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# (μ-4,4′-Bipyridine-κ²N:N′)bis[bis(N,N-dimethyldithiocarbamato-κ²S,S′)zinc(II)]

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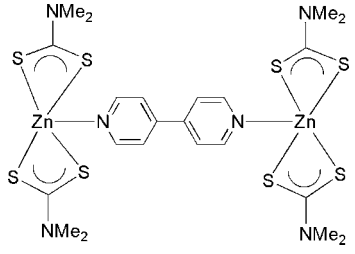
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.040; $wR$ factor = 0.101; data-to-parameter ratio = 22.1.

The title dinuclear $Zn^{II}$ complex, $[Zn_2(C_3H_6NS_2)_4(C_{10}H_8N_2)]$, is centrosymmetric; the mid-point of the C—C bond linking the two pyridine rings is located on an inversion center. The pyridine N atom coordinates to the $Zn^{II}$ cation, which is also chelated by two dimethyldithiocarbamate anions, giving a trigonal-bipyramidal $ZnNS_4$ geometry. Weak intermolecular C—H···S hydrogen bonding is present in the crystal structure.

## Related literature

Dialkyldithiocarbamates have strong metal-binding properties as well as biological functions, see: Jian *et al.* (2002); Arora *et al.* (2003); Hogarth & Richards (2006). For related zinc(II) dithiocarbamate compounds, see: Lai *et al.* (2002); Chen *et al.* (2006); Benson *et al.* (2007).




## Experimental

### Crystal data

$[Zn_2(C_3H_6NS_2)_4(C_{10}H_8N_2)]$
$M_r$ = 767.76
Monoclinic, $P2_1/c$
$a$ = 8.0490 (8) Å
$b$ = 13.8770 (14) Å
$c$ = 14.8134 (14) Å
$\beta$ = 100.070 (1)°
$V$ = 1629.1 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 2.01 mm$^{-1}$
$T$ = 173 K
0.34 × 0.26 × 0.13 mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min}$ = 0.540, $T_{max}$ = 0.770
14059 measured reflections
3754 independent reflections
3205 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.044

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.101
$S$ = 1.04
3754 reflections
170 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.95 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.064 (2) | Zn1—S3 | 2.3495 (8) |
| Zn1—S1 | 2.5909 (9) | Zn1—S4 | 2.6239 (9) |
| Zn1—S2 | 2.3488 (9) | | |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C4—H4$A$···S3$^{i}$ | 0.95 | 2.86 | 3.782 (3) | 164 |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5042).

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# supplementary materials

*Acta Cryst.* (2010). E**66**, m1465 [ **doi:10.1107/S1600536810042650** ]

# ($\mu$-4,4'-Bipyridine-$\kappa^2N$:$N'$)bis[bis(*N*,*N*-dimethyldithiocarbamato-$\kappa^2S$,$S'$)zinc(II)]

**M.-Q. Zha, X. Li, Y. Bing and Y. Lu**

## Comment

Dialkyldithiocarbamates, ($R_2$dtc) (where R is an alkyl group such as methyl, ethyl or propyl), have strong metal-binding properties as well as biological functions (Jian *et al.*, 2002; Arora *et al.*, 2003; Hogarth & Richards, 2006). Crystal engineering studies of zinc(II) dithiocarbamates ($^-S_2CNR_2$) are less well developed (Lai *et al.*, 2002; Chen *et al.*, 2006; Benson *et al.*, 2007), this is likely due to the stronger chelating ability of the dithiocarbamate ligand which tends to preclude incorporation of multiple bridging ligands within the Zn atom coordination sphere. Here, we report the crystal structure of the title zinc complex with 4,4'-bipy and dimethyldithiocarbamate ($Me_2$dtc), [$Zn_2(C_3H_6NS_2)_4(C_{10}H_8N_2)$], (I).

