

# catena-Poly[[[diaquairon(II)]- $\mu$ -pyridine-2,5-dicarboxylato-[tetraaquairon(II)]- $\mu$ -pyridine-2,5-dicarboxylato] tetrahydrate]

Hai-Yun Xu,\* Huai-Ling Ma, Mao-Tian Xu, Wen-Xian Zhao and Bao-Guo Guo

Department of Chemistry, Shangqiu Normal College, 476000 Shangqiu, Henan, People's Republic of China

Correspondence e-mail: xuhyun@yahoo.cn

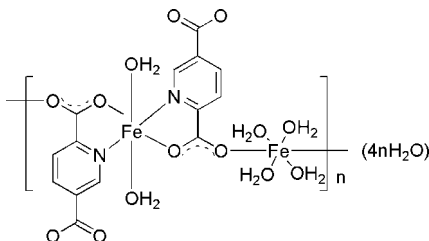
Received 22 December 2007; accepted 20 January 2008

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.043;  $wR$  factor = 0.125; data-to-parameter ratio = 12.0.

In the crystal structure of the title compound,  $\{[\text{Fe}_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}\}_n$ , there are two types of coordination for the  $\text{Fe}^{\text{II}}$  atoms. One  $\text{Fe}^{\text{II}}$  atom is in a distorted octahedral  $\text{N}_2\text{O}_4$  environment, with two chelating rings from the pyridine-dicarboxylate ligands and two O atoms from the water molecules, while the other is in a distorted octahedral  $\text{O}_6$  environment with two O atoms from the pyridinedicarboxylate ligands and four O atoms from the water molecules. Both  $\text{Fe}^{\text{II}}$  atoms lie on crystallographic centers of symmetry. The complex possesses an infinite chain structure running along the [101] direction. These chains are interconnected by the uncoordinated water molecules through  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds.

## Related literature

For related literature, see: Hill (1998); Liang *et al.* (2001); Mitzi *et al.* (1995); Moler *et al.* (2001); Zeng *et al.* (2003); Xu *et al.* (2004).



## Experimental

### Crystal data

$[\text{Fe}_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}$   
 $M_r = 622.06$   
 Triclinic,  $P\bar{1}$

$a = 7.098$  (3) Å  
 $b = 8.922$  (3) Å  
 $c = 9.720$  (2) Å

$\alpha = 90.942$  (6)°  
 $\beta = 101.375$  (6)°  
 $\gamma = 108.112$  (5)°  
 $V = 571.6$  (3) Å<sup>3</sup>  
 $Z = 1$

Mo  $K\alpha$  radiation  
 $\mu = 1.36$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.21 \times 0.20 \times 0.18$  mm

### Data collection

Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.763$ ,  $T_{\text{max}} = 0.792$

2866 measured reflections  
 1989 independent reflections  
 1757 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.062$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.124$   
 $S = 1.06$   
 1989 reflections

166 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.65$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.60$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                                       | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|-------|--------------|--------------|----------------|
| $\text{O9}-\text{H9B} \cdots \text{O8}$              | 0.85  | 2.32         | 3.159 (6)    | 171            |
| $\text{O9}-\text{H9A} \cdots \text{O6}^{\text{i}}$   | 0.85  | 2.06         | 2.849 (5)    | 154            |
| $\text{O8}-\text{H8B} \cdots \text{O5}^{\text{ii}}$  | 0.85  | 2.55         | 3.204 (4)    | 134            |
| $\text{O8}-\text{H8B} \cdots \text{O4}^{\text{iii}}$ | 0.85  | 2.51         | 3.171 (4)    | 136            |
| $\text{O8}-\text{H8A} \cdots \text{O3}$              | 0.85  | 2.55         | 3.177 (4)    | 132            |
| $\text{O8}-\text{H8A} \cdots \text{O2}$              | 0.85  | 2.44         | 3.201 (4)    | 149            |
| $\text{O5}-\text{H5B} \cdots \text{O7}^{\text{i}}$   | 0.85  | 2.22         | 2.706 (3)    | 116            |
| $\text{O2}-\text{H2B} \cdots \text{O9}^{\text{iii}}$ | 0.85  | 1.94         | 2.657 (5)    | 141            |
| $\text{O2}-\text{H2A} \cdots \text{O4}^{\text{iv}}$  | 0.85  | 1.99         | 2.758 (3)    | 150            |
| $\text{O1}-\text{H1B} \cdots \text{O6}^{\text{v}}$   | 0.85  | 1.92         | 2.715 (3)    | 156            |
| $\text{O1}-\text{H1A} \cdots \text{O8}^{\text{ii}}$  | 0.85  | 2.06         | 2.822 (4)    | 148            |

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); 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.

