

2-Aminopyridinium bis(pyridine-2,6-dicarboxylato)ferrate(III)

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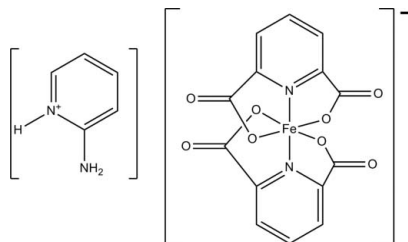
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.086; data-to-parameter ratio = 16.6.

In the title compound, $(\text{C}_5\text{H}_7\text{N}_2)[\text{Fe}(\text{C}_7\text{H}_3\text{NO}_4)_2]$ or $[2\text{-apyH}][\text{Fe}(\text{pydc})_2]$, the asymmetric unit contains an $[\text{Fe}(\text{pydc})_2]^-$ (pydc is pyridine-2,6-dicarboxylate) anion and a protonated 2-aminopyridine cation ($[2\text{-apyH}]^+$). The complex anion contains an Fe^{III} atom within a distorted octahedral FeN_2O_4 coordination geometry. $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding, offset $\pi-\pi$ stacking [centroid-centroid distance = 3.805 (13) Å] and $\text{C}=\text{O}\cdots\pi$ interactions [3.494 (14) Å] generate a three-dimensional network structure.

Related literature

For related structures, see: Mirzaei *et al.* (2011); Eshtiagh-Hosseini *et al.* (2010, 2011); Hseu *et al.* (1991); Marsh (1993); Aghabozorg, Nemati *et al.* (2007); Aghabozorg, Sadrkhanlou *et al.* (2007); Soleimannejad *et al.* (2010). For details on the importance of coordinative covalent bonds and weak intermolecular forces in forming extended organized networks, see: Steiner (2002). For graph-set analysis of hydrogen-bonding patterns, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$(\text{C}_5\text{H}_7\text{N}_2)[\text{Fe}(\text{C}_7\text{H}_3\text{NO}_4)_2]$
 $M_r = 481.18$
 Orthorhombic, $Pbca$
 $a = 7.9288$ (10) Å

$b = 15.881$ (2) Å
 $c = 30.069$ (4) Å
 $V = 3786.2$ (8) Å³
 $Z = 8$

Mo $K\alpha$ radiation
 $\mu = 0.86$ mm⁻¹

$T = 100$ K
 $0.34 \times 0.25 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: numerical (SADABS; Sheldrick, 2009)
 $T_{\text{min}} = 0.696$, $T_{\text{max}} = 0.932$

62788 measured reflections
 5007 independent reflections
 4354 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.086$
 $S = 1.05$
 5007 reflections
 301 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N3}-\text{H3A}\cdots\text{O2}^{\text{i}}$ | 0.85 (2) | 1.99 (2) | 2.7786 (18) | 153 (2) |
| $\text{N4}-\text{H4A}\cdots\text{O2}^{\text{i}}$ | 0.91 (3) | 2.07 (3) | 2.862 (2) | 145 (2) |
| $\text{N4}-\text{H4B}\cdots\text{O6}^{\text{ii}}$ | 0.83 (2) | 1.98 (2) | 2.8045 (19) | 171 (2) |
| $\text{C3}-\text{H3}\cdots\text{O4}^{\text{ii}}$ | 0.95 | 2.44 | 3.3466 (19) | 159 |
| $\text{C12}-\text{H12}\cdots\text{O5}^{\text{iii}}$ | 0.95 | 2.43 | 3.281 (2) | 150 |
| $\text{C10}-\text{H10}\cdots\text{O1}^{\text{iv}}$ | 0.95 | 2.58 | 3.2398 (19) | 127 |

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2009); 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: RZ2696).

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supplementary materials

Acta Cryst. (2012). E68, m174 [doi:10.1107/S1600536812001493]

2-Aminopyridinium bis(pyridine-2,6-dicarboxylato)ferrate(III)

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Comment

For the synthesis of supramolecular systems, coordinative covalent bonds and weak intermolecular forces are important to the assembly into extended organized networks (Steiner, 2002). Our research group has worked on the synthesis of supramolecular systems including proton transfer compounds and their complexes and are exploring the role of non-covalent interactions such as hydrogen bonding, ion pairing and π - π stacking in constructing the supramolecular crystalline compounds and their metal complexes (Mirzaei *et al.*, 2011; Eshtiagh-Hosseini *et al.*, 2011, Eshtiagh-Hosseini, *et al.*, 2010).

