

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

Diaquabis[5-(2-pyridyl)tetrazolato- $\kappa^2N^1, N^5$ ]iron(II)

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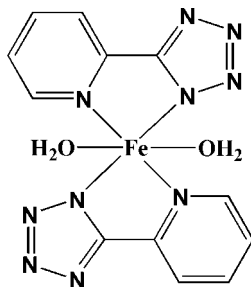
Received 23 February 2009; accepted 4 March 2009

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.003$  Å;  $R$  factor = 0.023;  $wR$  factor = 0.057; data-to-parameter ratio = 11.8.

The title complex,  $[Fe(C_6H_4N_5)_2(H_2O)_2]$ , was synthesized by the reaction of ferrous sulfate with 5-(2-pyridyl)-2H-tetrazole (HL). The  $Fe^{II}$  atom, located on a crystallographic center of inversion, is coordinated by four N-atom donors from two planar *trans*-related deprotonated *L* ligands and two O atoms from two axial water molecules in a distorted octahedral geometry. The  $Fe^{II}$  mononuclear units are further connected by intermolecular  $O-H \cdots N$  and  $C-H \cdots O$  hydrogen-bonding interactions, forming a three-dimensional framework.

## Related literature

For hydrogen bonds, see: Desiraju & Steiner (1999); Kitagawa & Uemura (2005); For general background, see: Rizk *et al.* (2005); Robin & Fromm (2006); For structurally related complexes with tetrazole ligands, see: Mo *et al.* (2004); Song *et al.* (2008); Tao *et al.* (2008); Wang *et al.* (2003); Wen (2008); Wu *et al.* (2007).



## Experimental

## Crystal data

$[Fe(C_6H_4N_5)_2(H_2O)_2]$   
 $M_r = 384.17$   
 Monoclinic,  $P2_1/c$   
 $a = 8.114$  (2) Å  
 $b = 12.924$  (3) Å

$c = 7.360$  (2) Å  
 $\beta = 96.021$  (3)°  
 $V = 767.5$  (3) Å³  
 $Z = 2$   
 Mo  $K\alpha$  radiation

$\mu = 1.02$  mm⁻¹  
 $T = 293$  K

0.29 × 0.14 × 0.11 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.757$ ,  $T_{max} = 0.897$

4287 measured reflections  
 1356 independent reflections  
 1204 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.017$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.057$   
 $S = 1.10$   
 1356 reflections

115 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{max} = 0.23$  e Å⁻³  
 $\Delta\rho_{min} = -0.24$  e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H11 \cdots N5^i$	0.85	1.91	2.764 (2)	177
$O1-H12 \cdots N4^{ii}$	0.85	2.00	2.823 (2)	162
$C2-H2 \cdots O1^{iii}$	0.93	2.56	3.362 (3)	145

Symmetry codes: (i)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $-x, y - \frac{1}{2}, -z + \frac{5}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 2$ .

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 (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

This work was supported by the Start-up Fund for PhDs in Natural Scientific Research of Zhengzhou University of Light Industry (grant No. 2006BSJJ001 to SMF). We also thank Dr Chun-Sen Liu for his helpful discussions and valuable suggestions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2104).

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**supplementary materials**

*Acta Cryst.* (2009). E65, m382 [ doi:10.1107/S1600536809007892 ]

## Diaquabis[5-(2-pyridyl)tetrazolato- $\kappa^2 N^1, N^5$ ]iron(II)

M. Hu, S.-T. Ma, L.-Q. Guo and S.-M. Fang

### Comment

Currently, there is considerable interest in self-assembly and construction of supramolecular complexes featuring fascinating architectures realized by noncovalent interactions such as coordination bonds, hydrogen bonds and other weak intermolecular interactions (Rizk *et al.*, 2005; Robin & Fromm, 2006). Hydrogen bonds, combining directionality, strength and selectivity, have been noted as the most versatile organizing force to assemble supramolecular structures (Kitagawa & Uemura, 2005). Due to their ability of providing multi-coordination sites as well as hydrogen bonding acceptors, tetrazole and its derivatives are receiving much attention in coordination and supramolecular chemistry (Mo *et al.*, 2004; Song *et al.*, 2008; Tao *et al.*, 2008; Wang *et al.*, 2003; Wen, 2008; Wu *et al.*, 2007). Herein we report the crystal structure of an iron(II) complex of 2-pyridyl-tetrazole *HL*, [Fe(*L*)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].