The authors thank the Natural Science Foundation of Henan Province (No. 0511020300) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2270).

## References

- Hill, C. L. (1998). *Chem. Rev.* **98**, 1–390.  
 Liang, Y.-C., Hong, M.-C., Su, W.-P., Cao, R. & Zhang, W.-J. (2001). *Inorg. Chem.* **40**, 4574–4582.  
 Mitzi, D. B., Wang, S., Field, C. A., Chess, C. A. & Guloy, A. M. (1995). *Science*, **267**, 1473–1476.  
 Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Xu, Y., Han, L., Lin, Z.-Z., Liu, C.-P., Yuan, D.-Q., Zhou, Y.-F. & Hong, M.-C. (2004). *Eur. J. Inorg. Chem.* pp. 4457–4462.  
 Zeng, M.-H., Gao, S., Yu, X.-L. & Chen, X.-M. (2003). *New J. Chem.* **27**, 1599–1602.

**supplementary materials**

*Acta Cryst.* (2008). E64, m413 [ doi:10.1107/S1600536808002043 ]

***catena*-Poly[[[diaquairon(II)]- $\mu$ -pyridine-2,5-dicarboxylato-[tetraaquairon(II)]- $\mu$ -pyridine-2,5-dicarboxylato] tetrahydrate]**

**H.-Y. Xu, H.-L. Ma, M.-T. Xu, W.-X. Zhao and B.-G. Guo**

**Comment**

Extended frameworks of coordination polymers based on transition metal ions and multifunctional bridging ligands are currently of great interest because of their intriguing topologies and their potential applications (Hill, 1998; Moler *et al.*, 2001; Mitzi *et al.*, 1995). Multi-carboxylate ligands may exhibit various coordination modes to furnish various structures. Recently, many transition metal-organic polymers constructed with multi-carboxylate ligands show various of novel topology and potential applications in catalysis, materials chemistry and biochemistry (Zeng *et al.*, 2003; Xu *et al.*, 2004; Liang *et al.*, 2001). Pyridine-2,5-dicarboxylic acid (H<sub>2</sub>pydc) has unique features because of the presence of two carboxylate groups (O donor atoms) and the pyridine ring (N donor atom), which aids to increase the dimensionality of the assembled covalent network. Therefore, it is most likely that pydc will form low symmetric structures with metals. In this paper, we report the preparation and crystal structure of a new three-dimensional supramolecular complex [Fe<sub>2</sub>(pydc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O, (I).

In the complex, (I), there exist two types of coordination geometries around the Fe(II) ions. The Fe1 ions are hexacoordinated in a N<sub>2</sub>O<sub>4</sub> environment with two chelating rings from the pydc ligands and two oxygen atoms from the water molecules. The Fe2 ions are also hexacoordinated in an O<sub>6</sub> environment with two oxygen atoms from the pydc ligands and four oxygen atoms from the water molecules. All Fe atoms lie on a crystallographic center of symmetry and the ligand lies on a crystallographic twofold axis. A perspective view of the local coordination environments around the Fe(II) atoms of (I) is shown in Fig. 1. For Fe1 and Fe2, the bond distances of Fe—O (water oxygen), 2.071–2.100 Å, are similar with those of Fe—O (carboxylate oxygen), 2.058–2.080 Å. As presented in Fig. 2, the two kinds of geometries around Fe(II) ions are arranged alternatively to give the one-dimensional polymeric chain. Interestingly, all Fe atoms of one polymeric chain are situated on one line and the neighboring Fe(II) atoms are *syn*-anti carboxylato bridged with the distance of 5.423 Å. These chains are interconnected by the uncoordinated water molecules through O—H...O hydrogen-bonding interactions and form a two-dimensional layer structure. A three-dimensional supramolecular network is obtained through O—H...O hydrogen-bonding interactions in the layers.