The asymmetric unit of the title compound (I) is shown in Fig. 1. The Fe atom is hexa-coordinated by two N and four O atoms from two (pydc)²⁻ ions resulting in a distorted octahedral coordination environment. Although it would be reasonable to consider O1, O3, O5, and O7 as the equatorial "plane" and the N1 and N2 atoms to occupy the apical positions, the geometric constraints of the pydc²⁻ ligand generate a considerable tetrahedral distortion of this "plane" as seen from the angles O1–Fe1–O3 and O5–Fe1–O7 which are, respectively 150.46 (5)° and 151.47 (5)°. Although the O1–Fe1–O3 and O5–Fe1–O7 planes are close to being orthogonal (dihedral angle = 88.49 (7)°), the remainder of the ligands are noticeably less so. In particular, the ligand containing N1 is folded along the O1...O3 line by 30.4 (1)° which is likely caused by a close contact with the carbonyl group containing O8 in the anion at 1 + x, y, z. This distortion is the largest of all those found in the related complexes [Cat][Fe(py-2,6-dc)₂] (Cat = (H₅O₂) (Hseu *et al.*, 1991, Marsh *et al.*, 1993), 2,9-dimethyl-1,10-phenanthroline (Aghabozorg, Sadrkhanlou *et al.*, 2007), piperazinium (Aghabozorg, Nemati *et al.*, 2007), 4,4'-bipyridinium (Soleimannejad *et al.*, 2010), 2-aminopyrimidinium (Eshtiagh-Hosseini *et al.*, 2011)).

The solid state architecture of I is generated *via* intermolecular N–H...O and C–H...O hydrogen bonding (Table 1 and Fig. 2) having the graph-set motifs $R_4^4(24)$ and $R_2^1(6)$ as well as offset π - π stacking interactions between the pyridine unit containing N2 and the cation at 1 - x, -y, 1 - z (centroid-centroid distance = 3.805 (13) Å) and a C14=O8... π interaction with the centroid of the pyridine ring containing N1 (3.494 (14) Å).

Experimental

A solution of 2-aminopyridine (0.06 g, 0.60 mmol) and pyridine-2,6-dicarboxylic acid (0.05 g, 0.30 mmol) was refluxed for 1 h. Then a solution of FeCl₃.6H₂O (0.04 g, 0.15 mmol) was added dropwise and the refluxing continued for 6 hrs at 60°C. The resulting solution was light green in colour. After slow evaporation of solvent at laboratory temperature plate-like yellow crystals were collected.

Refinement

The N-bound H atoms were located in a difference Fourier map and refined freely. The C-bound H-atoms were placed in calculated positions and treated as riding atoms, with C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

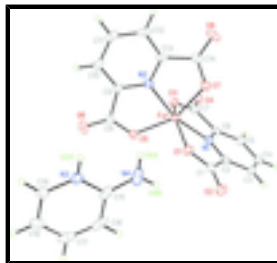


Fig. 1. Perspective view of I with 50% probability ellipsoids for the non-H atoms.

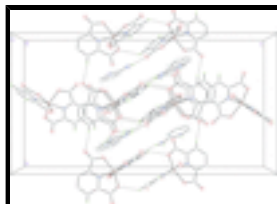


Fig. 2. Packing of I viewed down *a* with H-bonding interactions shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. H atoms not involved in hydrogen bonding are omitted. Key: Fe = brown, O = red, N = blue, C = grey, H = green.

2-Aminopyridinium bis(pyridine-2,6-dicarboxylato)ferrate(III)

Crystal data

(C₅H₇N₂)[Fe(C₇H₃NO₄)₂]

M_r = 481.18

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

a = 7.9288 (10) Å

b = 15.881 (2) Å

c = 30.069 (4) Å

V = 3786.2 (8) Å³

Z = 8

F(000) = 1960

D_x = 1.688 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9998 reflections

θ = 2.7–29.0°

μ = 0.86 mm⁻¹

T = 100 K

Plate, yellow

0.34 × 0.25 × 0.08 mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: numerical
(*SADABS*; Sheldrick, 2009)

T_{min} = 0.696, *T_{max}* = 0.932

62788 measured reflections

5007 independent reflections

4354 reflections with *I* > 2σ(*I*)

R_{int} = 0.051

θ_{max} = 29.1°, θ_{min} = 2.6°

h = -10→10

k = -21→21

l = -40→40

Refinement

Refinement on *F*²

Least-squares matrix: full

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.033$$

$$wR(F^2) = 0.086$$

$$S = 1.05$$

5007 reflections

301 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 2.8224P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5 °. in omega, collected at phi = 0.00, 90.00 and 180.00 °. and 2 sets of 800 frames, each of width 0.45 ° in phi, collected at omega = -30.00 and 210.00 °. The scan time was 10 sec/frame.

