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Bis[methyl 2-(2-pyridylmethylidene)-hydrazinecarbodithioato]zinc(II)

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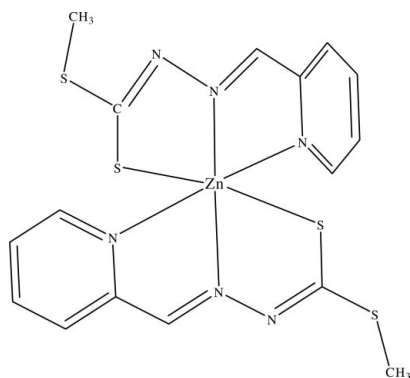
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.034; wR factor = 0.079; data-to-parameter ratio = 18.8.

In the title compound, $[\text{Zn}(\text{C}_8\text{H}_8\text{N}_3\text{S}_2)_2]$, the Zn atom is coordinated by the two ligands in a tridentate manner, *via* the pyridyl N, the azomethine N and the thiolate S atom; the coordination geometry is distorted octahedral, with the two ligands in the *mer* configuration (two S atoms and two pyridyl N atoms are *cis* with respect to each other and the azomethine N atoms is *trans*). The molecules are linked by C—H...S hydrogen bonds, forming a three-dimensional network structure.

Related literature

For general background, see: Akbar Ali *et al.* (2001); Casas *et al.* (2000); Kasuga *et al.* (2001); Tarafder *et al.* (2003). For related structures, see: Chen *et al.* (2003a,b); Lin *et al.* (2007).



Experimental

Crystal data

 $[\text{Zn}(\text{C}_8\text{H}_8\text{N}_3\text{S}_2)_2]$ $M_r = 487.97$ Orthorhombic, Pna_21 $a = 18.630$ (7) Å $b = 9.160$ (3) Å $c = 12.457$ (4) Å $V = 2125.8$ (13) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 1.56$ mm⁻¹ $T = 293$ (2) K $0.25 \times 0.22 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\min} = 0.745$, $T_{\max} = 0.777$

11500 measured reflections

4584 independent reflections

3257 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.079$ $S = 1.04$

4584 reflections

244 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Absolute structure: Flack (1983),

2122 Friedel pairs

Flack parameter: 0.013 (12)

Table 1

Selected geometric parameters (Å, °).

Zn1—N5	2.130 (3)	Zn1—N4	2.223 (3)
Zn1—N2	2.139 (3)	Zn1—S1	2.4584 (13)
Zn1—N1	2.219 (3)	Zn1—S3	2.4814 (13)
N5—Zn1—N2	173.15 (11)	N1—Zn1—S1	150.43 (8)
N5—Zn1—N1	107.46 (11)	N4—Zn1—S1	92.05 (8)
N2—Zn1—N1	74.43 (11)	N5—Zn1—S3	77.11 (8)
N5—Zn1—N4	74.61 (10)	N2—Zn1—S3	96.37 (9)
N2—Zn1—N4	112.15 (11)	N1—Zn1—S3	91.11 (8)
N1—Zn1—N4	88.90 (11)	N4—Zn1—S3	150.32 (8)
N5—Zn1—S1	101.26 (8)	S1—Zn1—S3	102.17 (4)
N2—Zn1—S1	77.89 (8)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2A}\cdots\text{S1}^i$	0.93	2.94	3.715 (3)	142
$\text{C12}-\text{H12A}\cdots\text{S3}^{ii}$	0.93	2.79	3.526 (4)	138

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL and local programs.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2230).

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supplementary materials

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Bis[methyl 2-(2-pyridylmethylidene)hydrazinecarbodithioato]zinc(II)

X.-X. Zhou, Z.-Y. Zhou, J.-Q. Chen, X.-M. Lin and Y.-P. Cai

Comment

The wide variety of biological activity exhibited by thiosemicarbazones (Kasuga *et al.*, 2001) and Schiff bases derived from *S*-alkyldithiocarbazates (Akbar Ali *et al.*, 2001) and their interesting coordination chemistry have stimulated considerable research interest in these compounds (Casas *et al.*, 2000). Some Schiff bases of *S*-alkyl esters of dithiocarbazic acid and their complexes were found to display antifungal and antibacterial properties (Tarafder *et al.*, 2003). Recently we reported the Co(II) complex of the S-containing Schiff base ligand methyl 2-pyridylmethylidenehydrazinecarbodithioate (NNS⁻) (Lin *et al.*, 2007). As a part of structural studies of compounds containing the sulfur-nitrogen chelating ligand (Chen *et al.*, 2003a,b), we report here the synthesis and structure of the compound, bis(methyl 2-pyridylmethylidenehydrazinecarbodithioato)zinc(II), Zn(NNS)₂.