**Experimental**

A mixture of H<sub>2</sub>pydc (0.34 g, 2 mmol), KOH (0.23 g, 4 mmol) and FeSO<sub>4</sub>·7H<sub>2</sub>O (0.55 g, 2 mmol) in 15 ml of MeOH/H<sub>2</sub>O (v/v, 1:1) was sealed in a 25-ml stainless-steel reactor with a teflon liner and was heated at 453 K for 72 h under autogenous pressure. Slow cooling to room temperature yielded 0.36 g (yield 40%) of block red crystals. Anal. Calc. for C<sub>7</sub>H<sub>13</sub>NO<sub>9</sub>Fe (%): C 27.03, H 4.21, N 4.50. Found (%): C 27.14, H 4.46, N 4.36.

**Refinement**

The H atoms were included in the riding-model approximation with C—H = 0.93 Å and O—H = 0.85 Å, and with  $U_{iso}(H) = 1.2U_{eq}(C, O)$ . Hydroxyl H atoms were allowed to rotate to best fit the experimental electron density.

## Figures

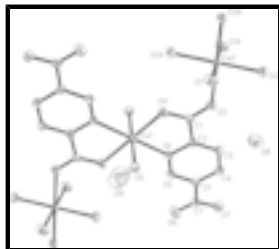


Fig. 1. Part of the polymeric structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. The H atoms are omitted for clarity. The suffix A corresponds to symmetry code (2 - x, 1 - y, 1 - z).

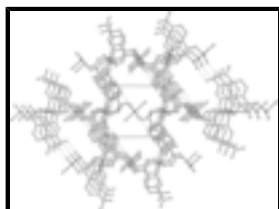


Fig. 2. The three-dimensional supramolecular structure of the title compound. Hydrogen bonds are shown by dashed lines.

## **catena-Poly[[[diaquairon(II)]- $\mu$ -pyridine-2,5-dicarboxylato- [tetraaquairon(II)]- $\mu$ -pyridine-2,5-dicarboxylato] tetrahydrate]**

### Crystal data

[Fe<sub>2</sub>(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] $\cdot$ 4H<sub>2</sub>O

$M_r$  = 622.06

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

$a$  = 7.098 (3) Å

$b$  = 8.922 (3) Å

$c$  = 9.720 (2) Å

$\alpha$  = 90.942 (6)°

$\beta$  = 101.375 (6)°

$\gamma$  = 108.112 (5)°

$V$  = 571.6 (3) Å<sup>3</sup>

$Z$  = 1

$F_{000}$  = 320

$D_x$  = 1.807 Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 714 reflections

$\theta$  = 2.4–28.2°

$\mu$  = 1.36 mm<sup>-1</sup>

$T$  = 298 (2) K

Block, red

0.21  $\times$  0.20  $\times$  0.18 mm

### Data collection

Bruker SMART APEX CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T$  = 298(2) K

$\phi$  and  $\omega$  scans

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

$T_{\min}$  = 0.763,  $T_{\max}$  = 0.792

2866 measured reflections

1989 independent reflections

1757 reflections with  $I > 2\sigma(I)$

$R_{\text{int}}$  = 0.062

$\theta_{\text{max}}$  = 25.0°

$\theta_{\text{min}}$  = 2.1°

$h$  = -8 $\rightarrow$ 6

$k$  = -10 $\rightarrow$ 10

$l$  = -11 $\rightarrow$ 10

Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.043$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.124$  | $w = 1/[\sigma^2(F_o^2) + (0.081P)^2 + 0.2244P]$         |
| $S = 1.06$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 1989 reflections   | $(\Delta/\sigma)_{\max} < 0.001$                         |
| 166 parameters   | $\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$    |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$   |
|  | 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.