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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 Å) and included as riding contributions with isotropic displacement parameters 1.2 times those of the attached atoms. Those attached to nitrogen were independently refined.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| Fe1 | 0.59560 (3) | 0.000219 (13) | 0.381592 (7) | 0.01464 (7) |
| O1 | 0.71089 (13) | 0.10747 (7) | 0.40025 (3) | 0.0189 (2) |
| O2 | 0.86897 (14) | 0.21717 (7) | 0.37918 (4) | 0.0207 (2) |
| O3 | 0.57386 (14) | -0.09825 (7) | 0.33979 (4) | 0.0193 (2) |
| O4 | 0.58951 (16) | -0.14205 (7) | 0.26911 (4) | 0.0260 (3) |
| O5 | 0.72260 (13) | -0.06573 (7) | 0.42789 (4) | 0.0200 (2) |
| O6 | 0.71032 (17) | -0.14212 (9) | 0.49034 (4) | 0.0340 (3) |
| O7 | 0.38240 (14) | 0.05590 (7) | 0.35875 (4) | 0.0203 (2) |
| O8 | 0.09948 (14) | 0.06009 (8) | 0.36268 (4) | 0.0282 (3) |
| N1 | 0.71877 (15) | 0.03920 (8) | 0.32474 (4) | 0.0151 (2) |
| N2 | 0.41237 (15) | -0.03392 (8) | 0.42709 (4) | 0.0155 (2) |
| C1 | 0.79204 (18) | 0.15161 (9) | 0.37119 (5) | 0.0169 (3) |
| C2 | 0.78632 (17) | 0.11562 (9) | 0.32459 (5) | 0.0152 (3) |
| C3 | 0.83948 (19) | 0.15243 (10) | 0.28506 (5) | 0.0182 (3) |
| H3 | 0.8871 | 0.2073 | 0.2846 | 0.022* |
| C4 | 0.8203 (2) | 0.10578 (10) | 0.24610 (5) | 0.0207 (3) |
| H4 | 0.8547 | 0.1293 | 0.2185 | 0.025* |
| C5 | 0.7509 (2) | 0.02482 (9) | 0.24716 (5) | 0.0196 (3) |

