

## Diazidobis[2,4-diamino-6-(2-pyridyl)-1,3,5-triazine- $\kappa^2N^1, N^6$ ]zinc(II)

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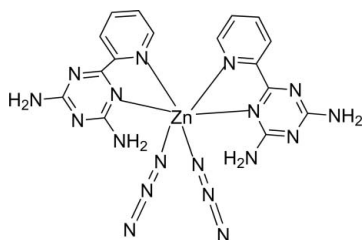
Received 12 April 2009; accepted 29 April 2009

 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.005$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.111; data-to-parameter ratio = 16.2.

In the title mononuclear complex,  $[Zn(N_3)_2(C_8H_8N_6)_2]$ , the  $Zn^{II}$  atom, lying on a twofold rotation axis, is six-coordinated in a distorted octahedral environment by four N atoms from two 2,4-diamino-6-(2-pyridyl)-1,3,5-triazine ligands and two N atoms from two end-on-coordinated azide ions.  $N-H \cdots N$  hydrogen bonds between the ligand and azide ion link the complex molecules into a three-dimensional network.

### Related literature

For general background to organic-inorganic hybrid complexes with azide ligands, see: Carranza *et al.* (2008); Gadad *et al.* (2000, 2004); Sun & Du (2005).



### Experimental

#### Crystal data

 $[Zn(N_3)_2(C_8H_8N_6)_2]$ 
 $M_r = 525.86$ 

 Monoclinic,  $C2/c$ 
 $a = 18.288$  (9) Å

 $b = 14.231$  (7) Å

 $c = 9.144$  (4) Å

 $\beta = 115.382$  (5)°

 $V = 2150.2$  (18) Å<sup>3</sup>
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 1.19$  mm<sup>-1</sup>
 $T = 293$  K

 $0.20 \times 0.18 \times 0.08$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.588$ ,  $T_{\max} = 0.841$ 

(expected range = 0.636–0.909)

9145 measured reflections

2569 independent reflections

 1766 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.056$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.045$ 
 $wR(F^2) = 0.111$ 
 $S = 1.00$ 

2569 reflections

159 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.51$  e Å<sup>-3</sup>
 $\Delta\rho_{\text{min}} = -0.41$  e Å<sup>-3</sup>
**Table 1**

Selected bond lengths (Å).

|        |           |        |           |
|--------|-----------|--------|-----------|
| Zn1–N7 | 2.153 (3) | Zn1–N1 | 2.202 (2) |
| Zn1–N4 | 2.166 (2) |        |           |

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                    | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------------|-------|--------------|--------------|----------------|
| N5–H5A $\cdots$ N3 <sup>i</sup>   | 0.86  | 2.19         | 3.042 (4)    | 175            |
| N5–H5B $\cdots$ N7 <sup>ii</sup>  | 0.86  | 2.31         | 3.060 (4)    | 147            |
| N6–H6A $\cdots$ N9 <sup>iii</sup> | 0.86  | 2.34         | 3.025 (4)    | 137            |
| N6–H6B $\cdots$ N7 <sup>iv</sup>  | 0.86  | 2.10         | 2.939 (4)    | 164            |

 Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 3$ ; (ii)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 2$ ; (iii)  $x, -y + 1, z + \frac{1}{2}$ ; (iv)  $-x + 1, y, -z + \frac{3}{2}$ .

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: HY2194).

### References

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**supplementary materials**

*Acta Cryst.* (2009). E65, m622 [ doi:10.1107/S1600536809016055 ]

## Diazidobis[2,4-diamino-6-(2-pyridyl)-1,3,5-triazine- $\kappa^2N^1,N^6$ ]zinc(II)

Q.-H. Zhao, A.-L. Fan, L.-N. Li and M.-J. Xie

### Comment

At present, the design and synthesis of organic–inorganic hybrid compounds have drawn considerable attention. It was reported that 1*H*-1,3,5-triazole derivatives are a type of heterocyclic compounds with widely biological activity and outstanding capability. Meanwhile, a large number of complexes with azide ligands have been structurally and magnetically characterized (Carranza *et al.*, 2008; Gadad *et al.*, 2000, 2004; Sun & Du, 2005). Herein we report the synthesis and crystal structure of the title compound.

