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2,6-Diaminopyridinium bis(4-hydroxypyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)-ferrate(III) dihydrate

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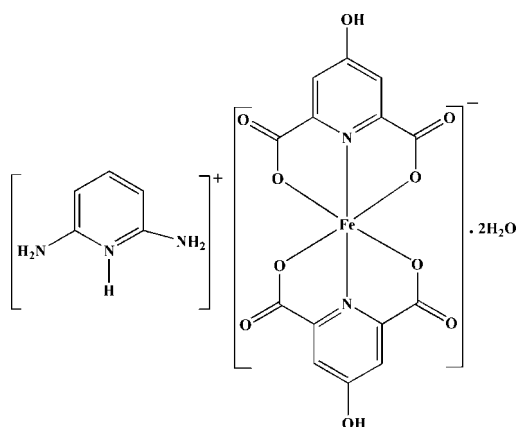
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.046; wR factor = 0.110; data-to-parameter ratio = 23.9.

The reaction of iron(II) sulfate heptahydrate with the proton-transfer compound (pydaH)(hypydCH) (pyda = pyridine-2,6-diamine; hypydCH₂ = 4-hydroxypyridine-2,6-dicarboxylic acid) in an aqueous solution led to the formation of the title compound, (C₅H₈N₃)[Fe(C₇H₃NO₅)₂].2H₂O. The anion is a six-coordinated complex with a distorted octahedral geometry around the Fe^{III} atom. Extensive intermolecular O—H...O, N—H...O and C—H...O hydrogen bonds, involving the complex anion, (pydaH)⁺ counter-ion and two uncoordinated water molecules, and π — π [centroid-to-centroid distance 3.323 (11) Å] and C—O... π [O—centroid distance 3.150 (15) Å] interactions connect the various components into a supramolecular structure.

Related literature

For other complexes with pyridinedicarboxylic acids, see: Rafizadeh *et al.* (2004, 2006, 2007*a,b*); Rafizadeh & Amani (2006).



Experimental

Crystal data

(C₅H₈N₃)[Fe(C₇H₃NO₅)₂].2H₂O

$M_r = 564.23$

Monoclinic, $P2_1/n$

$a = 6.9389$ (4) Å

$b = 20.8845$ (12) Å

$c = 14.9908$ (8) Å

$\beta = 96.371$ (1)°

$V = 2159.0$ (2) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.78$ mm⁻¹

$T = 100$ (2) K

0.40 × 0.40 × 0.20 mm

Data collection

Bruker SMART APEXII CCD

area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

$T_{\min} = 0.746$, $T_{\max} = 0.860$

33555 measured reflections

8157 independent reflections

5648 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.073$

Refinement

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

$wR(F^2) = 0.110$

$S = 1.02$

8157 reflections

342 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.49$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.61$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1—O3	2.0101 (13)	Fe1—O6	2.0413 (13)
Fe1—O8	2.0135 (14)	Fe1—N1	2.0478 (14)
Fe1—N2	2.0392 (15)	Fe1—O1	2.0544 (13)
O3—Fe1—O8	95.80 (6)	N2—Fe1—N1	175.34 (6)
O3—Fe1—N2	107.52 (6)	O6—Fe1—N1	102.08 (5)
O8—Fe1—N2	76.88 (6)	O3—Fe1—O1	151.34 (5)
O3—Fe1—O6	91.49 (5)	O8—Fe1—O1	94.61 (5)
O8—Fe1—O6	152.40 (5)	N2—Fe1—O1	100.83 (5)
N2—Fe1—O6	75.54 (6)	O6—Fe1—O1	91.53 (5)
O3—Fe1—N1	76.40 (5)	N1—Fe1—O1	75.10 (5)
O8—Fe1—N1	105.50 (6)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3N...O2 ⁱ	0.92	2.00	2.8431 (19)	152
N4—H4NA...O2W ⁱⁱ	0.92	2.04	2.957 (2)	173
N4—H4NB...O3	0.92	2.33	3.139 (2)	147
O5—H5...O1W	0.85	1.74	2.566 (2)	164
O10—H10...O2W	0.85	1.80	2.614 (2)	159
N5—H5NA...O2 ⁱ	0.92	1.98	2.800 (2)	148
N5—H5NB...O6 ⁱⁱⁱ	0.92	1.96	2.832 (2)	157
O1W—H1WA...O7 ^{iv}	0.85	1.98	2.826 (2)	173
O1W—H1WB...O4 ⁱⁱ	0.85	2.05	2.877 (2)	166
O2W—H2WA...O1 ^v	0.85	1.88	2.716 (2)	168
O2W—H2WB...O9 ^{vi}	0.85	1.87	2.709 (2)	168
C16—H16A...O3	0.95	2.55	3.323 (2)	139

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2152).