In the title complex, the Fe<sup>II</sup> atom is located on a crystallographic center of inversion. It is six-coordinated by two O atoms from water molecules and four N-atom donors from two deprotonated *N,N'*-chelating *L* ligands binding *via* the pyridyl nitrogen and the tetrazole nitrogen in 1-position, in a *transoid* pseudo-octahedral geometry (Fig. 1).

Each Fe<sup>II</sup> mononuclear unit exhibits both proton donors (water molecules) and acceptors (uncoordinated N atoms on the tetrazole rings) and can therefore act as a good building unit for hydrogen bonded networks. As shown in Fig. 2 the O—H $\cdots$ N hydrogen bonds (Table 1) between tetrazole rings and coordinated water molecules link neighboring mononuclear [Fe(*L*)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] units resulting in an infinite hydrogen bonded layer running parallel to the crystallographic (100) plane. Furthermore, the crystal structure of (I) also contains intermolecular C—H $\cdots$ O (Table 1) hydrogen-bonding interactions (Desiraju & Steiner, 1999), between the *L* ligands and the coordinated water molecules that interlink the twodimensional layers to form a three dimensional supramolecular framework.

### Experimental

A solution of *HL* (0.05 mmol) in CH<sub>3</sub>OH (10 ml) in the presence of excess 2,6-dimethylpyridine (*ca* 0.05 ml for adjusting the pH value of the reaction system to basic conditions) was carefully layered on top of an aqueous solution (15 ml) of FeSO<sub>4</sub> (0.1 mmol) in a test tube. Yellow single crystals suitable for X-ray analysis appeared at the tube wall after *ca* one month at room temperature (yield ~30% based on *HL*). Elemental analysis calculated for (C<sub>12</sub>H<sub>12</sub>FeN<sub>10</sub>O<sub>2</sub>): H 3.15, C 37.52, N 36.46%; found: H 3.08, C 37.37, N 36.68%.

### Refinement

H atoms of the water molecules were located from the difference Fourier map and were allowed to ride on the O atom, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$ . The remaining H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 (aromatic), and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ .

## Figures

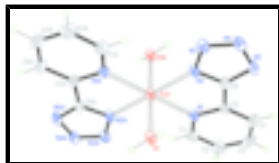


Fig. 1. The molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A are generated by the symmetry operation  $(-x, -y + 1, -z + 2)$ .

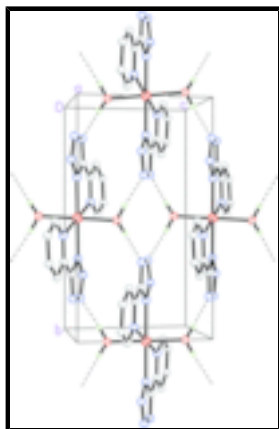


Fig. 2. Two dimensional network, parallel to the (100) plane, formed by the intermolecular O—H...N (fine dashed lines) interactions. For clarity, only H atoms involved in the interactions are shown.

## Diaquabis[5-(2-pyridyl)tetrazolato- $\kappa^2N^1, N^5$ ]iron(II)

### Crystal data

$[\text{Fe}(\text{C}_6\text{H}_4\text{N}_5)_2(\text{H}_2\text{O})_2]$

$M_r = 384.17$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 8.114\ (2)\ \text{\AA}$

$b = 12.924\ (3)\ \text{\AA}$

$c = 7.360\ (2)\ \text{\AA}$

$\beta = 96.021\ (3)^\circ$

$V = 767.5\ (3)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 392$

$D_x = 1.662\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

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

Cell parameters from 2211 reflections

$\theta = 3.0\text{--}28.3^\circ$

$\mu = 1.02\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, yellow

$0.29 \times 0.14 \times 0.11\ \text{mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ \text{K}$