As shown in Fig. 1, the central Zn<sup>II</sup> atom is coordinated by six N atoms and assumes a distorted octahedral geometry. The Zn—N(amide) bond [2.166 (2) Å] and the Zn—N(azide) bond [2.153 (3) Å] are significantly shorter than the Zn—N(pyridine) bond [2.202 (2) Å] (Table 1). The pyridyl and triazine rings of the ligand are essentially planar. The C3 atom shows an evident deviation of 0.1264 (3) Å from the mean plane through all atoms of the ligand. The two ligands coordinated to the Zn atom form a dihedral angle of 74.80 (7)°. The molecules are connected into a three-dimensional network through N—H⋯N hydrogen bonds (Table 2 and Fig. 2).

### Experimental

All chemicals used (reagent grade) were commercially available. The compound was synthesized by heating a mixture of Zn(CH<sub>3</sub>COO)<sub>2</sub> (30 mg, 0.15 mmol), 2,4-diamino-6-pyridyl-1,3,5-triazine (17.6 mg, 0.1 mmol), CH<sub>3</sub>OH (5 ml) and H<sub>2</sub>O (15 ml) at 338 K in stirring condition. After a few minutes, an aqueous solution (2 ml) of sodium azide (6.5 mg, 0.1 mmol) was added to it and stirred for 30 min. Colourless single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature for three weeks.

### Refinement

H atoms were positioned geometrically and treated as riding on their parent atoms, with N—H = 0.86 and C—H = 0.93 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$ .

Figures

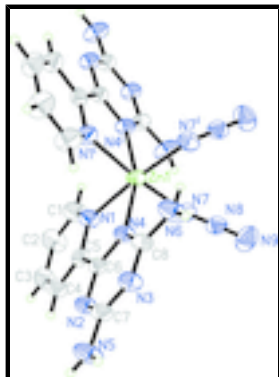


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i)  $-x+1, y, -z+3/2$ .]

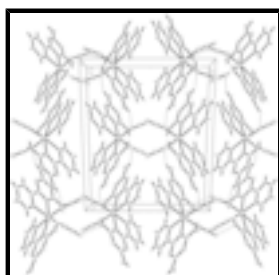


Fig. 2. The crystal packing diagram of the title compound, showing hydrogen bonds (dashed lines).

**Diazidobis[2,4-diamino-6-(2-pyridyl)-1,3,5-triazine- $\kappa^2$ N<sup>1</sup>,N<sup>6</sup>]zinc(II)**

*Crystal data*

$[\text{Zn}(\text{N}_3)_2(\text{C}_8\text{H}_8\text{N}_6)_2]$

$M_r = 525.86$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 18.288\ (9)\ \text{\AA}$

$b = 14.231\ (7)\ \text{\AA}$

$c = 9.144\ (4)\ \text{\AA}$

$\beta = 115.382\ (5)^\circ$

$V = 2150.2\ (18)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1072$

$D_x = 1.624\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2266 reflections

$\theta = 1.9\text{--}28.6^\circ$

$\mu = 1.19\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.20 \times 0.18 \times 0.08\ \text{mm}$

*Data collection*

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

2569 independent reflections

1766 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\text{max}} = 28.6^\circ$

$\theta_{\text{min}} = 1.9^\circ$

$h = -24 \rightarrow 24$

(SADABS; Sheldrick, 1996)

$T_{\min} = 0.588$ ,  $T_{\max} = 0.841$

9145 measured reflections

$k = -18 \rightarrow 19$

$l = -12 \rightarrow 12$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.111$

$S = 1.00$

2569 reflections

159 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.3944P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