Complex (I) is a binuclear structure, in which Zn1A is symmetrical component related by Zn1 (Symmetry code: -*x*, *y* + 1/2, -*z* + 3/2), and the two $Zn^{2+}$ ions possess the same coordination environment (Fig. 1). The $Zn^{2+}$ ion adopts a distorted square-pyramidal coordination geometry comprising two S,*S*'- bidentate dimethyldithiocarbamate ($Me_2$dtc) ligands, one N atom from 4,4'-bipy ligand, the N atom in the apical site, Zn—O distances ranging from 2.349 to 2.624 Å and Cd –N distance being 2.064 Å. In the crystal, the molecules are generate to a one-dimensional chain, which is further extended into two-dimensional supramolecular network *via* weak C—H···S contacts (Fig. 2), and finally assembled into three-dimensional supramolecular network by C—H···π interactions (Fig. 3).

## Experimental

Tetramethylthiuram monosulfide (5.0 mg, 0.024 mmol) dissolved in *N*,*N*-dimethylformamide (DMF) (2 ml) was mixed with a DMF solution (1 ml) of 4,4'-bipy (2.38 mg, 0.012 mmol) and stirred for 20 min at room temperature. A DMF solution (0.2 ml) of $Zn(NO_3)_2.6H_2O$ (3.57 mg, 0.012 mmol) was then added dropwise and the mixture was allowed to react for 15 min. The solution was left at room temperature to allow slow evaporation. After a few days, pale yellow block crystals of (I) were obtained from the mother liquor.

## Refinement

H atoms were placed in calculated positions and treated using a riding-model approximation with C–H = 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$.

**Figures**

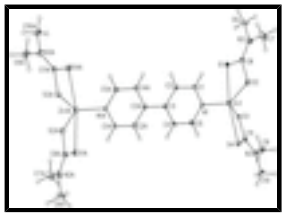

Fig. 1. The molcular structure of (I) showing displacement ellipsoids at the 30% probability level.

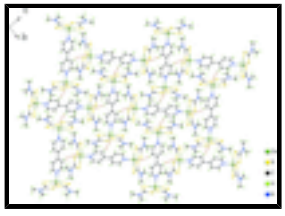

Fig. 2. Two-dimensional supramolecular framework for (I) by C—H···S interactions (orange dashed lines).

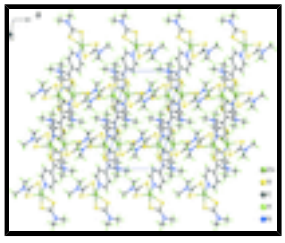

Fig. 3. Unit-cell contents for (I) viewed in projection down the *b* axis.

## (μ-4,4'-Bipyridine-κ$^2$*N*:*N*')bis[bis(*N*,*N*- dimethyldithiocarbamato-κ$^2$*S*,*S*')zinc(II)]

*Crystal data*

| | |
|---|---|
| $[Zn_2(C_3H_6NS_2)_4(C_{10}H_8N_2)]$ | $F(000) = 788$ |
| $M_r = 767.76$ | $D_x = 1.565$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 14059 reflections |
| $a = 8.0490\ (8)$ Å | $\theta = 2.0–27.5°$ |
| $b = 13.8770\ (14)$ Å | $\mu = 2.01$ mm$^{-1}$ |
| $c = 14.8134\ (14)$ Å | $T = 173$ K |
| $\beta = 100.070\ (1)°$ | Block, yellow |
| $V = 1629.1\ (3)$ Å$^3$ | 0.34 × 0.26 × 0.13 mm |
| $Z = 2$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART 1000 CCD area-detector diffractometer | 3754 independent reflections |
| Radiation source: fine-focus sealed tube | 3205 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.044$ |
| φ and ω scans | $\theta_{max} = 27.5°$, $\theta_{min} = 2.0°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2001) | $h = -10\rightarrow10$ |
| $T_{min} = 0.540$, $T_{max} = 0.770$ | $k = -18\rightarrow15$ |

| | |
|---|---|
| 14059 measured reflections | $l = -18 \rightarrow 19$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.101$ | H-atom parameters constrained |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 3.8184P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 3754 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 170 parameters | $\Delta\rho_{max} = 1.21$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -1.95$ e Å$^{-3}$ |