The Zn atom is six-coordinated by the two tridentate NNS⁻ anions in a distorted octahedral geometry (Fig. 1). The ligands chelate the Zn(II) ion *via* the pyridyl N, the azomethine N, and the thiolate S atoms in a *mer*-configuration with four five-membered rings. The two azomethine N atoms (N2 and N5) are *trans* to each other, while the sulfur atoms (S1 and S3) and pyridyl N atoms (N1 and N4) are in *cis* positions. The two almost planar ligands [maximum deviation from their least-squares planes is 0.038 (3) Å] approach the central Zn(II) atom in an orthogonal orientation. The pyridyl ring and the two five-membered chelate rings formed by each ligand display very small dihedral angles between the planes. For each ligand, the maximum dihedral angle of 2.5 (1)° is between two neighbouring five-membered chelate rings (*viz.* Zn1—S1—C7—N3—N2 and Zn1—N1—C5—C6—N2).

The molecules are linked by C—H...S hydrogen bonds. As shown in Fig. 2, each molecular unit forms four acceptor/donor hydrogen bonds with four neighboring molecular units, resulting in a three-dimensional network structure.

Experimental

A solution of Zn(ClO₄)₂ (363 mg, 1.00 mmol) in CH₃OH (20 ml) was slowly added to a solution of methyl 2-pyridylmethylidenehydrazinecarbodithioate (HNNS) (410 mg, 1.95 mmol) in CH₃OH (10 ml). The resultant black-purple solution was stirred under N₂ for 2 h at 323 K and then filtered. After addition of diethyl ether (20 ml), the filtrate was cooled to 253 K. A microcrystalline solid was collected after 24 h and dried under vacuum (yield: 264 mg, 55%). Brown block-shaped crystals suitable for X-ray diffraction were obtained in 2 d by slow diffusion of diethyl ether into a dilute solution of the title complex in methanol. The assigned structure was substantiated by elemental analysis; calculated for C₁₆H₁₆N₆ZnS₄: C 39.51, H 3.30, N 17.29%; found: C 39.46, H 3.38, N 17.23%.

Refinement

All H atoms were placed in idealized positions (C—H = 0.93 or 0.97 Å), and refined in the riding-model approximation. $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier atom})$, where $x = 1.5$ for methyl and 1.2 for all other H atoms.

Figures

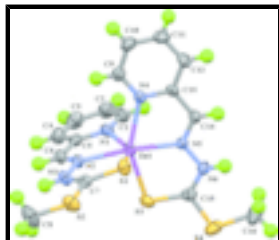


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

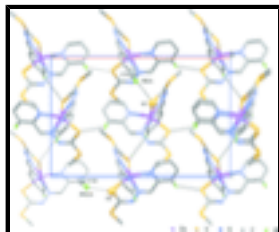


Fig. 2. A view of the three-dimensional molecular network parallel to (010), formed by weak intermolecular C—H...S hydrogen bonds (dotted lines). Hydrogen atoms not involved in hydrogen bonds have been omitted.