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supplementary materials

Acta Cryst. (2008). E64, m1300-m1301 [doi:10.1107/S1600536808029280]

2,6-Diaminopyridinium bis(4-hydroxypyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)ferrate(III) dihydrate

M. Rafizadeh, Z. Derikvand and A. Nemati

Comment

Noncovalent interactions including hydrogen bonding, ion pairing, hydrophobic or hydrophilic and donor–acceptor interactions play a key role in chemical, catalytic and biochemical processes, as well as supramolecular chemistry and crystal engineering. Our research group has recently focused on synthesis of water soluble self-assembly systems that can function as suitable ligands in the synthesis of metal complexes. We have reported some complexes with pyridinedicarboxylic acids (Rafizadeh *et al.*, 2004, 2006, 2007*a,b*; Rafizadeh & Amani, 2006).

In the title compound (Fig. 1), the Fe^{III} atom has a distorted octahedral geometry. The bond angles (Table 1) and the torsion angles O6—Fe1—O1—C1 [100.80 (13)°], O1—Fe1—O6—C8 [103.59 (13)°], O8—Fe1—O3—C7 [104.38 (13)°] and O3—Fe1—O8—C14 [106.46 (14)°] indicate that two dianionic hypydc ligands are almost perpendicular to each other. In this work we used Fe^{II} ions as starting material. Most probably during the synthesis process, Fe^{II} was oxidized into Fe^{III}. There are a large number of O—H \cdots O, N—H \cdots O and C—H \cdots O hydrogen bonds between the cations, anions and water molecules (Table 2). Considerable π – π interaction [centroid–centroid distance = 3.323 (11) Å] between the cation and anion, and C—O \cdots π interaction [O–centroid distance = 3.150 (15) Å] between two anions are observed (Fig. 2). Hydrogen bonds, π – π and C—O \cdots π interactions result in the formation of a supramolecular structure (Fig. 3).

Experimental

The reaction of FeSO₄·7H₂O (0.139 g, 0.5 mmol) in water (20 ml) with (pydaH)(hypydcH) (0.264 g, 1.0 mmol) in water (20 ml) gave colorless crystal of the title compound. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at room temperature.

Refinement

H atoms attached to O and N atoms and water molecules are located from difference Fourier maps and refined isotropically with their coordinates fixed. H atoms on C atoms were positioned geometrically and refined in riding model, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

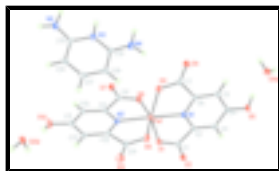


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

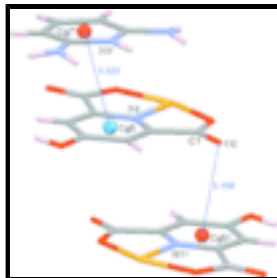


Fig. 2. π - π Stacking interaction ($Cg5 \cdots Cg7^i$) and $C-O \cdots \pi$ interaction ($C1-O2 \cdots Cg5^{ii}$) in the title compound. [$Cg5$: N1/C2-C6, $Cg7$: N3/C15-C19. Symmetry codes: (i) $1/2 + x, 1/2 - y, 1/2 + z$; (ii) $-x, -y, 1 - z$.]

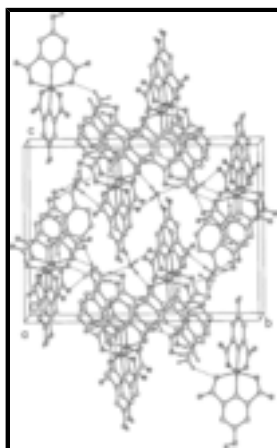


Fig. 3. Crystal packing of the title compound. Hydrogen bonds are shown by dashed lines.