*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 $F^2 > \sigma(F^2)$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.13314 (4) | 0.27435 (3) | 0.24330 (2) | 0.02256 (11) |
| S1 | 0.08181 (9) | 0.16003 (5) | 0.10290 (5) | 0.02256 (11) |
| S2 | −0.12799 (10) | 0.31820 (6) | 0.15575 (6) | 0.02636 (18) |
| S3 | 0.39861 (9) | 0.33093 (6) | 0.22187 (5) | 0.02260 (17) |
| S4 | 0.21808 (10) | 0.41611 (6) | 0.35942 (6) | 0.02694 (18) |
| C1 | −0.0291 (4) | 0.1060 (2) | 0.3154 (2) | 0.0286 (7) |
| H1A | −0.0887 | 0.1049 | 0.2541 | 0.034* |
| C2 | −0.0689 (4) | 0.0385 (2) | 0.3764 (2) | 0.0292 (7) |
| H2A | −0.1562 | −0.0069 | 0.3570 | 0.035* |
| C3 | 0.0183 (4) | 0.0363 (2) | 0.46632 (19) | 0.0183 (6) |
| C4 | 0.1429 (4) | 0.1065 (2) | 0.4901 (2) | 0.0236 (6) |
| H4A | 0.2065 | 0.1084 | 0.5504 | 0.028* |
| C5 | 0.1731 (4) | 0.1731 (2) | 0.4255 (2) | 0.0235 (6) |
| H5A | 0.2568 | 0.2209 | 0.4434 | 0.028* |
| C6 | −0.1905 (5) | 0.1389 (3) | −0.0636 (3) | 0.0444 (10) |
| H6A | −0.0751 | 0.1136 | −0.0503 | 0.067* |
| H6B | −0.2123 | 0.1658 | −0.1257 | 0.067* |