Bis[methyl 2-(2-pyridylmethylidene)hydrazinecarbodithioato]zinc(II)

Crystal data

[Zn(C₈H₈N₃S₂)₂]

M_r = 487.97

Orthorhombic, *Pna*2₁

Hall symbol: P2c-2n

a = 18.630 (7) Å

b = 9.160 (3) Å

c = 12.457 (4) Å

V = 2125.8 (13) Å³

Z = 4

*F*₀₀₀ = 1000

D_x = 1.525 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 5120 reflections

θ = 2.8–26.8°

μ = 1.56 mm⁻¹

T = 293 (2) K

Block, colorless

0.25 × 0.22 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 293(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

*T*_{min} = 0.745, *T*_{max} = 0.777

11500 measured reflections

4584 independent reflections

3257 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.028

θ_{max} = 27.1°

θ_{min} = 2.2°

h = -23→13

k = -11→11

l = -15→15

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.1243P]$
$wR(F^2) = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\max} < 0.001$
4584 reflections	$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
244 parameters	$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 2122 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.013 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.056290 (19)	0.37624 (4)	-0.00480 (4)	0.05017 (12)
S1	0.06703 (6)	0.16722 (11)	-0.12754 (9)	0.0649 (3)
S2	0.16269 (7)	0.12965 (14)	-0.30631 (10)	0.0782 (4)
S3	0.15974 (5)	0.33863 (11)	0.11758 (9)	0.0641 (3)
S4	0.16648 (8)	0.15980 (16)	0.30963 (11)	0.0885 (4)
N1	0.05862 (16)	0.6151 (3)	0.0248 (2)	0.0548 (9)
N2	0.11660 (15)	0.4672 (3)	-0.1347 (2)	0.0494 (7)
N3	0.14624 (17)	0.3833 (4)	-0.2142 (2)	0.0587 (8)
H3A	0.1757	0.4172	-0.2611	0.070*
N4	-0.06136 (14)	0.3920 (3)	-0.0321 (2)	0.0527 (8)
N5	0.00813 (14)	0.2761 (3)	0.1317 (2)	0.0468 (7)
N6	0.04532 (16)	0.2141 (3)	0.2144 (2)	0.0563 (8)
H6A	0.0252	0.1636	0.2642	0.068*
C1	0.0304 (2)	0.6883 (5)	0.1059 (4)	0.0695 (11)
H1A	-0.0021	0.6405	0.1504	0.083*
C2	0.0468 (3)	0.8328 (5)	0.1276 (4)	0.0782 (13)