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|-----|--------------|---------------|-------------|------------|
| H5 | 0.7388 | -0.0075 | 0.2208 | 0.024* |
| C6 | 0.70041 (18) | -0.00665 (9) | 0.28810 (5) | 0.0165 (3) |
| C7 | 0.61493 (19) | -0.09005 (9) | 0.29832 (5) | 0.0182 (3) |
| C8 | 0.6451 (2) | -0.09916 (10) | 0.46131 (5) | 0.0205 (3) |
| C9 | 0.4578 (2) | -0.08052 (10) | 0.46189 (5) | 0.0182 (3) |
| C10 | 0.3381 (2) | -0.10642 (11) | 0.49278 (5) | 0.0242 (3) |
| H10 | 0.3692 | -0.1383 | 0.5182 | 0.029* |
| C11 | 0.1704 (2) | -0.08385 (11) | 0.48508 (6) | 0.0278 (4) |
| H11 | 0.0858 | -0.1009 | 0.5056 | 0.033* |
| C12 | 0.1253 (2) | -0.03686 (11) | 0.44795 (6) | 0.0244 (3) |
| H12 | 0.0109 | -0.0224 | 0.4423 | 0.029* |
| C13 | 0.25309 (19) | -0.01181 (10) | 0.41939 (5) | 0.0178 (3) |
| C14 | 0.23732 (19) | 0.03925 (10) | 0.37688 (5) | 0.0192 (3) |
| N3 | 0.69376 (17) | 0.22722 (8) | 0.63929 (4) | 0.0190 (3) |
| H3A | 0.589 (3) | 0.2371 (14) | 0.6420 (7) | 0.030 (6)* |
| N4 | 0.6725 (2) | 0.28438 (10) | 0.56932 (5) | 0.0301 (3) |
| H4A | 0.561 (3) | 0.2940 (15) | 0.5747 (8) | 0.043 (7)* |
| H4B | 0.712 (3) | 0.3010 (15) | 0.5452 (8) | 0.039 (6)* |
| C15 | 0.7672 (2) | 0.24858 (9) | 0.60028 (5) | 0.0212 (3) |
| C16 | 0.9402 (2) | 0.22941 (10) | 0.59494 (6) | 0.0276 (4) |
| H16 | 0.9963 | 0.2433 | 0.5680 | 0.033* |
| C17 | 1.0264 (2) | 0.19094 (11) | 0.62851 (7) | 0.0288 (4) |
| H17 | 1.1421 | 0.1772 | 0.6246 | 0.035* |
| C18 | 0.9461 (2) | 0.17143 (11) | 0.66875 (6) | 0.0264 (3) |
| H18 | 1.0067 | 0.1456 | 0.6924 | 0.032* |
| C19 | 0.7792 (2) | 0.19028 (10) | 0.67326 (5) | 0.0218 (3) |
| H19 | 0.7225 | 0.1775 | 0.7003 | 0.026* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|-------------|-------------|-------------|
| Fe1 | 0.01050 (11) | 0.01760 (12) | 0.01583 (12) | 0.00026 (7) | 0.00200 (7) | 0.00414 (7) |
| O1 | 0.0182 (5) | 0.0206 (5) | 0.0178 (5) | -0.0026 (4) | 0.0036 (4) | 0.0010 (4) |
| O2 | 0.0186 (5) | 0.0173 (5) | 0.0261 (6) | -0.0019 (4) | 0.0028 (4) | -0.0004 (4) |
| O3 | 0.0194 (5) | 0.0171 (5) | 0.0214 (5) | -0.0013 (4) | 0.0020 (4) | 0.0041 (4) |
| O4 | 0.0326 (7) | 0.0191 (6) | 0.0264 (6) | -0.0023 (5) | 0.0022 (5) | -0.0028 (4) |
| O5 | 0.0121 (5) | 0.0254 (6) | 0.0225 (5) | 0.0011 (4) | -0.0011 (4) | 0.0070 (4) |
| O6 | 0.0318 (7) | 0.0410 (7) | 0.0292 (6) | 0.0014 (6) | -0.0093 (5) | 0.0163 (6) |
| O7 | 0.0160 (5) | 0.0248 (6) | 0.0199 (5) | 0.0043 (4) | 0.0001 (4) | 0.0054 (4) |
| O8 | 0.0168 (6) | 0.0336 (7) | 0.0342 (7) | 0.0092 (5) | -0.0079 (5) | -0.0039 (5) |
| N1 | 0.0108 (5) | 0.0165 (6) | 0.0180 (6) | 0.0019 (5) | 0.0024 (4) | 0.0023 (4) |
| N2 | 0.0119 (6) | 0.0195 (6) | 0.0152 (6) | -0.0014 (5) | 0.0005 (4) | 0.0000 (5) |
| C1 | 0.0122 (6) | 0.0178 (7) | 0.0206 (7) | 0.0029 (5) | 0.0022 (5) | 0.0023 (5) |
| C2 | 0.0105 (6) | 0.0165 (7) | 0.0186 (7) | 0.0017 (5) | 0.0021 (5) | 0.0022 (5) |
| C3 | 0.0146 (7) | 0.0178 (7) | 0.0222 (7) | 0.0007 (5) | 0.0026 (5) | 0.0047 (5) |
| C4 | 0.0207 (7) | 0.0234 (7) | 0.0179 (7) | 0.0017 (6) | 0.0056 (6) | 0.0051 (6) |
| C5 | 0.0208 (7) | 0.0196 (7) | 0.0184 (7) | 0.0029 (6) | 0.0034 (6) | 0.0008 (6) |
| C6 | 0.0131 (6) | 0.0165 (7) | 0.0199 (7) | 0.0026 (5) | 0.0016 (5) | 0.0015 (5) |