| | | | | |
|---|---|---|---|---|
| H6C | −0.2706 | 0.0867 | −0.0591 | 0.067* |
| C7 | −0.3640 (5) | 0.2736 (4) | −0.0185 (3) | 0.0495 (11) |
| H7A | −0.4042 | 0.2895 | 0.0385 | 0.074* |
| H7B | −0.4514 | 0.2375 | −0.0591 | 0.074* |
| H7C | −0.3387 | 0.3332 | −0.0489 | 0.074* |
| C8 | −0.0971 (4) | 0.2285 (2) | 0.0785 (2) | 0.0230 (6) |
| C9 | 0.6095 (5) | 0.5119 (3) | 0.2449 (3) | 0.0372 (8) |
| H9A | 0.5971 | 0.4609 | 0.1985 | 0.056* |
| H9B | 0.7211 | 0.5072 | 0.2836 | 0.056* |
| H9C | 0.5976 | 0.5750 | 0.2147 | 0.056* |
| C10 | 0.4667 (5) | 0.5812 (3) | 0.3652 (3) | 0.0362 (8) |
| H10A | 0.3668 | 0.5723 | 0.3939 | 0.054* |
| H10B | 0.4570 | 0.6421 | 0.3312 | 0.054* |
| H10C | 0.5680 | 0.5825 | 0.4127 | 0.054* |
| C11 | 0.3763 (4) | 0.4248 (2) | 0.2965 (2) | 0.0206 (6) |
| N1 | 0.0906 (3) | 0.17348 (17) | 0.33906 (17) | 0.0203 (5) |
| N2 | −0.2105 (3) | 0.2147 (2) | 0.0027 (2) | 0.0331 (7) |
| N3 | 0.4789 (3) | 0.50091 (19) | 0.30182 (18) | 0.0255 (6) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.02293 (17) | 0.02255 (18) | 0.02164 (18) | −0.00291 (12) | 0.00229 (12) | 0.00392 (12) |
| S1 | 0.02293 (17) | 0.02255 (18) | 0.02164 (18) | −0.00291 (12) | 0.00229 (12) | 0.00392 (12) |
| S2 | 0.0227 (4) | 0.0276 (4) | 0.0287 (4) | 0.0040 (3) | 0.0042 (3) | 0.0005 (3) |
| S3 | 0.0212 (3) | 0.0237 (4) | 0.0230 (4) | −0.0016 (3) | 0.0042 (3) | −0.0034 (3) |
| S4 | 0.0300 (4) | 0.0249 (4) | 0.0284 (4) | −0.0040 (3) | 0.0119 (3) | −0.0024 (3) |
| C1 | 0.0389 (18) | 0.0250 (16) | 0.0183 (15) | −0.0113 (13) | −0.0045 (13) | 0.0017 (12) |
| C2 | 0.0391 (18) | 0.0238 (16) | 0.0216 (15) | −0.0152 (14) | −0.0032 (13) | 0.0036 (12) |
| C3 | 0.0251 (14) | 0.0133 (13) | 0.0171 (13) | −0.0003 (11) | 0.0055 (11) | −0.0020 (11) |
| C4 | 0.0269 (15) | 0.0259 (16) | 0.0167 (14) | −0.0071 (12) | 0.0002 (11) | 0.0008 (12) |
| C5 | 0.0240 (14) | 0.0245 (16) | 0.0217 (15) | −0.0074 (12) | 0.0032 (12) | −0.0016 (12) |
| C6 | 0.039 (2) | 0.065 (3) | 0.0268 (18) | −0.0130 (19) | 0.0011 (15) | −0.0150 (18) |
| C7 | 0.0289 (19) | 0.072 (3) | 0.043 (2) | 0.0039 (19) | −0.0056 (17) | 0.006 (2) |
| C8 | 0.0222 (14) | 0.0263 (16) | 0.0213 (15) | −0.0054 (12) | 0.0057 (11) | 0.0024 (12) |
| C9 | 0.0364 (18) | 0.036 (2) | 0.043 (2) | −0.0150 (15) | 0.0175 (16) | −0.0078 (16) |
| C10 | 0.042 (2) | 0.0242 (17) | 0.045 (2) | −0.0088 (15) | 0.0146 (16) | −0.0106 (15) |
| C11 | 0.0202 (13) | 0.0212 (14) | 0.0190 (14) | 0.0016 (11) | −0.0004 (11) | 0.0035 (11) |
| N1 | 0.0254 (12) | 0.0168 (12) | 0.0186 (12) | −0.0027 (10) | 0.0034 (10) | 0.0014 (9) |
| N2 | 0.0236 (13) | 0.0464 (18) | 0.0279 (15) | −0.0042 (12) | 0.0005 (11) | 0.0005 (13) |
| N3 | 0.0268 (13) | 0.0219 (13) | 0.0290 (14) | −0.0045 (10) | 0.0082 (11) | −0.0022 (11) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.064 (2) | C5—H5A | 0.9500 |
| Zn1—S1 | 2.5909 (9) | C6—N2 | 1.467 (5) |
| Zn1—S2 | 2.3488 (9) | C6—H6A | 0.9800 |
| Zn1—S3 | 2.3495 (8) | C6—H6B | 0.9800 |
| Zn1—S4 | 2.6239 (9) | C6—H6C | 0.9800 |