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

|     | $x$        | $y$         | $z$         | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|-------------|-------------|----------------------------------|
| Fe1 | 0.5000     | 0.5000      | 0.0000      | 0.0222 (2)                       |
| Fe2 | 1.0000     | 0.5000      | 0.5000      | 0.0258 (2)                       |
| C1  | 0.6446 (4) | 0.3738 (3)  | 0.2523 (3)  | 0.0270 (6)                       |
| C2  | 0.4924 (4) | 0.2309 (3)  | 0.1667 (3)  | 0.0275 (6)                       |
| C3  | 0.4514 (5) | 0.0824 (3)  | 0.2147 (3)  | 0.0330 (7)                       |
| H3  | 0.5126     | 0.0679      | 0.3050      | 0.040*                           |
| C4  | 0.3189 (5) | -0.0438 (3) | 0.1270 (3)  | 0.0331 (7)                       |
| H4  | 0.2889     | -0.1449     | 0.1579      | 0.040*                           |
| C5  | 0.2302 (4) | -0.0216 (3) | -0.0065 (3) | 0.0278 (6)                       |
| C6  | 0.2767 (4) | 0.1328 (3)  | -0.0474 (3) | 0.0279 (6)                       |
| H6  | 0.2161     | 0.1496      | -0.1372     | 0.033*                           |
| C7  | 0.0905 (4) | -0.1587 (4) | -0.1093 (3) | 0.0318 (7)                       |
| N1  | 0.4039 (3) | 0.2565 (3)  | 0.0369 (3)  | 0.0261 (5)                       |
| O1  | 0.8315 (4) | 0.6187 (3)  | 0.5803 (3)  | 0.0448 (6)                       |
| H1A | 0.7132     | 0.6145      | 0.5373      | 0.054*                           |
| H1B | 0.9150     | 0.7017      | 0.6279      | 0.054*                           |
| O2  | 0.9411 (3) | 0.3350 (3)  | 0.6494 (2)  | 0.0425 (6)                       |
| H2B | 0.8576     | 0.2419      | 0.6286      | 0.051*                           |

## supplementary materials

---

|     |            |             |             |             |
|-----|------------|-------------|-------------|-------------|
| H2A | 1.0460     | 0.3570      | 0.7156      | 0.051*      |
| O3  | 0.7348 (3) | 0.3533 (2)  | 0.3701 (2)  | 0.0352 (5)  |
| O4  | 0.6748 (3) | 0.5047 (2)  | 0.1970 (2)  | 0.0334 (5)  |
| O5  | 0.2787 (3) | 0.5429 (3)  | 0.0954 (2)  | 0.0361 (5)  |
| H5A | 0.1792     | 0.5354      | 0.0276      | 0.043*      |
| H5B | 0.2288     | 0.4806      | 0.1537      | 0.043*      |
| O6  | 0.0097 (4) | -0.1287 (3) | -0.2262 (3) | 0.0473 (6)  |
| O7  | 0.0653 (4) | -0.2939 (3) | -0.0688 (3) | 0.0430 (6)  |
| O8  | 0.4663 (4) | 0.2880 (4)  | 0.6019 (3)  | 0.0640 (8)  |
| H8B | 0.4601     | 0.3105      | 0.6859      | 0.077*      |
| H8A | 0.5871     | 0.3270      | 0.5904      | 0.077*      |
| O9  | 0.1591 (7) | -0.0327 (5) | 0.4428 (6)  | 0.1112 (15) |
| H9B | 0.2489     | 0.0471      | 0.4912      | 0.133*      |
| H9A | 0.1463     | 0.0205      | 0.3718      | 0.133*      |