| | | | | | | |
|-----|-------------|------------|-------------|-------------|-------------|-------------|
| C7 | 0.0152 (7) | 0.0161 (7) | 0.0234 (7) | 0.0022 (5) | 0.0014 (6) | 0.0025 (5) |
| C8 | 0.0190 (7) | 0.0228 (7) | 0.0198 (7) | -0.0016 (6) | -0.0036 (6) | 0.0044 (6) |
| C9 | 0.0189 (7) | 0.0203 (7) | 0.0153 (7) | -0.0038 (6) | 0.0004 (5) | 0.0008 (5) |
| C10 | 0.0296 (9) | 0.0250 (8) | 0.0180 (7) | -0.0064 (7) | 0.0055 (6) | 0.0020 (6) |
| C11 | 0.0241 (8) | 0.0305 (9) | 0.0289 (8) | -0.0085 (7) | 0.0144 (7) | -0.0030 (7) |
| C12 | 0.0137 (7) | 0.0286 (8) | 0.0310 (8) | -0.0035 (6) | 0.0064 (6) | -0.0081 (7) |
| C13 | 0.0116 (6) | 0.0204 (7) | 0.0215 (7) | -0.0006 (5) | 0.0006 (5) | -0.0049 (5) |
| C14 | 0.0151 (7) | 0.0208 (7) | 0.0218 (7) | 0.0030 (6) | -0.0020 (5) | -0.0044 (6) |
| N3 | 0.0149 (6) | 0.0207 (6) | 0.0214 (6) | 0.0011 (5) | 0.0045 (5) | 0.0024 (5) |
| N4 | 0.0420 (10) | 0.0285 (8) | 0.0197 (7) | 0.0062 (7) | 0.0093 (6) | 0.0062 (6) |
| C15 | 0.0270 (8) | 0.0136 (7) | 0.0228 (8) | -0.0013 (6) | 0.0083 (6) | 0.0000 (5) |
| C16 | 0.0289 (9) | 0.0194 (8) | 0.0344 (9) | -0.0062 (7) | 0.0188 (7) | -0.0033 (6) |
| C17 | 0.0164 (8) | 0.0205 (8) | 0.0494 (11) | -0.0024 (6) | 0.0084 (7) | -0.0074 (7) |
| C18 | 0.0189 (8) | 0.0239 (8) | 0.0365 (9) | 0.0012 (6) | -0.0024 (7) | -0.0004 (7) |
| C19 | 0.0182 (7) | 0.0233 (8) | 0.0239 (8) | -0.0004 (6) | 0.0007 (6) | 0.0028 (6) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|-----------|-------------|
| Fe1—O5 | 2.0122 (11) | C5—H5 | 0.9500 |
| Fe1—O1 | 2.0128 (11) | C6—C7 | 1.519 (2) |
| Fe1—O3 | 2.0137 (11) | C8—C9 | 1.514 (2) |
| Fe1—O7 | 2.0277 (11) | C9—C10 | 1.390 (2) |
| Fe1—N1 | 2.0638 (12) | C10—C11 | 1.396 (3) |
| Fe1—N2 | 2.0679 (12) | C10—H10 | 0.9500 |
| O1—C1 | 1.2919 (18) | C11—C12 | 1.390 (3) |
| O2—C1 | 1.2305 (19) | C11—H11 | 0.9500 |
| O3—C7 | 1.2954 (19) | C12—C13 | 1.387 (2) |
| O4—C7 | 1.2221 (19) | C12—H12 | 0.9500 |
| O5—C8 | 1.2920 (19) | C13—C14 | 1.519 (2) |
| O6—C8 | 1.2227 (19) | N3—C15 | 1.353 (2) |
| O7—C14 | 1.3002 (19) | N3—C19 | 1.359 (2) |
| O8—C14 | 1.2192 (19) | N3—H3A | 0.85 (2) |
| N1—C2 | 1.3266 (19) | N4—C15 | 1.324 (2) |
| N1—C6 | 1.3287 (19) | N4—H4A | 0.91 (3) |
| N2—C13 | 1.3311 (19) | N4—H4B | 0.83 (2) |
| N2—C9 | 1.3316 (19) | C15—C16 | 1.414 (2) |
| C1—C2 | 1.514 (2) | C16—C17 | 1.364 (3) |
| C2—C3 | 1.390 (2) | C16—H16 | 0.9500 |
| C3—C4 | 1.395 (2) | C17—C18 | 1.402 (3) |
| C3—H3 | 0.9500 | C17—H17 | 0.9500 |
| C4—C5 | 1.399 (2) | C18—C19 | 1.363 (2) |
| C4—H4 | 0.9500 | C18—H18 | 0.9500 |
| C5—C6 | 1.388 (2) | C19—H19 | 0.9500 |
| O5—Fe1—O1 | 91.17 (5) | O4—C7—C6 | 121.15 (14) |
| O5—Fe1—O3 | 94.04 (5) | O3—C7—C6 | 113.23 (13) |
| O1—Fe1—O3 | 150.46 (4) | O6—C8—O5 | 125.69 (15) |
| O5—Fe1—O7 | 151.47 (4) | O6—C8—C9 | 121.04 (15) |
| O1—Fe1—O7 | 95.97 (5) | O5—C8—C9 | 113.27 (13) |
| O3—Fe1—O7 | 93.20 (5) | N2—C9—C10 | 120.29 (15) |

