray study

$T = 180\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$

Disorder in main residue

R factor = 0.066

wR factor = 0.196

Data-to-parameter ratio = 27.2

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

The first dinuclear zinc(II) dithiocarbamate complex with butyl substituent groups

The crystal structure of the title compound, bis(μ - N,N -dibutyldithiocarbamato- $\kappa^2S:S'$)bis[(N,N -dibutyldithiocarbamato- κ^2S,S')zinc(II)], $[\text{Zn}_2(\text{C}_9\text{H}_{18}\text{NS}_2)_4]$, has been determined at 180 K. The structure contains two crystallographically unique Zn^{2+} metal centres, showing almost identical slightly distorted tetrahedral coordination environments, and forming a dinuclear complex with two skew-bridging $\text{syn-}N,N$ -dibutyldithiocarbamate ligands. Two other dithiocarbamate ligands are connected to the Zn^{2+} centres in a syn,syn -chelate coordination mode.

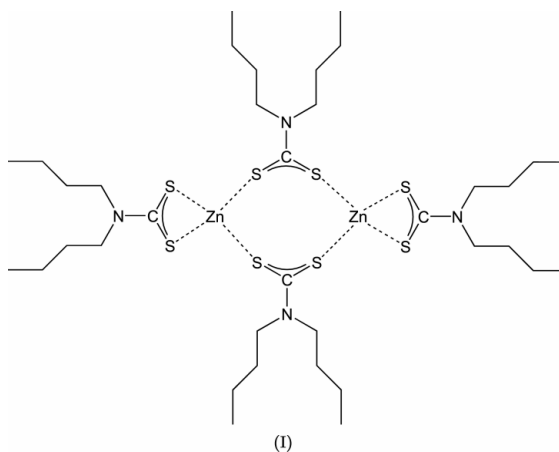
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Comment

Metal dithiocarbamate complexes have been known for a long time, with the first crystallographic result dating back 50 years, when Simonsen & Ho (1953) reported the space group and unit-cell parameters for the structure of the ethyl analogue of the title compound. There has been a recent renewal of interest in this type of compound, which can act as a molecular precursor in the synthesis of novel metal sulfide nanomaterials (Trindade *et al.*, 2001). Such compounds have been successfully used as single-molecule precursors to prepare a wide range of nanocrystalline semiconductors, such as ZnS (Malik *et al.*, 2001), CdS (Monteiro *et al.*, 2002; Lazzel & O'Brien, 1999; Trindade, O'Brien & Zhang, 1997), PbS (Trindade, O'Brien, Zhang & Motevalli, 1997) and Bi_2S_3 (Monteiro *et al.*, 2001). ZnS, a technologically important material as a phosphor and as a white pigment, can be prepared from a well known



zinc(II) diethyldithiocarbamate complex $[\text{Zn}_2(\text{C}_5\text{H}_{10}\text{NS}_2)_4]$, the crystal structure of which has been extensively studied (Simonsen & Ho, 1953; Bonamico *et al.*, 1965; Zvonkova *et al.*, 1967; Tiekink, 2000). A search in the Cambridge Structural Database (Allen, 2002) reveals that an analogous compound containing methyl substituents, *viz.* $[\text{Zn}_2(\text{C}_3\text{H}_6\text{NS}_2)_4]$, has

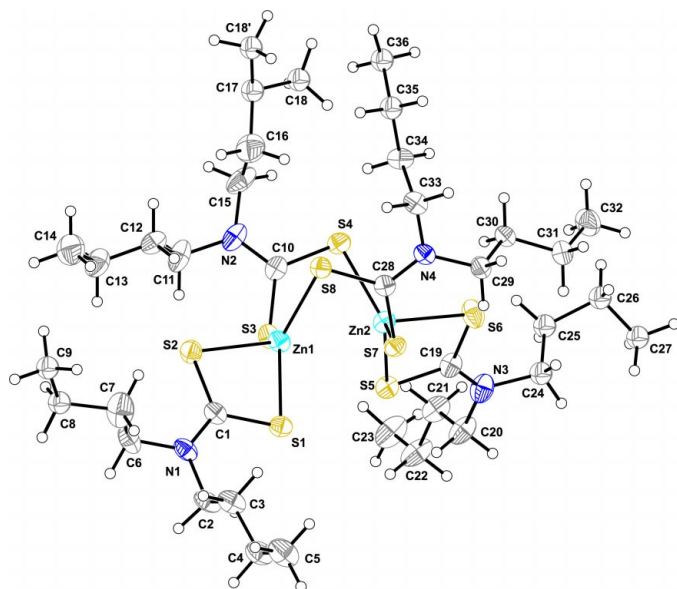


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level, H atoms as small spheres, and the labelling scheme for all non-H atoms. Disordered H atoms on C17 have been omitted for clarity; atom C18 is disordered over two different positions.