$\varphi$  and  $\omega$  scans

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

$T_{\min} = 0.757, T_{\max} = 0.897$

1356 independent reflections

1204 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 3.0^\circ$

$h = -9 \rightarrow 8$

$k = -15 \rightarrow 15$

4287 measured reflections

$l = -8 \rightarrow 8$

*Refinement*

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.023$

H-atom parameters constrained

$wR(F^2) = 0.057$

$$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 0.3154P]$$

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

$S = 1.10$

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

1356 reflections

$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$

115 parameters

$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Primary atom site location: structure-invariant direct methods

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.

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.0000	0.5000	1.0000	0.02908 (12)
C1	0.3360 (2)	0.51552 (16)	0.8123 (3)	0.0456 (5)
H1	0.3306	0.4437	0.8065	0.055*
C2	0.4708 (3)	0.56508 (19)	0.7511 (3)	0.0565 (6)
H2	0.5543	0.5270	0.7050	0.068*
C3	0.4800 (3)	0.67167 (19)	0.7593 (3)	0.0539 (6)
H3	0.5708	0.7063	0.7213	0.065*
C4	0.3524 (2)	0.72590 (16)	0.8246 (3)	0.0440 (5)
H4	0.3550	0.7978	0.8296	0.053*
C5	0.2204 (2)	0.67171 (13)	0.8826 (2)	0.0318 (4)
C6	0.0757 (2)	0.72097 (12)	0.9502 (2)	0.0304 (4)
N1	0.21327 (18)	0.56715 (11)	0.87949 (19)	0.0332 (3)
N2	-0.04622 (17)	0.66384 (10)	1.00861 (18)	0.0308 (3)
N3	-0.15883 (19)	0.73201 (11)	1.0590 (2)	0.0367 (4)
N4	-0.1046 (2)	0.82582 (11)	1.0311 (2)	0.0396 (4)
N5	0.0442 (2)	0.82160 (11)	0.9625 (2)	0.0375 (4)
O1	0.13384 (15)	0.50897 (8)	1.26584 (16)	0.0340 (3)

## supplementary materials

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H11	0.1091	0.5606	1.3292	0.041*
H12	0.1461	0.4509	1.3199	0.041*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Fe1	0.0345 (2)	0.01947 (19)	0.0352 (2)	0.00073 (14)	0.01281 (15)	0.00110 (14)
C1	0.0410 (11)	0.0464 (12)	0.0517 (12)	0.0074 (9)	0.0153 (9)	0.0027 (9)
C2	0.0407 (13)	0.0745 (16)	0.0573 (13)	0.0099 (11)	0.0195 (10)	0.0056 (12)
C3	0.0357 (11)	0.0773 (17)	0.0497 (12)	-0.0136 (11)	0.0102 (9)	0.0086 (11)
C4	0.0444 (12)	0.0457 (11)	0.0423 (10)	-0.0154 (9)	0.0069 (9)	0.0037 (9)
C5	0.0352 (9)	0.0332 (10)	0.0268 (8)	-0.0052 (7)	0.0020 (7)	0.0027 (7)
C6	0.0409 (10)	0.0249 (9)	0.0253 (8)	-0.0037 (7)	0.0028 (7)	0.0007 (7)
N1	0.0343 (8)	0.0313 (8)	0.0355 (8)	0.0010 (6)	0.0099 (6)	0.0028 (6)
N2	0.0378 (8)	0.0215 (7)	0.0346 (8)	0.0018 (6)	0.0103 (6)	-0.0002 (6)
N3	0.0449 (9)	0.0274 (8)	0.0390 (8)	0.0062 (7)	0.0091 (7)	-0.0022 (6)
N4	0.0564 (10)	0.0255 (8)	0.0371 (8)	0.0046 (7)	0.0064 (7)	-0.0017 (6)
N5	0.0543 (10)	0.0223 (7)	0.0358 (8)	-0.0032 (7)	0.0040 (7)	0.0015 (6)
O1	0.0434 (7)	0.0226 (6)	0.0373 (7)	0.0035 (5)	0.0105 (5)	0.0006 (5)