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

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|-------------|--------------|--------------|
| Fe1 | 0.0226 (3)  | 0.0153 (3)  | 0.0243 (3)  | 0.0050 (2)  | -0.0034 (2)  | -0.0004 (2)  |
| Fe2 | 0.0269 (4)  | 0.0200 (3)  | 0.0247 (3)  | 0.0056 (2)  | -0.0043 (2)  | -0.0003 (2)  |
| C1  | 0.0253 (14) | 0.0248 (14) | 0.0301 (15) | 0.0088 (12) | 0.0027 (11)  | -0.0011 (11) |
| C2  | 0.0261 (14) | 0.0260 (14) | 0.0284 (15) | 0.0082 (12) | 0.0021 (11)  | -0.0013 (11) |
| C3  | 0.0369 (17) | 0.0282 (15) | 0.0302 (16) | 0.0083 (13) | 0.0019 (13)  | 0.0059 (12)  |
| C4  | 0.0357 (16) | 0.0215 (14) | 0.0403 (17) | 0.0090 (13) | 0.0041 (13)  | 0.0059 (12)  |
| C5  | 0.0251 (14) | 0.0225 (14) | 0.0355 (16) | 0.0079 (12) | 0.0054 (12)  | 0.0003 (12)  |
| C6  | 0.0277 (15) | 0.0226 (13) | 0.0314 (15) | 0.0088 (12) | 0.0006 (12)  | -0.0004 (11) |
| C7  | 0.0242 (14) | 0.0258 (15) | 0.0432 (18) | 0.0083 (12) | 0.0023 (13)  | -0.0049 (13) |
| N1  | 0.0259 (12) | 0.0187 (11) | 0.0308 (13) | 0.0071 (10) | -0.0003 (10) | 0.0014 (9)   |
| O1  | 0.0403 (13) | 0.0383 (13) | 0.0492 (14) | 0.0153 (11) | -0.0089 (11) | -0.0151 (11) |
| O2  | 0.0407 (13) | 0.0349 (12) | 0.0411 (13) | 0.0033 (10) | -0.0026 (10) | 0.0113 (10)  |
| O3  | 0.0366 (12) | 0.0278 (11) | 0.0308 (11) | 0.0047 (9)  | -0.0072 (9)  | 0.0010 (8)   |
| O4  | 0.0367 (12) | 0.0228 (10) | 0.0314 (11) | 0.0071 (9)  | -0.0096 (9)  | -0.0011 (8)  |
| O5  | 0.0320 (11) | 0.0320 (12) | 0.0439 (13) | 0.0104 (10) | 0.0072 (10)  | 0.0046 (10)  |
| O6  | 0.0572 (15) | 0.0302 (12) | 0.0434 (14) | 0.0136 (11) | -0.0134 (11) | -0.0088 (10) |
| O7  | 0.0367 (13) | 0.0198 (11) | 0.0632 (16) | 0.0040 (10) | -0.0020 (11) | -0.0008 (10) |
| O8  | 0.0469 (16) | 0.075 (2)   | 0.066 (2)   | 0.0196 (16) | 0.0038 (14)  | 0.0019 (16)  |
| O9  | 0.116 (3)   | 0.054 (2)   | 0.163 (5)   | 0.019 (2)   | 0.041 (3)    | 0.000 (2)    |

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

|                      |           |       |           |
|----------------------|-----------|-------|-----------|
| Fe1—O4               | 2.058 (2) | C4—C5 | 1.372 (4) |
| Fe1—O4 <sup>i</sup>  | 2.058 (2) | C4—H4 | 0.9300    |
| Fe1—O5 <sup>i</sup>  | 2.100 (2) | C5—C6 | 1.397 (4) |
| Fe1—O5               | 2.100 (2) | C5—C7 | 1.515 (4) |
| Fe1—N1               | 2.125 (2) | C6—N1 | 1.328 (4) |
| Fe1—N1 <sup>i</sup>  | 2.125 (2) | C6—H6 | 0.9300    |
| Fe2—O1               | 2.071 (2) | C7—O6 | 1.241 (4) |
| Fe2—O1 <sup>ii</sup> | 2.071 (2) | C7—O7 | 1.245 (4) |