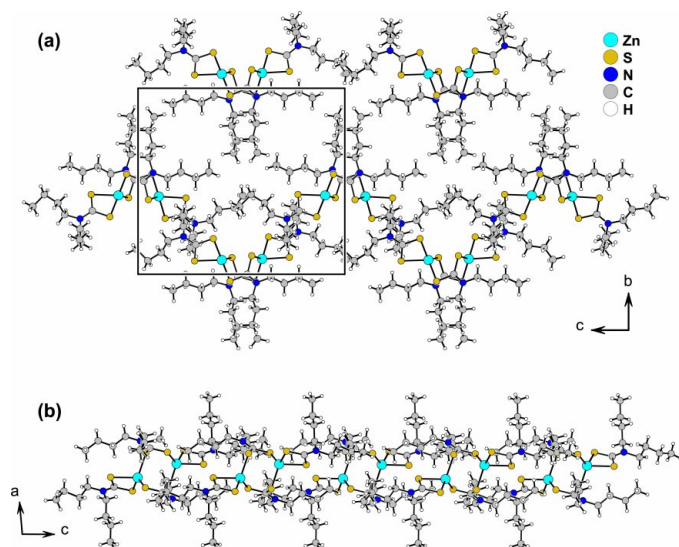


Figure 2
Perspective views, along the *a* (top) and *b* (bottom) axes, of the layers in the *bc* plane, formed by the parallel stacking of $[\text{Zn}_2(\text{C}_9\text{H}_{18}\text{NS}_2)_4]$ molecules related by the 2_1 screw axis.

been described (Klug, 1966; Ramalingam *et al.*, 1998). We report here the first crystal structure of a dinuclear zinc(II) dithiocarbamate complex with butyl substituent groups, $[\text{Zn}_2(\text{C}_9\text{H}_{18}\text{NS}_2)_4]$, (I).

Compound (I) crystallizes in the monoclinic space group $P2_1/c$, with one complete dinuclear $[\text{Zn}_2(\text{C}_9\text{H}_{18}\text{NS}_2)_4]$ complex molecule in the asymmetric unit (Fig. 1). The crystallographically unique Zn^{2+} metal centres have approximately identical distorted tetrahedral coordination environments

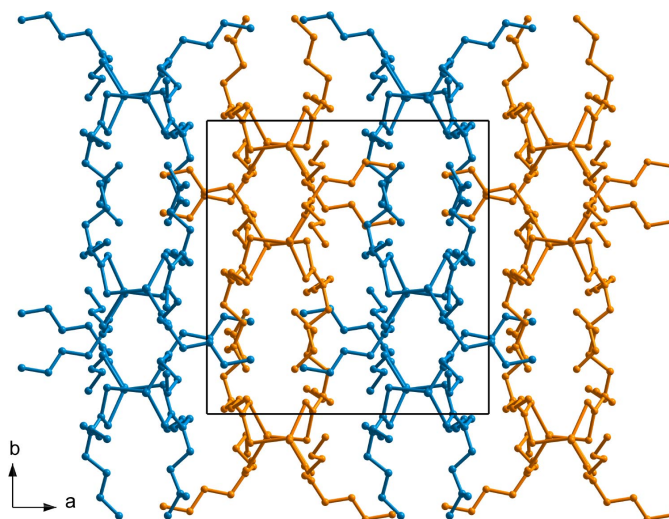


Figure 3
Schematic representation of the alternation in an *ABAB*... fashion along the *a* axis (due to the *c*-glide plane), of layers (in blue and orange) of $[\text{Zn}_2(\text{C}_9\text{H}_{18}\text{NS}_2)_4]$ molecules. H atoms have been omitted for clarity.

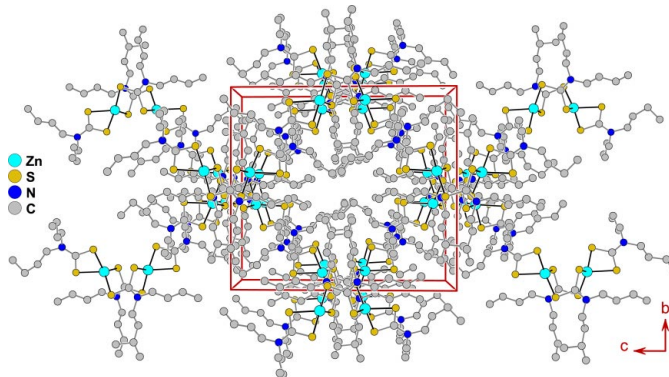


Figure 4
Perspective view of (I) along the *a* axis. H atoms have been omitted for clarity.