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

Fe1—O1 <sup>i</sup>	2.1389 (13)	C3—H3	0.9300
Fe1—O1	2.1389 (13)	C4—C5	1.384 (2)
Fe1—N2	2.1526 (14)	C4—H4	0.9300
Fe1—N2 <sup>i</sup>	2.1526 (14)	C5—N1	1.353 (2)
Fe1—N1 <sup>i</sup>	2.2037 (14)	C5—C6	1.468 (2)
Fe1—N1	2.2037 (14)	C6—N5	1.330 (2)
C1—N1	1.336 (2)	C6—N2	1.341 (2)
C1—C2	1.383 (3)	N2—N3	1.3489 (19)
C1—H1	0.9300	N3—N4	1.313 (2)
C2—C3	1.380 (3)	N4—N5	1.358 (2)
C2—H2	0.9300	O1—H11	0.8501
C3—C4	1.378 (3)	O1—H12	0.8500
O1 <sup>i</sup> —Fe1—O1	180.0	C2—C3—H3	120.5
O1 <sup>i</sup> —Fe1—N2	90.40 (5)	C3—C4—C5	118.96 (19)
O1—Fe1—N2	89.60 (5)	C3—C4—H4	120.5
O1 <sup>i</sup> —Fe1—N2 <sup>i</sup>	89.60 (5)	C5—C4—H4	120.5
O1—Fe1—N2 <sup>i</sup>	90.40 (5)	N1—C5—C4	122.25 (17)
N2—Fe1—N2 <sup>i</sup>	180.0	N1—C5—C6	113.85 (14)
O1 <sup>i</sup> —Fe1—N1 <sup>i</sup>	90.12 (5)	C4—C5—C6	123.89 (16)
O1—Fe1—N1 <sup>i</sup>	89.88 (5)	N5—C6—N2	111.28 (15)
N2—Fe1—N1 <sup>i</sup>	103.24 (5)	N5—C6—C5	127.83 (15)
N2 <sup>i</sup> —Fe1—N1 <sup>i</sup>	76.76 (5)	N2—C6—C5	120.89 (14)
O1 <sup>i</sup> —Fe1—N1	89.89 (5)	C1—N1—C5	118.22 (16)
O1—Fe1—N1	90.11 (5)	C1—N1—Fe1	126.83 (13)