### 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.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | x            | y            | z          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|------------|----------------------------------|
| Zn1 | 0.5000       | 0.26762 (3)  | 0.7500     | 0.03110 (17)                     |
| N1  | 0.57688 (14) | 0.16446 (17) | 0.7022 (3) | 0.0345 (6)                       |
| N2  | 0.72454 (13) | 0.16338 (16) | 1.1155 (3) | 0.0317 (6)                       |
| N3  | 0.67379 (15) | 0.25546 (16) | 1.2722 (3) | 0.0335 (6)                       |
| N4  | 0.59865 (13) | 0.24286 (16) | 0.9857 (3) | 0.0295 (6)                       |
| N5  | 0.79367 (15) | 0.17410 (19) | 1.3913 (3) | 0.0466 (7)                       |
| H5A | 0.7994       | 0.1940       | 1.4845     | 0.056*                           |
| H5B | 0.8297       | 0.1380       | 1.3842     | 0.056*                           |
| N6  | 0.55659 (15) | 0.33821 (19) | 1.1393 (3) | 0.0463 (7)                       |
| H6A | 0.5622       | 0.3608       | 1.2308     | 0.056*                           |
| H6B | 0.5157       | 0.3542       | 1.0517     | 0.056*                           |
| N7  | 0.56565 (14) | 0.37551 (19) | 0.6915 (3) | 0.0370 (6)                       |
| N8  | 0.58831 (15) | 0.43984 (19) | 0.7856 (3) | 0.0372 (6)                       |
| N9  | 0.61108 (18) | 0.5009 (2)   | 0.8783 (4) | 0.0554 (8)                       |
| C1  | 0.5666 (2)   | 0.1303 (2)   | 0.5574 (4) | 0.0486 (9)                       |
| H1A | 0.5178       | 0.1421       | 0.4682     | 0.058*                           |
| C2  | 0.6245 (2)   | 0.0791 (3)   | 0.5352 (4) | 0.0536 (10)                      |
| H2A | 0.6149       | 0.0572       | 0.4327     | 0.064*                           |
| C3  | 0.6968 (2)   | 0.0602 (2)   | 0.6659 (4) | 0.0452 (8)                       |
| H3A | 0.7370       | 0.0257       | 0.6537     | 0.054*                           |