supplementary materials

H2A	0.0268	0.8802	0.1864	0.094*
C3	0.0925 (3)	0.9028 (5)	0.0616 (4)	0.0806 (13)
H3B	0.1043	0.9998	0.0746	0.097*
C4	0.1219 (2)	0.8307 (4)	-0.0255 (4)	0.0708 (12)
H4A	0.1532	0.8780	-0.0723	0.085*
C5	0.1034 (2)	0.6868 (4)	-0.0407 (3)	0.0519 (9)
C6	0.13319 (19)	0.6008 (4)	-0.1282 (3)	0.0540 (9)
H6B	0.1638	0.6431	-0.1783	0.065*
C7	0.1259 (2)	0.2492 (5)	-0.2121 (3)	0.0513 (10)
C8	0.2232 (3)	0.2385 (6)	-0.3797 (5)	0.123 (2)
H8A	0.2461	0.1801	-0.4337	0.185*
H8B	0.2589	0.2776	-0.3320	0.185*
H8C	0.1976	0.3172	-0.4133	0.185*
C9	-0.0957 (2)	0.4483 (5)	-0.1153 (4)	0.0715 (11)
H9A	-0.0695	0.4984	-0.1670	0.086*
C10	-0.1684 (2)	0.4357 (5)	-0.1283 (4)	0.0832 (14)
H10A	-0.1906	0.4778	-0.1876	0.100*
C11	-0.2080 (2)	0.3619 (5)	-0.0549 (4)	0.0846 (15)
H11A	-0.2573	0.3521	-0.0632	0.102*
C12	-0.1735 (2)	0.3019 (5)	0.0324 (4)	0.0729 (12)
H12A	-0.1993	0.2519	0.0848	0.087*
C13	-0.09986 (19)	0.3174 (4)	0.0405 (3)	0.0529 (9)
C14	-0.05961 (18)	0.2558 (4)	0.1289 (3)	0.0543 (9)
H14A	-0.0826	0.2026	0.1824	0.065*
C15	0.1136 (2)	0.2385 (4)	0.2107 (3)	0.0535 (10)
C16	0.1042 (3)	0.0692 (7)	0.3960 (4)	0.131 (2)
H16A	0.1298	0.0223	0.4533	0.197*
H16B	0.0781	-0.0027	0.3558	0.197*
H16C	0.0713	0.1393	0.4253	0.197*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0438 (2)	0.0553 (2)	0.0514 (2)	-0.00346 (17)	0.0087 (2)	0.0044 (2)
S1	0.0754 (7)	0.0579 (6)	0.0615 (6)	-0.0133 (5)	0.0076 (6)	-0.0041 (5)
S2	0.0750 (8)	0.0874 (9)	0.0721 (7)	0.0010 (6)	0.0107 (6)	-0.0295 (6)
S3	0.0393 (5)	0.0865 (7)	0.0665 (6)	0.0000 (5)	0.0002 (5)	-0.0022 (6)
S4	0.0793 (9)	0.0942 (9)	0.0921 (9)	0.0049 (7)	-0.0400 (8)	0.0142 (7)
N1	0.0497 (16)	0.0497 (16)	0.065 (3)	0.0043 (15)	0.0092 (15)	-0.0022 (14)
N2	0.0492 (16)	0.053 (2)	0.0462 (16)	-0.0006 (14)	0.0097 (14)	0.0008 (15)
N3	0.0558 (19)	0.071 (2)	0.0496 (18)	-0.0080 (16)	0.0192 (15)	-0.0006 (16)
N4	0.0441 (16)	0.0578 (18)	0.056 (2)	-0.0011 (14)	0.0030 (14)	0.0111 (14)
N5	0.0418 (17)	0.0534 (17)	0.0451 (15)	-0.0013 (13)	0.0030 (14)	0.0051 (14)
N6	0.057 (2)	0.065 (2)	0.0474 (17)	-0.0068 (15)	-0.0047 (15)	0.0106 (15)
C1	0.066 (3)	0.073 (3)	0.070 (3)	0.007 (2)	0.016 (2)	-0.002 (2)
C2	0.097 (3)	0.068 (3)	0.070 (3)	0.021 (2)	0.008 (3)	-0.011 (2)
C3	0.101 (4)	0.058 (3)	0.083 (3)	0.007 (3)	-0.005 (3)	-0.009 (2)
C4	0.080 (3)	0.057 (2)	0.076 (4)	-0.004 (2)	0.002 (2)	0.005 (2)

C5	0.051 (2)	0.044 (2)	0.060 (2)	0.0033 (17)	-0.0019 (17)	0.0037 (16)
C6	0.056 (2)	0.052 (2)	0.055 (2)	-0.0081 (17)	0.0097 (19)	0.0076 (18)
C7	0.051 (2)	0.058 (3)	0.045 (2)	-0.0007 (19)	-0.0046 (16)	-0.0083 (18)
C8	0.119 (4)	0.148 (5)	0.103 (4)	-0.015 (4)	0.053 (4)	-0.024 (4)
C9	0.060 (3)	0.079 (3)	0.076 (3)	0.000 (2)	-0.003 (2)	0.026 (3)
C10	0.066 (3)	0.089 (3)	0.095 (3)	0.001 (2)	-0.026 (3)	0.032 (3)
C11	0.047 (2)	0.093 (4)	0.114 (4)	-0.004 (2)	-0.018 (3)	0.023 (3)
C12	0.048 (2)	0.090 (3)	0.080 (3)	-0.019 (2)	0.002 (2)	0.016 (2)
C13	0.039 (2)	0.060 (2)	0.059 (2)	0.0024 (17)	0.0026 (17)	0.0065 (18)
C14	0.045 (2)	0.069 (2)	0.049 (2)	-0.0080 (17)	0.0058 (19)	0.0063 (18)
C15	0.051 (2)	0.056 (3)	0.054 (2)	0.0061 (19)	-0.0101 (19)	-0.0152 (17)
C16	0.158 (6)	0.146 (5)	0.090 (4)	-0.045 (4)	-0.054 (4)	0.052 (4)

Geometric parameters (Å, °)