N2—Fe1—N1	76.76 (5)	C5—N1—Fe1	114.89 (11)
N2 <sup>i</sup> —Fe1—N1	103.24 (5)	C6—N2—N3	105.81 (13)
N1 <sup>i</sup> —Fe1—N1	180.000 (1)	C6—N2—Fe1	113.29 (11)
N1—C1—C2	122.33 (19)	N3—N2—Fe1	140.87 (11)
N1—C1—H1	118.8	N4—N3—N2	108.19 (14)
C2—C1—H1	118.8	N3—N4—N5	110.28 (13)
C3—C2—C1	119.3 (2)	C6—N5—N4	104.44 (14)
C3—C2—H2	120.4	Fe1—O1—H11	114.7
C1—C2—H2	120.4	Fe1—O1—H12	113.8
C4—C3—C2	118.92 (19)	H11—O1—H12	117.3
C4—C3—H3	120.5		
N1—C1—C2—C3	0.0 (3)	N2—Fe1—N1—C5	5.08 (12)
C1—C2—C3—C4	-1.4 (3)	N2 <sup>i</sup> —Fe1—N1—C5	-174.92 (12)
C2—C3—C4—C5	1.0 (3)	N5—C6—N2—N3	0.17 (19)
C3—C4—C5—N1	0.8 (3)	C5—C6—N2—N3	-179.46 (14)
C3—C4—C5—C6	-178.37 (17)	N5—C6—N2—Fe1	-178.30 (11)
N1—C5—C6—N5	-177.20 (16)	C5—C6—N2—Fe1	2.07 (19)
C4—C5—C6—N5	2.1 (3)	O1 <sup>i</sup> —Fe1—N2—C6	-93.43 (12)
N1—C5—C6—N2	2.4 (2)	O1—Fe1—N2—C6	86.57 (12)
C4—C5—C6—N2	-178.36 (16)	N1 <sup>i</sup> —Fe1—N2—C6	176.36 (11)
C2—C1—N1—C5	1.8 (3)	N1—Fe1—N2—C6	-3.64 (11)
C2—C1—N1—Fe1	-175.34 (15)	O1 <sup>i</sup> —Fe1—N2—N3	88.90 (18)
C4—C5—N1—C1	-2.2 (3)	O1—Fe1—N2—N3	-91.10 (18)
C6—C5—N1—C1	177.07 (16)	N1 <sup>i</sup> —Fe1—N2—N3	-1.31 (18)
C4—C5—N1—Fe1	175.23 (13)	N1—Fe1—N2—N3	178.69 (18)
C6—C5—N1—Fe1	-5.48 (18)	C6—N2—N3—N4	-0.01 (18)
O1 <sup>i</sup> —Fe1—N1—C1	-87.30 (16)	Fe1—N2—N3—N4	177.76 (13)
O1—Fe1—N1—C1	92.70 (16)	N2—N3—N4—N5	-0.15 (19)
N2—Fe1—N1—C1	-177.74 (17)	N2—C6—N5—N4	-0.26 (19)
N2 <sup>i</sup> —Fe1—N1—C1	2.26 (17)	C5—C6—N5—N4	179.35 (16)
O1 <sup>i</sup> —Fe1—N1—C5	95.51 (12)	N3—N4—N5—C6	0.25 (19)
O1—Fe1—N1—C5	-84.49 (12)		

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

*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>
O1—H11 $\cdots$ N5 <sup>ii</sup>	0.85	1.91	2.764 (2)	177
O1—H12 $\cdots$ N4 <sup>iii</sup>	0.85	2.00	2.823 (2)	162
C2—H2 $\cdots$ O1 <sup>iv</sup>	0.93	2.56	3.362 (3)	145

Symmetry codes: (ii)  $x, -y+3/2, z+1/2$ ; (iii)  $-x, y-1/2, -z+5/2$ ; (iv)  $-x+1, -y+1, -z+2$ .

Fig. 1

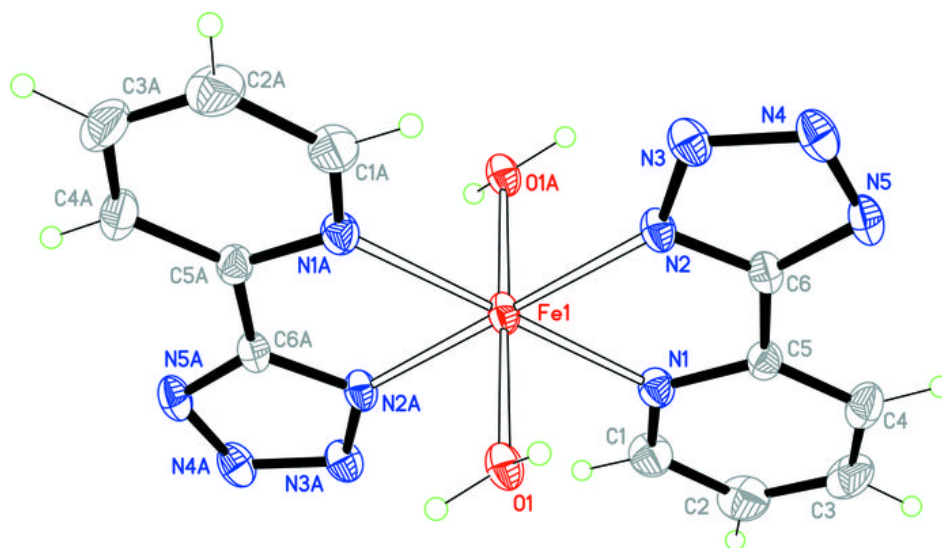


Fig. 2