| | | | |
|---|---|---|---|
| S1—C8 | 1.710 (3) | C7—N2 | 1.468 (5) |
| S2—C8 | 1.738 (3) | C7—H7A | 0.9800 |
| S3—C11 | 1.738 (3) | C7—H7B | 0.9800 |
| S4—C11 | 1.708 (3) | C7—H7C | 0.9800 |
| C1—N1 | 1.345 (4) | C8—N2 | 1.331 (4) |
| C1—C2 | 1.378 (4) | C9—N3 | 1.466 (4) |
| C1—H1A | 0.9500 | C9—H9A | 0.9800 |
| C2—C3 | 1.393 (4) | C9—H9B | 0.9800 |
| C2—H2A | 0.9500 | C9—H9C | 0.9800 |
| C3—C4 | 1.398 (4) | C10—N3 | 1.471 (4) |
| C3—C3$^{i}$ | 1.483 (6) | C10—H10A | 0.9800 |
| C4—C5 | 1.383 (4) | C10—H10B | 0.9800 |
| C4—H4A | 0.9500 | C10—H10C | 0.9800 |
| C5—N1 | 1.335 (4) | C11—N3 | 1.334 (4) |
| N1—Zn1—S2 | 108.37 (7) | H6B—C6—H6C | 109.5 |
| N1—Zn1—S3 | 125.72 (7) | N2—C7—H7A | 109.5 |
| S2—Zn1—S3 | 125.87 (3) | N2—C7—H7B | 109.5 |
| N1—Zn1—S1 | 96.55 (7) | H7A—C7—H7B | 109.5 |
| S2—Zn1—S1 | 73.36 (3) | N2—C7—H7C | 109.5 |
| S3—Zn1—S1 | 96.74 (3) | H7A—C7—H7C | 109.5 |
| N1—Zn1—S4 | 96.52 (7) | H7B—C7—H7C | 109.5 |
| S2—Zn1—S4 | 105.85 (3) | N2—C8—S1 | 121.7 (3) |
| S3—Zn1—S4 | 72.49 (3) | N2—C8—S2 | 120.2 (3) |
| S1—Zn1—S4 | 166.41 (3) | S1—C8—S2 | 118.10 (18) |
| C8—S1—Zn1 | 80.77 (11) | N3—C9—H9A | 109.5 |
| C8—S2—Zn1 | 87.75 (11) | N3—C9—H9B | 109.5 |
| C11—S3—Zn1 | 88.10 (10) | H9A—C9—H9B | 109.5 |
| C11—S4—Zn1 | 80.15 (10) | N3—C9—H9C | 109.5 |
| N1—C1—C2 | 122.7 (3) | H9A—C9—H9C | 109.5 |
| N1—C1—H1A | 118.6 | H9B—C9—H9C | 109.5 |
| C2—C1—H1A | 118.6 | N3—C10—H10A | 109.5 |
| C1—C2—C3 | 120.4 (3) | N3—C10—H10B | 109.5 |
| C1—C2—H2A | 119.8 | H10A—C10—H10B | 109.5 |
| C3—C2—H2A | 119.8 | N3—C10—H10C | 109.5 |
| C2—C3—C4 | 116.4 (3) | H10A—C10—H10C | 109.5 |
| C2—C3—C3$^{i}$ | 122.1 (3) | H10B—C10—H10C | 109.5 |
| C4—C3—C3$^{i}$ | 121.5 (3) | N3—C11—S4 | 122.4 (2) |
| C5—C4—C3 | 119.8 (3) | N3—C11—S3 | 119.9 (2) |
| C5—C4—H4A | 120.1 | S4—C11—S3 | 117.64 (17) |
| C3—C4—H4A | 120.1 | C5—N1—C1 | 117.4 (3) |
| N1—C5—C4 | 123.2 (3) | C5—N1—Zn1 | 123.2 (2) |
| N1—C5—H5A | 118.4 | C1—N1—Zn1 | 119.4 (2) |
| C4—C5—H5A | 118.4 | C8—N2—C6 | 121.9 (3) |
| N2—C6—H6A | 109.5 | C8—N2—C7 | 121.8 (3) |
| N2—C6—H6B | 109.5 | C6—N2—C7 | 116.3 (3) |
| H6A—C6—H6B | 109.5 | C11—N3—C9 | 123.2 (3) |
| N2—C6—H6C | 109.5 | C11—N3—C10 | 121.8 (3) |
| H6A—C6—H6C | 109.5 | C9—N3—C10 | 115.0 (3) |

Symmetry codes: (i) −*x*, −*y*, −*z*+1.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C4—H4A···S3$^{ii}$ | 0.95 | 2.86 | 3.782 (3) | 164 |

Symmetry codes: (ii) *x*, −*y*+1/2, *z*+1/2.