supplementary materials

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| O5—Fe1—N1 | 119.50 (5) | N2—C9—C8 | 111.41 (13) |
| O1—Fe1—N1 | 76.24 (5) | C10—C9—C8 | 128.29 (15) |
| O3—Fe1—N1 | 75.90 (5) | C9—C10—C11 | 117.61 (15) |
| O7—Fe1—N1 | 89.03 (5) | C9—C10—H10 | 121.2 |
| O5—Fe1—N2 | 75.96 (5) | C11—C10—H10 | 121.2 |
| O1—Fe1—N2 | 110.89 (5) | C12—C11—C10 | 121.09 (15) |
| O3—Fe1—N2 | 98.58 (5) | C12—C11—H11 | 119.5 |
| O7—Fe1—N2 | 75.68 (5) | C10—C11—H11 | 119.5 |
| N1—Fe1—N2 | 163.55 (5) | C13—C12—C11 | 117.59 (15) |
| C1—O1—Fe1 | 119.79 (10) | C13—C12—H12 | 121.2 |
| C7—O3—Fe1 | 120.09 (10) | C11—C12—H12 | 121.2 |
| C8—O5—Fe1 | 120.93 (10) | N2—C13—C12 | 120.67 (15) |
| C14—O7—Fe1 | 120.45 (10) | N2—C13—C14 | 111.43 (13) |
| C2—N1—C6 | 122.87 (13) | C12—C13—C14 | 127.89 (15) |
| C2—N1—Fe1 | 117.92 (10) | O8—C14—O7 | 126.22 (15) |
| C6—N1—Fe1 | 118.08 (10) | O8—C14—C13 | 120.90 (15) |
| C13—N2—C9 | 122.70 (13) | O7—C14—C13 | 112.88 (13) |
| C13—N2—Fe1 | 118.84 (10) | C15—N3—C19 | 123.04 (14) |
| C9—N2—Fe1 | 118.39 (10) | C15—N3—H3A | 117.3 (15) |
| O2—C1—O1 | 125.02 (14) | C19—N3—H3A | 119.6 (15) |
| O2—C1—C2 | 121.01 (13) | C15—N4—H4A | 119.9 (15) |
| O1—C1—C2 | 113.98 (13) | C15—N4—H4B | 122.3 (16) |
| N1—C2—C3 | 120.67 (14) | H4A—N4—H4B | 118 (2) |
| N1—C2—C1 | 110.75 (12) | N4—C15—N3 | 118.23 (15) |
| C3—C2—C1 | 128.58 (14) | N4—C15—C16 | 124.22 (16) |
| C2—C3—C4 | 117.51 (14) | N3—C15—C16 | 117.53 (16) |
| C2—C3—H3 | 121.2 | C17—C16—C15 | 119.88 (15) |
| C4—C3—H3 | 121.2 | C17—C16—H16 | 120.1 |
| C3—C4—C5 | 120.81 (14) | C15—C16—H16 | 120.1 |
| C3—C4—H4 | 119.6 | C16—C17—C18 | 120.70 (16) |
| C5—C4—H4 | 119.6 | C16—C17—H17 | 119.7 |
| C6—C5—C4 | 117.69 (14) | C18—C17—H17 | 119.7 |
| C6—C5—H5 | 121.2 | C19—C18—C17 | 118.55 (17) |
| C4—C5—H5 | 121.2 | C19—C18—H18 | 120.7 |
| N1—C6—C5 | 120.44 (13) | C17—C18—H18 | 120.7 |
| N1—C6—C7 | 111.03 (13) | N3—C19—C18 | 120.28 (15) |
| C5—C6—C7 | 128.48 (14) | N3—C19—H19 | 119.9 |
| O4—C7—O3 | 125.61 (14) | C18—C19—H19 | 119.9 |
| O5—Fe1—O1—C1 | 124.47 (11) | N1—C2—C3—C4 | -0.5 (2) |
| O3—Fe1—O1—C1 | 24.16 (16) | C1—C2—C3—C4 | -179.94 (14) |
| O7—Fe1—O1—C1 | -83.20 (11) | C2—C3—C4—C5 | -0.4 (2) |
| N1—Fe1—O1—C1 | 4.33 (11) | C3—C4—C5—C6 | 0.8 (2) |
| N2—Fe1—O1—C1 | -160.13 (10) | C2—N1—C6—C5 | -0.7 (2) |
| O5—Fe1—O3—C7 | -130.21 (11) | Fe1—N1—C6—C5 | 166.92 (11) |
| O1—Fe1—O3—C7 | -30.65 (16) | C2—N1—C6—C7 | -178.35 (12) |
| O7—Fe1—O3—C7 | 77.40 (11) | Fe1—N1—C6—C7 | -10.74 (15) |
| N1—Fe1—O3—C7 | -10.79 (11) | C4—C5—C6—N1 | -0.3 (2) |
| N2—Fe1—O3—C7 | 153.40 (11) | C4—C5—C6—C7 | 176.96 (14) |
| O1—Fe1—O5—C8 | 113.09 (12) | Fe1—O3—C7—O4 | -171.34 (12) |