|  |             |            |             |
|--|-------------|------------|-------------|
| Fe2—O3 <sup>ii</sup>                   | 2.080 (2)   | O1—H1A     | 0.8499      |
| Fe2—O3                                 | 2.080 (2)   | O1—H1B     | 0.8499      |
| Fe2—O2                                 | 2.092 (2)   | O2—H2B     | 0.8500      |
| Fe2—O2 <sup>ii</sup>                   | 2.092 (2)   | O2—H2A     | 0.8501      |
| C1—O3                                  | 1.242 (3)   | O5—H5A     | 0.8499      |
| C1—O4                                  | 1.268 (4)   | O5—H5B     | 0.8500      |
| C1—C2                                  | 1.496 (4)   | O8—H8B     | 0.8500      |
| C2—N1                                  | 1.351 (4)   | O8—H8A     | 0.8499      |
| C2—C3                                  | 1.376 (4)   | O9—H9B     | 0.8499      |
| C3—C4                                  | 1.368 (4)   | O9—H9A     | 0.8500      |
| C3—H3                                  | 0.9300      |            |             |
| O4—Fe1—O4 <sup>i</sup>                 | 180.00 (11) | N1—C2—C1   | 115.5 (2)   |
| O4—Fe1—O5 <sup>i</sup>                 | 90.89 (9)   | C3—C2—C1   | 122.3 (3)   |
| O4 <sup>i</sup> —Fe1—O5 <sup>i</sup>   | 89.11 (9)   | C4—C3—C2   | 118.8 (3)   |
| O4—Fe1—O5                              | 89.11 (9)   | C4—C3—H3   | 120.6       |
| O4 <sup>i</sup> —Fe1—O5                | 90.89 (9)   | C2—C3—H3   | 120.6       |
| O5 <sup>i</sup> —Fe1—O5                | 180.00 (6)  | C3—C4—C5   | 120.2 (3)   |
| O4—Fe1—N1                              | 79.00 (8)   | C3—C4—H4   | 119.9       |
| O4 <sup>i</sup> —Fe1—N1                | 101.00 (8)  | C5—C4—H4   | 119.9       |
| O5 <sup>i</sup> —Fe1—N1                | 88.20 (9)   | C4—C5—C6   | 117.9 (3)   |
| O5—Fe1—N1                              | 91.80 (9)   | C4—C5—C7   | 121.9 (3)   |
| O4—Fe1—N1 <sup>i</sup>                 | 101.00 (8)  | C6—C5—C7   | 120.2 (3)   |
| O4 <sup>i</sup> —Fe1—N1 <sup>i</sup>   | 79.00 (8)   | N1—C6—C5   | 122.5 (3)   |
| O5 <sup>i</sup> —Fe1—N1 <sup>i</sup>   | 91.80 (9)   | N1—C6—H6   | 118.7       |
| O5—Fe1—N1 <sup>i</sup>                 | 88.20 (9)   | C5—C6—H6   | 118.7       |
| N1—Fe1—N1 <sup>i</sup>                 | 180.0       | O6—C7—O7   | 125.1 (3)   |
| O1—Fe2—O1 <sup>ii</sup>                | 180.00 (12) | O6—C7—C5   | 118.1 (3)   |
| O1—Fe2—O3 <sup>ii</sup>                | 90.59 (9)   | O7—C7—C5   | 116.8 (3)   |
| O1 <sup>ii</sup> —Fe2—O3 <sup>ii</sup> | 89.41 (9)   | C6—N1—C2   | 118.4 (2)   |
| O1—Fe2—O3                              | 89.41 (9)   | C6—N1—Fe1  | 129.8 (2)   |
| O1 <sup>ii</sup> —Fe2—O3               | 90.59 (9)   | C2—N1—Fe1  | 111.81 (18) |
| O3 <sup>ii</sup> —Fe2—O3               | 180.0       | Fe2—O1—H1A | 122.3       |
| O1—Fe2—O2                              | 89.15 (10)  | Fe2—O1—H1B | 107.1       |
| O1 <sup>ii</sup> —Fe2—O2               | 90.85 (10)  | H1A—O1—H1B | 122.4       |
| O3 <sup>ii</sup> —Fe2—O2               | 93.74 (9)   | Fe2—O2—H2B | 122.9       |
| O3—Fe2—O2                              | 86.26 (9)   | Fe2—O2—H2A | 108.0       |
| O1—Fe2—O2 <sup>ii</sup>                | 90.85 (10)  | H2B—O2—H2A | 122.9       |
| O1 <sup>ii</sup> —Fe2—O2 <sup>ii</sup> | 89.15 (10)  | C1—O3—Fe2  | 129.74 (18) |
| O3 <sup>ii</sup> —Fe2—O2 <sup>ii</sup> | 86.26 (9)   | C1—O4—Fe1  | 116.24 (18) |
| O3—Fe2—O2 <sup>ii</sup>                | 93.74 (9)   | Fe1—O5—H5A | 104.8       |
| O2—Fe2—O2 <sup>ii</sup>                | 180.0       | Fe1—O5—H5B | 119.7       |
| O3—C1—O4                               | 125.5 (3)   | H5A—O5—H5B | 105.0       |
| O3—C1—C2                               | 117.1 (2)   | H8B—O8—H8A | 110.3       |

## supplementary materials

---

|          |           |            |      |
|----------|-----------|------------|------|
| O4—C1—C2 | 117.3 (2) | H9B—O9—H9A | 91.5 |
| N1—C2—C3 | 122.2 (3) |            |      |