Zn1—N5	2.130 (3)	C1—H1A	0.9300
Zn1—N2	2.139 (3)	C2—C3	1.346 (7)
Zn1—N1	2.219 (3)	C2—H2A	0.9300
Zn1—N4	2.223 (3)	C3—C4	1.384 (6)
Zn1—S1	2.4584 (13)	C3—H3B	0.9300
Zn1—S3	2.4814 (13)	C4—C5	1.376 (5)
S1—C7	1.697 (4)	C4—H4A	0.9300
S2—C7	1.744 (4)	C5—C6	1.456 (5)
S2—C8	1.761 (5)	C6—H6B	0.9300
S3—C15	1.710 (4)	C8—H8A	0.9600
S4—C15	1.735 (4)	C8—H8B	0.9600
S4—C16	1.786 (6)	C8—H8C	0.9600
N1—C1	1.321 (5)	C9—C10	1.368 (5)
N1—C5	1.339 (4)	C9—H9A	0.9300
N2—C6	1.264 (4)	C10—C11	1.356 (6)
N2—N3	1.370 (4)	C10—H10A	0.9300
N3—C7	1.286 (5)	C11—C12	1.377 (6)
N3—H3A	0.8600	C11—H11A	0.9300
N4—C9	1.323 (5)	C12—C13	1.384 (5)
N4—C13	1.341 (4)	C12—H12A	0.9300
N5—C14	1.276 (4)	C13—C14	1.447 (5)
N5—N6	1.365 (4)	C14—H14A	0.9300
N6—C15	1.293 (4)	C16—H16A	0.9600
N6—H6A	0.8600	C16—H16B	0.9600
C1—C2	1.385 (6)	C16—H16C	0.9600
N5—Zn1—N2	173.15 (11)	C5—C4—C3	117.7 (4)
N5—Zn1—N1	107.46 (11)	C5—C4—H4A	121.1
N2—Zn1—N1	74.43 (11)	C3—C4—H4A	121.1
N5—Zn1—N4	74.61 (10)	N1—C5—C4	122.9 (4)
N2—Zn1—N4	112.15 (11)	N1—C5—C6	115.4 (3)
N1—Zn1—N4	88.90 (11)	C4—C5—C6	121.7 (4)
N5—Zn1—S1	101.26 (8)	N2—C6—C5	118.6 (3)
N2—Zn1—S1	77.89 (8)	N2—C6—H6B	120.7
N1—Zn1—S1	150.43 (8)	C5—C6—H6B	120.7

supplementary materials

N4—Zn1—S1	92.05 (8)	N3—C7—S1	128.7 (3)
N5—Zn1—S3	77.11 (8)	N3—C7—S2	118.1 (3)
N2—Zn1—S3	96.37 (9)	S1—C7—S2	113.2 (2)
N1—Zn1—S3	91.11 (8)	S2—C8—H8A	109.5
N4—Zn1—S3	150.32 (8)	S2—C8—H8B	109.5
S1—Zn1—S3	102.17 (4)	H8A—C8—H8B	109.5
C7—S1—Zn1	95.42 (14)	S2—C8—H8C	109.5
C7—S2—C8	104.2 (2)	H8A—C8—H8C	109.5
C15—S3—Zn1	95.79 (13)	H8B—C8—H8C	109.5
C15—S4—C16	104.6 (2)	N4—C9—C10	122.6 (4)
C1—N1—C5	117.7 (3)	N4—C9—H9A	118.7
C1—N1—Zn1	128.3 (3)	C10—C9—H9A	118.7
C5—N1—Zn1	113.2 (2)	C11—C10—C9	120.0 (4)
C6—N2—N3	119.4 (3)	C11—C10—H10A	120.0
C6—N2—Zn1	117.2 (2)	C9—C10—H10A	120.0
N3—N2—Zn1	122.7 (2)	C10—C11—C12	118.6 (4)
C7—N3—N2	113.8 (3)	C10—C11—H11A	120.7
C7—N3—H3A	123.1	C12—C11—H11A	120.7
N2—N3—H3A	123.1	C11—C12—C13	118.6 (4)
C9—N4—C13	117.9 (3)	C11—C12—H12A	120.7
C9—N4—Zn1	128.5 (3)	C13—C12—H12A	120.7
C13—N4—Zn1	113.0 (2)	N4—C13—C12	122.3 (4)
C14—N5—N6	117.5 (3)	N4—C13—C14	115.8 (3)
C14—N5—Zn1	117.2 (2)	C12—C13—C14	122.0 (4)
N6—N5—Zn1	124.6 (2)	N5—C14—C13	118.5 (3)
C15—N6—N5	113.6 (3)	N5—C14—H14A	120.8
C15—N6—H6A	123.2	C13—C14—H14A	120.8
N5—N6—H6A	123.2	N6—C15—S3	127.7 (3)
N1—C1—C2	123.1 (4)	N6—C15—S4	117.5 (3)
N1—C1—H1A	118.5	S3—C15—S4	114.8 (2)
C2—C1—H1A	118.5	S4—C16—H16A	109.5
C3—C2—C1	118.4 (4)	S4—C16—H16B	109.5
C3—C2—H2A	120.8	H16A—C16—H16B	109.5
C1—C2—H2A	120.8	S4—C16—H16C	109.5
C2—C3—C4	120.2 (4)	H16A—C16—H16C	109.5
C2—C3—H3B	119.9	H16B—C16—H16C	109.5
C4—C3—H3B	119.9		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2A \cdots S1 ⁱ	0.93	2.94	3.715 (3)	142
C12—H12A \cdots S3 ⁱⁱ	0.93	2.79	3.526 (4)	138