**Fig. 1**

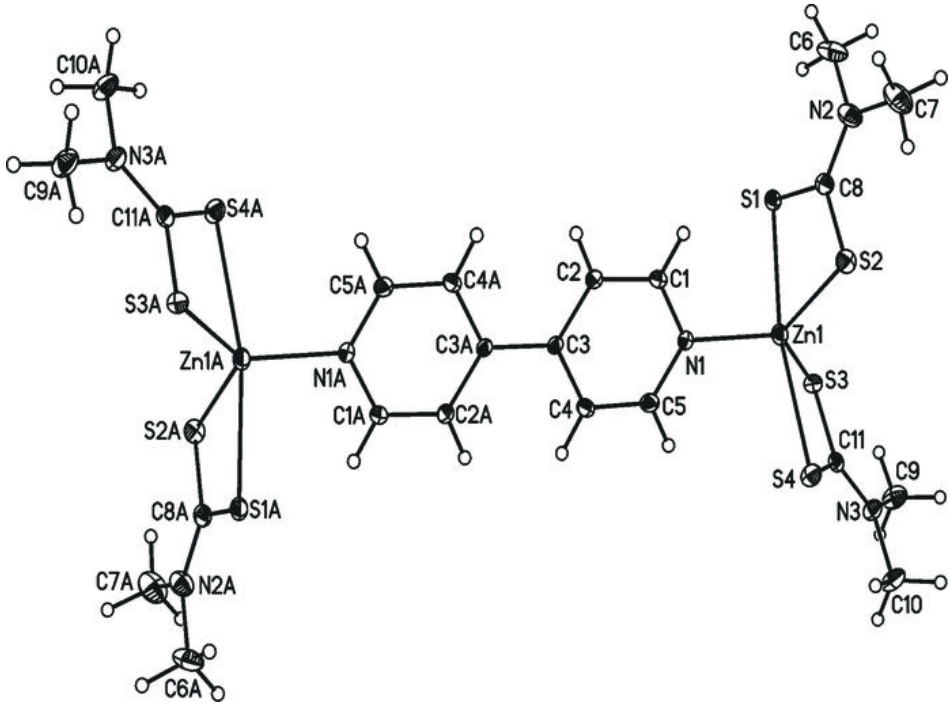
C10A
N3A
C9A
C11A
S4A
S3A
Zn1A
S2A
C8A
S1A
C7A
N2A
C6A
C5A
C4A
N1A
C1A
C2A
C3A
C3
C2
C1
N1
C4
C5
C6
N2
C7
S1
C8
S2
Zn1
S3
C11
S4
C9
N3
C10

**Fig. 2**

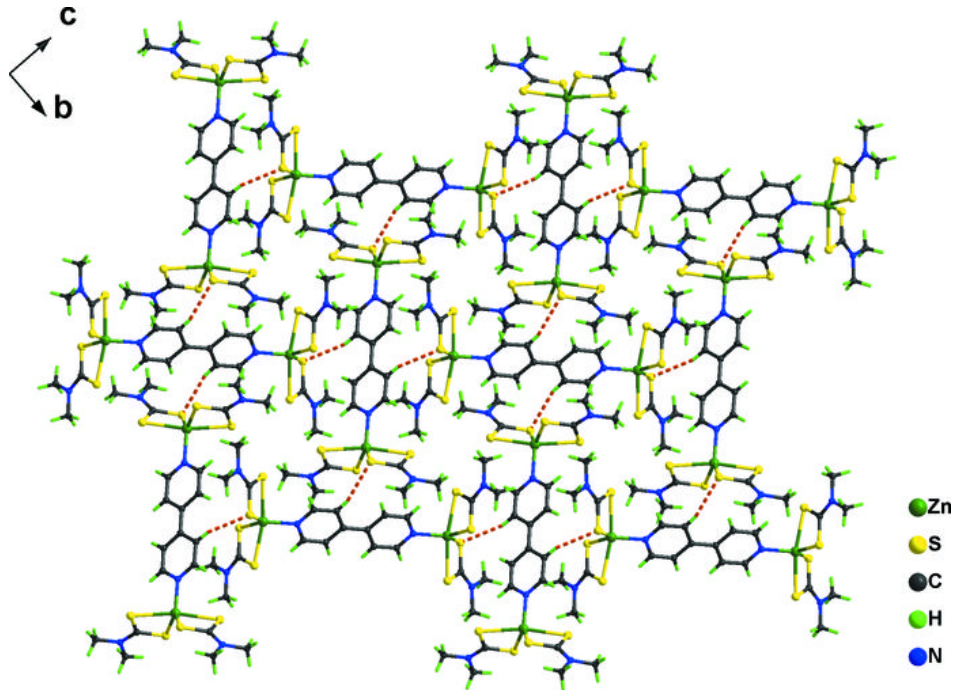

Fig. 3