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

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

| $D-H\cdots A$                     | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| O9—H9B $\cdots$ O8                | 0.85  | 2.32        | 3.159 (6)   | 171           |
| O9—H9A $\cdots$ O6 <sup>iii</sup> | 0.85  | 2.06        | 2.849 (5)   | 154           |
| O8—H8B $\cdots$ O5 <sup>iv</sup>  | 0.85  | 2.55        | 3.204 (4)   | 134           |
| O8—H8B $\cdots$ O4 <sup>iv</sup>  | 0.85  | 2.51        | 3.171 (4)   | 136           |
| O8—H8A $\cdots$ O3                | 0.85  | 2.55        | 3.177 (4)   | 132           |
| O8—H8A $\cdots$ O2                | 0.85  | 2.44        | 3.201 (4)   | 149           |
| O5—H5B $\cdots$ O7 <sup>iii</sup> | 0.85  | 2.22        | 2.706 (3)   | 116           |
| O2—H2B $\cdots$ O9 <sup>v</sup>   | 0.85  | 1.94        | 2.657 (5)   | 141           |
| O2—H2A $\cdots$ O4 <sup>ii</sup>  | 0.85  | 1.99        | 2.758 (3)   | 150           |
| O1—H1B $\cdots$ O6 <sup>vi</sup>  | 0.85  | 1.92        | 2.715 (3)   | 156           |
| O1—H1A $\cdots$ O8 <sup>iv</sup>  | 0.85  | 2.06        | 2.822 (4)   | 148           |

Symmetry codes: (iii)  $-x, -y, -z$ ; (iv)  $-x+1, -y+1, -z+1$ ; (v)  $-x+1, -y, -z+1$ ; (ii)  $-x+2, -y+1, -z+1$ ; (vi)  $x+1, y+1, z+1$ .

Fig. 1

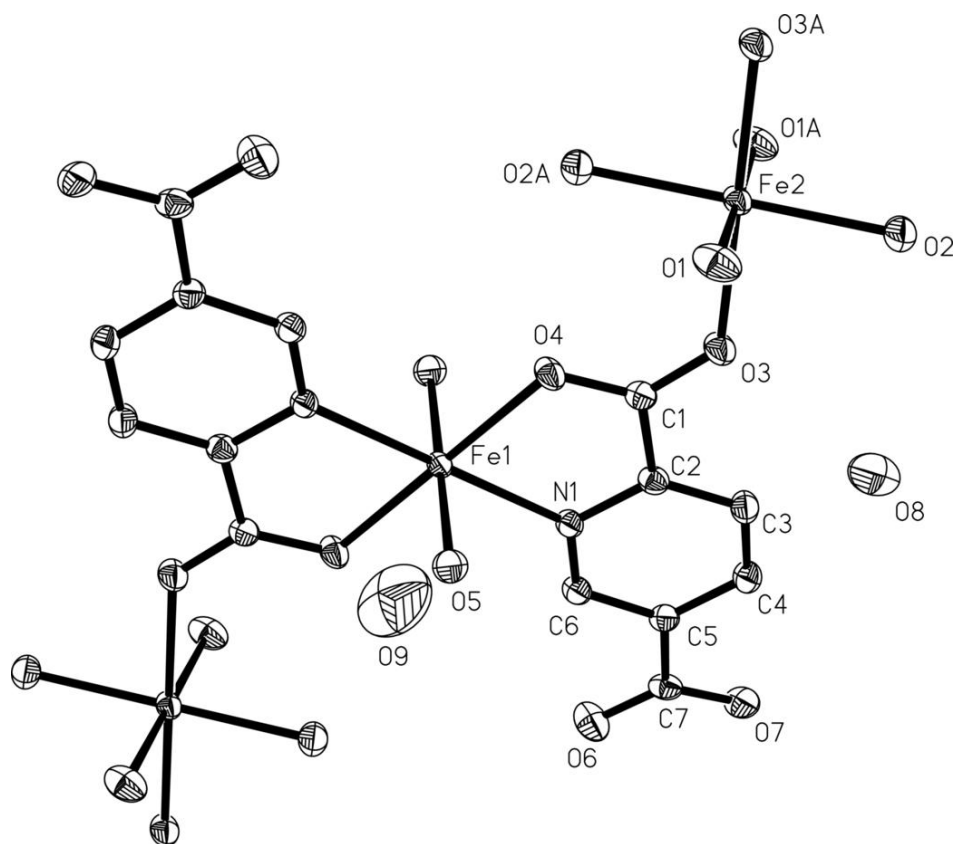


Fig. 2