Symmetry codes: (i) $x+1/2, -y+1/2, z$; (ii) $x-1/2, -y+1/2, z$.

Fig. 1

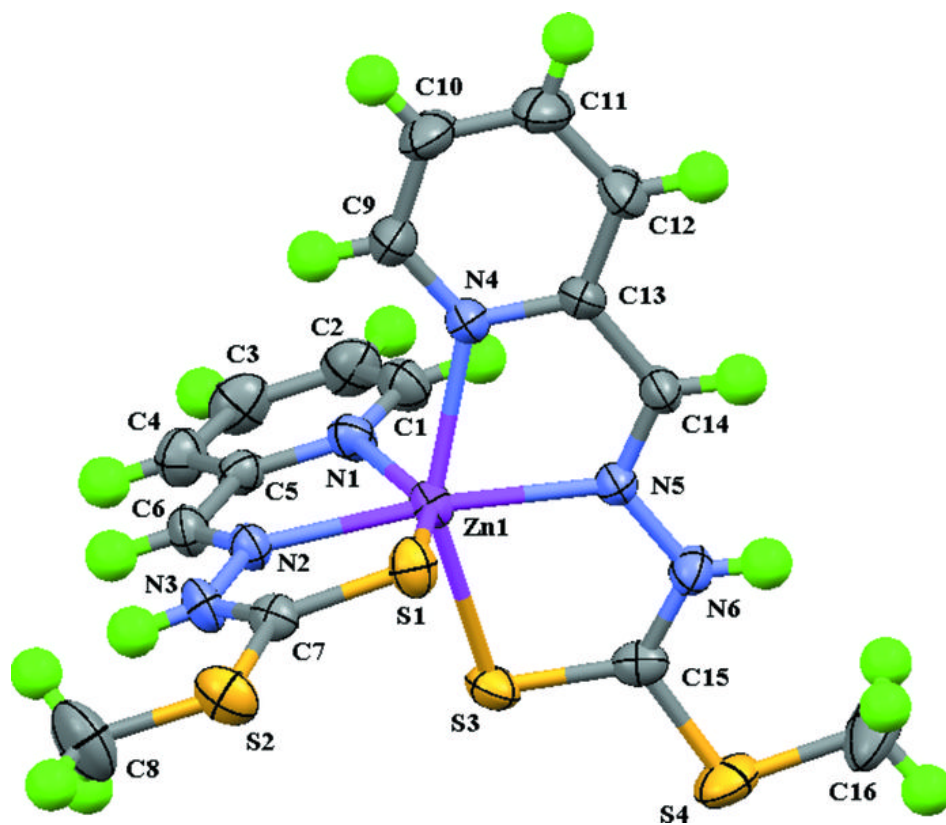


Fig. 2