| | | | |
|---------------|--------------|-----------------|--------------|
| O3—Fe1—O5—C8 | -96.00 (12) | Fe1—O3—C7—C6 | 8.32 (16) |
| O7—Fe1—O5—C8 | 8.31 (18) | N1—C6—C7—O4 | -178.53 (14) |
| N1—Fe1—O5—C8 | -172.08 (11) | C5—C6—C7—O4 | 4.0 (2) |
| N2—Fe1—O5—C8 | 1.84 (12) | N1—C6—C7—O3 | 1.79 (18) |
| O5—Fe1—O7—C14 | -14.53 (18) | C5—C6—C7—O3 | -175.64 (15) |
| O1—Fe1—O7—C14 | -118.14 (11) | Fe1—O5—C8—O6 | 177.84 (14) |
| O3—Fe1—O7—C14 | 89.99 (12) | Fe1—O5—C8—C9 | -1.99 (18) |
| N1—Fe1—O7—C14 | 165.81 (12) | C13—N2—C9—C10 | -1.8 (2) |
| N2—Fe1—O7—C14 | -8.06 (11) | Fe1—N2—C9—C10 | -178.61 (12) |
| O5—Fe1—N1—C2 | -93.42 (11) | C13—N2—C9—C8 | 177.56 (14) |
| O1—Fe1—N1—C2 | -9.99 (10) | Fe1—N2—C9—C8 | 0.72 (17) |
| O3—Fe1—N1—C2 | 179.94 (11) | O6—C8—C9—N2 | -179.09 (15) |
| O7—Fe1—N1—C2 | 86.39 (11) | O5—C8—C9—N2 | 0.76 (19) |
| N2—Fe1—N1—C2 | 107.84 (19) | O6—C8—C9—C10 | 0.2 (3) |
| O5—Fe1—N1—C6 | 98.35 (11) | O5—C8—C9—C10 | -179.99 (16) |
| O1—Fe1—N1—C6 | -178.22 (11) | N2—C9—C10—C11 | 1.8 (2) |
| O3—Fe1—N1—C6 | 11.71 (10) | C8—C9—C10—C11 | -177.39 (16) |
| O7—Fe1—N1—C6 | -81.84 (11) | C9—C10—C11—C12 | -0.3 (3) |
| N2—Fe1—N1—C6 | -60.4 (2) | C10—C11—C12—C13 | -1.3 (3) |
| O5—Fe1—N2—C13 | -178.28 (12) | C9—N2—C13—C12 | 0.1 (2) |
| O1—Fe1—N2—C13 | 95.90 (12) | Fe1—N2—C13—C12 | 176.91 (12) |
| O3—Fe1—N2—C13 | -86.23 (12) | C9—N2—C13—C14 | -178.55 (13) |
| O7—Fe1—N2—C13 | 4.90 (11) | Fe1—N2—C13—C14 | -1.72 (17) |
| N1—Fe1—N2—C13 | -17.3 (3) | C11—C12—C13—N2 | 1.4 (2) |
| O5—Fe1—N2—C9 | -1.31 (11) | C11—C12—C13—C14 | 179.82 (15) |
| O1—Fe1—N2—C9 | -87.13 (12) | Fe1—O7—C14—O8 | -170.02 (13) |
| O3—Fe1—N2—C9 | 90.74 (12) | Fe1—O7—C14—C13 | 9.43 (17) |
| O7—Fe1—N2—C9 | -178.13 (12) | N2—C13—C14—O8 | 174.77 (15) |
| N1—Fe1—N2—C9 | 159.71 (16) | C12—C13—C14—O8 | -3.7 (3) |
| Fe1—O1—C1—O2 | -178.75 (12) | N2—C13—C14—O7 | -4.71 (18) |
| Fe1—O1—C1—C2 | 1.11 (16) | C12—C13—C14—O7 | 176.78 (15) |
| C6—N1—C2—C3 | 1.1 (2) | C19—N3—C15—N4 | -179.95 (15) |
| Fe1—N1—C2—C3 | -166.53 (11) | C19—N3—C15—C16 | 1.4 (2) |
| C6—N1—C2—C1 | -179.40 (13) | N4—C15—C16—C17 | -178.71 (16) |
| Fe1—N1—C2—C1 | 12.98 (15) | N3—C15—C16—C17 | -0.1 (2) |
| O2—C1—C2—N1 | 170.78 (13) | C15—C16—C17—C18 | -1.2 (3) |
| O1—C1—C2—N1 | -9.09 (17) | C16—C17—C18—C19 | 1.2 (3) |
| O2—C1—C2—C3 | -9.8 (2) | C15—N3—C19—C18 | -1.3 (2) |
| O1—C1—C2—C3 | 170.37 (14) | C17—C18—C19—N3 | 0.0 (3) |