## supplementary materials

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|     |              |              |            |            |
|-----|--------------|--------------|------------|------------|
| C4  | 0.70815 (19) | 0.0941 (2)   | 0.8161 (4) | 0.0375 (7) |
| H4A | 0.7560       | 0.0818       | 0.9071     | 0.045*     |
| C5  | 0.64771 (17) | 0.14623 (19) | 0.8293 (3) | 0.0294 (6) |
| C6  | 0.65790 (16) | 0.18691 (19) | 0.9882 (3) | 0.0276 (6) |
| C7  | 0.72914 (17) | 0.1992 (2)   | 1.2585 (3) | 0.0320 (7) |
| C8  | 0.61087 (17) | 0.2789 (2)   | 1.1335 (3) | 0.0311 (7) |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Zn1 | 0.0264 (3)  | 0.0377 (3)  | 0.0228 (3)  | 0.000        | 0.00450 (19) | 0.000        |
| N1  | 0.0326 (13) | 0.0405 (15) | 0.0225 (13) | 0.0043 (11)  | 0.0043 (11)  | -0.0033 (10) |
| N2  | 0.0282 (13) | 0.0402 (15) | 0.0218 (13) | 0.0042 (10)  | 0.0060 (10)  | 0.0004 (10)  |
| N3  | 0.0307 (13) | 0.0454 (16) | 0.0206 (12) | 0.0050 (11)  | 0.0075 (10)  | 0.0004 (10)  |
| N4  | 0.0244 (12) | 0.0399 (15) | 0.0198 (12) | 0.0021 (10)  | 0.0052 (10)  | -0.0012 (10) |
| N5  | 0.0393 (15) | 0.070 (2)   | 0.0202 (13) | 0.0202 (14)  | 0.0027 (11)  | -0.0020 (13) |
| N6  | 0.0393 (15) | 0.070 (2)   | 0.0212 (13) | 0.0195 (14)  | 0.0050 (12)  | -0.0045 (12) |
| N7  | 0.0326 (14) | 0.0448 (16) | 0.0321 (14) | -0.0050 (12) | 0.0123 (11)  | -0.0025 (12) |
| N8  | 0.0285 (14) | 0.0446 (17) | 0.0338 (15) | -0.0006 (12) | 0.0089 (11)  | 0.0082 (13)  |
| N9  | 0.061 (2)   | 0.0489 (18) | 0.0433 (17) | -0.0132 (15) | 0.0104 (15)  | -0.0083 (15) |
| C1  | 0.0435 (19) | 0.063 (2)   | 0.0272 (17) | 0.0092 (17)  | 0.0041 (15)  | -0.0105 (16) |
| C2  | 0.059 (2)   | 0.065 (2)   | 0.0317 (18) | 0.0114 (19)  | 0.0149 (17)  | -0.0161 (16) |
| C3  | 0.051 (2)   | 0.046 (2)   | 0.042 (2)   | 0.0076 (16)  | 0.0222 (17)  | -0.0088 (15) |
| C4  | 0.0379 (17) | 0.0382 (18) | 0.0335 (17) | 0.0037 (14)  | 0.0125 (14)  | -0.0006 (14) |
| C5  | 0.0316 (15) | 0.0283 (15) | 0.0265 (15) | -0.0020 (12) | 0.0108 (12)  | -0.0022 (12) |
| C6  | 0.0265 (14) | 0.0303 (15) | 0.0244 (15) | -0.0014 (12) | 0.0094 (12)  | 0.0012 (12)  |
| C7  | 0.0291 (15) | 0.0372 (17) | 0.0246 (15) | 0.0008 (13)  | 0.0066 (12)  | 0.0047 (12)  |
| C8  | 0.0284 (15) | 0.0384 (17) | 0.0231 (15) | 0.0021 (13)  | 0.0078 (12)  | 0.0020 (12)  |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|                        |            |            |           |
|------------------------|------------|------------|-----------|
| Zn1—N7                 | 2.153 (3)  | N5—H5B     | 0.8600    |
| Zn1—N7 <sup>i</sup>    | 2.153 (3)  | N6—C8      | 1.322 (4) |
| Zn1—N4 <sup>i</sup>    | 2.166 (2)  | N6—H6A     | 0.8600    |
| Zn1—N4                 | 2.166 (2)  | N6—H6B     | 0.8600    |
| Zn1—N1                 | 2.202 (2)  | N7—N8      | 1.202 (4) |
| Zn1—N1 <sup>i</sup>    | 2.202 (2)  | N8—N9      | 1.159 (4) |
| N1—C5                  | 1.343 (3)  | C1—C2      | 1.371 (5) |
| N1—C1                  | 1.346 (4)  | C1—H1A     | 0.9300    |
| N2—C6                  | 1.318 (3)  | C2—C3      | 1.377 (5) |
| N2—C7                  | 1.372 (4)  | C2—H2A     | 0.9300    |
| N3—C7                  | 1.338 (4)  | C3—C4      | 1.385 (4) |
| N3—C8                  | 1.339 (4)  | C3—H3A     | 0.9300    |
| N4—C6                  | 1.337 (3)  | C4—C5      | 1.379 (4) |
| N4—C8                  | 1.371 (4)  | C4—H4A     | 0.9300    |
| N5—C7                  | 1.329 (3)  | C5—C6      | 1.500 (4) |
| N5—H5A                 | 0.8600     |            |           |
| N7—Zn1—N7 <sup>i</sup> | 89.01 (14) | H6A—N6—H6B | 120.0     |