(Table 1), and are bridged by two *N,N*-dibutyldithiocarbamate ligands in a skew *syn* coordination fashion, imposing a $\text{Zn1}\cdots\text{Zn2}$ separation of 3.7141 (12) Å (Fig. 1). Each metal centre is further connected to another organic ligand in a *syn,syn*-chelating coordination fashion. Molecules related by the 2_1 screw axis close-pack in the *bc* plane to form layers (Fig. 2), which alternate in an *ABAB*... fashion along the *a*-axis direction (Fig. 3), leading to the complete crystal structure of (I) (Fig. 4).

Experimental

All chemicals were purchased from Aldrich and used without further purification. CS_2 (4.13 mmol) was added to an ethanol suspension (*ca* 50 ml) containing dibutylamine ($\text{C}_8\text{H}_{19}\text{N}$, 4.13 mmol) and freshly prepared zinc(II) hydroxide $[\text{Zn}(\text{OH})_2]$, 2.07 mmol, and the resulting mixture was stirred overnight at ambient temperature. A white precipitate was isolated by vacuum filtration and was air-dried at 333 K. Moderate-quality colourless crystals of the title compound suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2 over a period of 2 d.

Crystal data

[Zn₂(C₉H₁₈NS₂)₄]
 $M_r = 948.20$
 Monoclinic, $P2_1/c$
 $a = 16.036$ (3) Å
 $b = 16.604$ (3) Å
 $c = 18.487$ (4) Å
 $\beta = 95.10$ (3)°
 $V = 4902.7$ (17) Å³
 $Z = 4$

$D_x = 1.285$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 22557 reflections
 $\theta = 1.0$ – 27.5°
 $\mu = 1.35$ mm⁻¹
 $T = 180$ (2) K
 Block, colourless
 $0.14 \times 0.12 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.748$, $T_{\max} = 0.877$
 30156 measured reflections
 11123 independent reflections

7744 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -20 \rightarrow 20$
 $k = -20 \rightarrow 21$
 $l = -18 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.196$
 $S = 1.04$
 11123 reflections
 409 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2 + 11.7125P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.64$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.86$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—S8	2.3164 (14)	N1—C1	1.329 (5)
Zn1—S1	2.3468 (13)	S3—C10	1.755 (5)
Zn1—S3	2.3659 (13)	S4—C10	1.722 (5)
Zn1—S2	2.4365 (14)	N2—C10	1.316 (6)
Zn2—S4	2.3118 (14)	S5—C19	1.723 (5)
Zn2—S5	2.3406 (13)	S6—C19	1.723 (5)
Zn2—S7	2.3660 (13)	N3—C19	1.332 (6)
Zn2—S6	2.4390 (16)	S7—C28	1.747 (5)
S1—C1	1.734 (5)	S8—C28	1.722 (4)
S2—C1	1.719 (5)	N4—C28	1.320 (5)
S8—Zn1—S1	125.51 (5)	S5—Zn2—S7	119.42 (5)
S8—Zn1—S3	112.59 (5)	S4—Zn2—S6	109.85 (6)
S1—Zn1—S3	116.50 (5)	S5—Zn2—S6	75.99 (5)
S8—Zn1—S2	110.67 (5)	S7—Zn2—S6	106.59 (6)
S1—Zn1—S2	76.05 (5)	S2—C1—S1	117.2 (3)
S3—Zn1—S2	107.05 (5)	S4—C10—S3	118.4 (3)
S4—Zn2—S5	123.14 (5)	S6—C19—S5	117.3 (3)
S4—Zn2—S7	112.71 (5)	S8—C28—S7	118.6 (3)

All H atoms were positioned geometrically and refined in the riding-model approximation, with $U_{\text{iso}}(\text{H})$ values fixed at 1.2 (methylene H atoms) or 1.5 (methyl H atoms) times U_{eq} of the parent atom. The alkyl chains were found to be severely affected by disorder, with some C atoms showing extended ellipsoids when treated with anisotropic displacement parameters. Attempts to model disorder for these alkyl chains resulted in a negligible improvement;

the crystal used for data collection, the best from several batches, was a very small block of only moderate quality. However, refinement of the crystal structure with strong geometrical restraints for the alkyl chains (approximately equal C—C bond lengths and C—C—C angles), and common isotropic displacement parameters for some C atoms, resulted in a satisfactory solution. Disorder for atom C18 was successfully modelled over two different positions (C18 and C18') with occupancy factors of 0.600 (13) and 0.400 (13), respectively. The highest peak in the final difference map is located 0.09 Å from C36, and the deepest hole is 0.75 Å from S6.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL (Bruker, 2001); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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