Hydrogen-bond geometry (Å, °)

| <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> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N3—H3A \cdots O2 ⁱ | 0.85 (2) | 1.99 (2) | 2.7786 (18) | 153 (2) |
| N4—H4A \cdots O2 ⁱ | 0.91 (3) | 2.07 (3) | 2.862 (2) | 145 (2) |
| N4—H4B \cdots O6 ⁱⁱ | 0.83 (2) | 1.98 (2) | 2.8045 (19) | 171 (2) |
| C3—H3 \cdots O4 ⁱⁱ | 0.95 | 2.44 | 3.3466 (19) | 159 |
| C12—H12 \cdots O5 ⁱⁱⁱ | 0.95 | 2.43 | 3.281 (2) | 150 |

supplementary materials

C10—H10...O1^{iv}

0.95

2.58

3.2398 (19)

127

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

Fig. 1

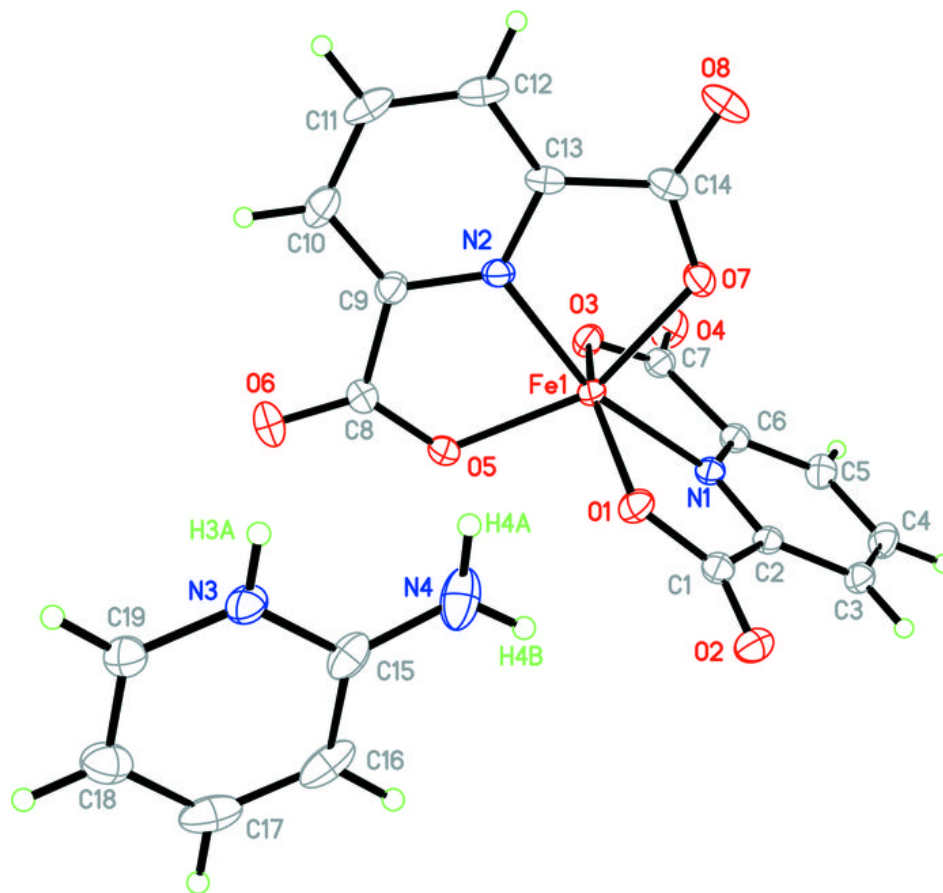


Fig. 2