|                                      |             |           |           |
|--------------------------------------|-------------|-----------|-----------|
| N7—Zn1—N4 <sup>i</sup>               | 100.61 (9)  | N8—N7—Zn1 | 115.1 (2) |
| N7 <sup>i</sup> —Zn1—N4 <sup>i</sup> | 92.75 (9)   | N9—N8—N7  | 178.8 (3) |
| N7—Zn1—N4                            | 92.75 (9)   | N1—C1—C2  | 123.1 (3) |
| N7 <sup>i</sup> —Zn1—N4              | 100.61 (9)  | N1—C1—H1A | 118.4     |
| N4 <sup>i</sup> —Zn1—N4              | 161.28 (13) | C2—C1—H1A | 118.4     |
| N7—Zn1—N1                            | 87.41 (10)  | C1—C2—C3  | 119.4 (3) |
| N7 <sup>i</sup> —Zn1—N1              | 174.96 (9)  | C1—C2—H2A | 120.3     |
| N4 <sup>i</sup> —Zn1—N1              | 91.39 (9)   | C3—C2—H2A | 120.3     |
| N4—Zn1—N1                            | 76.04 (9)   | C2—C3—C4  | 118.2 (3) |
| N7—Zn1—N1 <sup>i</sup>               | 174.96 (9)  | C2—C3—H3A | 120.9     |
| N7 <sup>i</sup> —Zn1—N1 <sup>i</sup> | 87.41 (10)  | C4—C3—H3A | 120.9     |
| N4 <sup>i</sup> —Zn1—N1 <sup>i</sup> | 76.04 (9)   | C5—C4—C3  | 119.3 (3) |
| N4—Zn1—N1 <sup>i</sup>               | 91.39 (9)   | C5—C4—H4A | 120.4     |
| N1—Zn1—N1 <sup>i</sup>               | 96.38 (14)  | C3—C4—H4A | 120.4     |
| C5—N1—C1                             | 117.3 (3)   | N1—C5—C4  | 122.7 (3) |
| C5—N1—Zn1                            | 114.71 (18) | N1—C5—C6  | 115.9 (2) |
| C1—N1—Zn1                            | 127.1 (2)   | C4—C5—C6  | 121.4 (3) |
| C6—N2—C7                             | 113.8 (2)   | N2—C6—N4  | 127.0 (2) |
| C7—N3—C8                             | 115.9 (2)   | N2—C6—C5  | 116.2 (2) |
| C6—N4—C8                             | 114.7 (2)   | N4—C6—C5  | 116.8 (2) |
| C6—N4—Zn1                            | 115.90 (17) | N5—C7—N3  | 119.1 (3) |
| C8—N4—Zn1                            | 129.38 (19) | N5—C7—N2  | 116.0 (3) |
| C7—N5—H5A                            | 120.0       | N3—C7—N2  | 124.9 (2) |
| C7—N5—H5B                            | 120.0       | N6—C8—N3  | 118.4 (3) |
| H5A—N5—H5B                           | 120.0       | N6—C8—N4  | 118.1 (2) |
| C8—N6—H6A                            | 120.0       | N3—C8—N4  | 123.5 (3) |
| C8—N6—H6B                            | 120.0       |           |           |

Symmetry codes: (i)  $-x+1, y, -z+3/2$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

| <i>D</i> —H $\cdots$ <i>A</i>     | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N5—H5A $\cdots$ N3 <sup>ii</sup>  | 0.86        | 2.19                | 3.042 (4)                  | 175                           |
| N5—H5B $\cdots$ N7 <sup>iii</sup> | 0.86        | 2.31                | 3.060 (4)                  | 147                           |
| N6—H6A $\cdots$ N9 <sup>iv</sup>  | 0.86        | 2.34                | 3.025 (4)                  | 137                           |
| N6—H6B $\cdots$ N7 <sup>i</sup>   | 0.86        | 2.10                | 2.939 (4)                  | 164                           |

Symmetry codes: (ii)  $-x+3/2, -y+1/2, -z+3$ ; (iii)  $-x+3/2, -y+1/2, -z+2$ ; (iv)  $x, -y+1, z+1/2$ ; (i)  $-x+1, y, -z+3/2$ .

Fig. 1

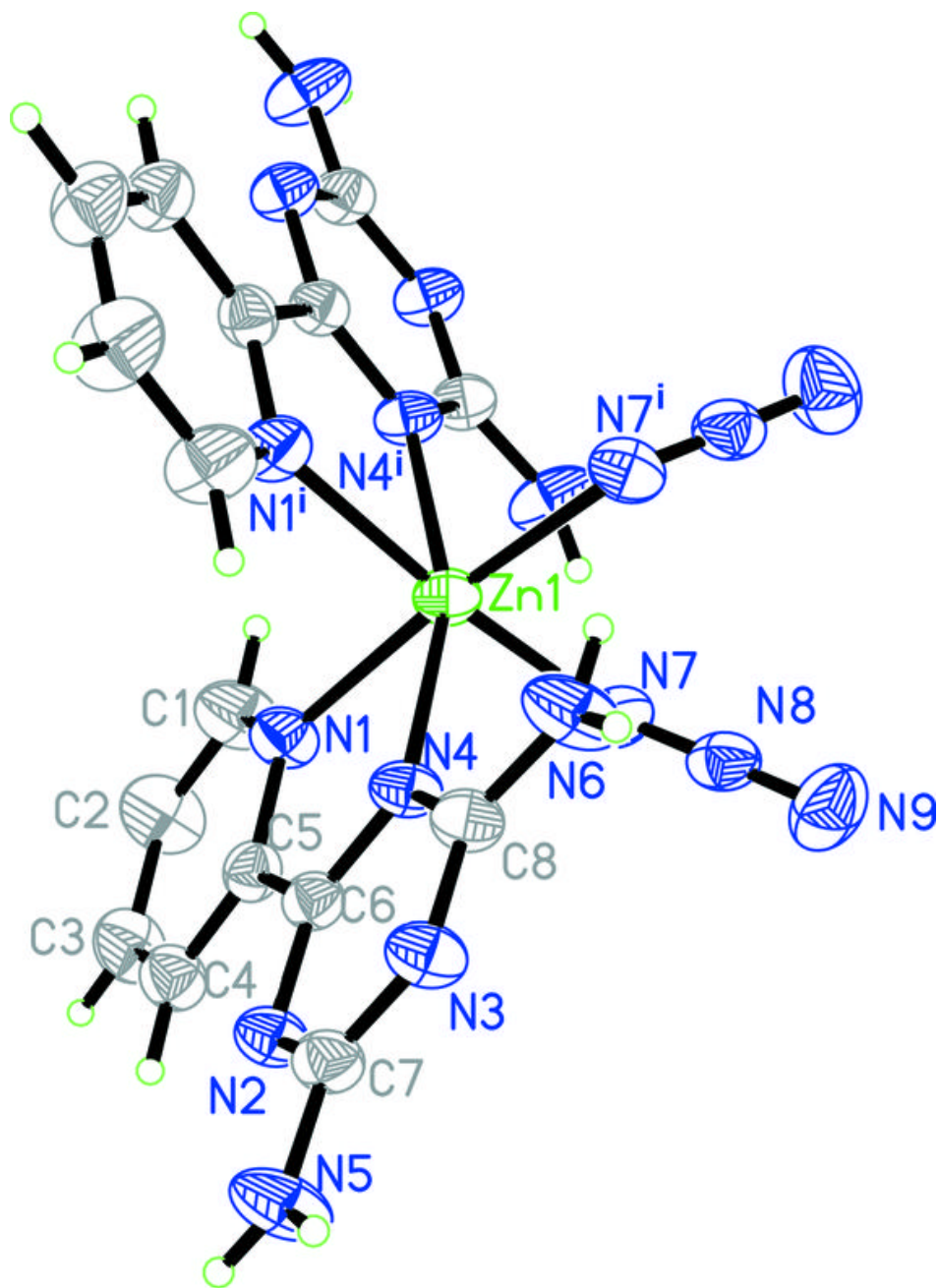


Fig. 2