2,6-Diaminopyridinium bis(4-hydroxypyridine-2,6-dicarboxylato- $\kappa^3 O^2, N, O^6$)ferrate(III) dihydrate

Crystal data

$(C_5H_8N_3)[Fe(C_7H_3NO_5)_2] \cdot 2H_2O$

$M_r = 564.23$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2yn$

$a = 6.9389\ (4)\ \text{\AA}$

$b = 20.8845\ (12)\ \text{\AA}$

$c = 14.9908\ (8)\ \text{\AA}$

$\beta = 96.371\ (1)^\circ$

$V = 2159.0\ (2)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1156$

$D_x = 1.736\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

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

Cell parameters from 4719 reflections

$\theta = 2.4\text{--}31.9^\circ$

$\mu = 0.78\ \text{mm}^{-1}$

$T = 100\ (2)\ \text{K}$

Prism, colourless

$0.40 \times 0.40 \times 0.20\ \text{mm}$

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100\ (2)\ \text{K}$

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

8157 independent reflections

5648 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.073$

$\theta_{\text{max}} = 33.1^\circ$

$\theta_{\text{min}} = 1.7^\circ$

$h = -10 \rightarrow 10$

$T_{\min} = 0.746$, $T_{\max} = 0.860$
33555 measured reflections

$k = -31 \rightarrow 32$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.110$

$S = 1.02$

8157 reflections

342 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.6357P]$$

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

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

$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.03345 (4)	0.098201 (12)	0.291874 (16)	0.01147 (7)
O1	0.18095 (19)	0.01628 (6)	0.33338 (8)	0.0138 (3)
O2	0.31460 (19)	-0.04217 (6)	0.44867 (9)	0.0154 (3)
O3	-0.08559 (19)	0.18304 (6)	0.31759 (8)	0.0147 (3)
O4	-0.1601 (2)	0.25261 (6)	0.42183 (9)	0.0164 (3)
O5	0.1267 (2)	0.11113 (7)	0.70162 (8)	0.0179 (3)
H5	0.0929	0.1486	0.7156	0.041 (8)*
N1	0.0599 (2)	0.10213 (7)	0.42918 (9)	0.0104 (3)
C1	0.2245 (3)	0.00489 (8)	0.41778 (12)	0.0119 (3)
C2	0.1537 (3)	0.05567 (8)	0.47787 (11)	0.0105 (3)
C3	0.1796 (3)	0.05772 (8)	0.56992 (11)	0.0120 (3)
H3A	0.2470	0.0246	0.6037	0.014*
C4	0.1027 (3)	0.11076 (8)	0.61299 (12)	0.0120 (3)
C5	0.0084 (3)	0.15997 (8)	0.56065 (12)	0.0119 (3)
H5A	-0.0422	0.1965	0.5879	0.014*
C6	-0.0080 (3)	0.15336 (8)	0.46877 (11)	0.0110 (3)
C7	-0.0940 (3)	0.20139 (9)	0.39982 (12)	0.0128 (3)
O6	0.28312 (19)	0.14151 (6)	0.26334 (8)	0.0149 (3)
O7	0.4605 (2)	0.17585 (7)	0.15648 (9)	0.0187 (3)
O8	-0.2194 (2)	0.05293 (6)	0.25578 (8)	0.0158 (3)
O9	-0.4188 (2)	0.01213 (7)	0.14115 (9)	0.0205 (3)

supplementary materials

O10	-0.0042 (2)	0.09000 (7)	-0.11598 (9)	0.0201 (3)
H10	-0.1192	0.0795	-0.1361	0.039 (8)*
N2	0.0277 (2)	0.09017 (7)	0.15604 (10)	0.0117 (3)
C8	0.3215 (3)	0.14715 (9)	0.18084 (12)	0.0133 (3)
C9	0.1707 (3)	0.11574 (8)	0.11447 (12)	0.0120 (3)
C10	0.1645 (3)	0.11537 (9)	0.02270 (12)	0.0142 (3)
H10A	0.2677	0.1328	-0.0063	0.017*
C11	0.0007 (3)	0.08840 (9)	-0.02725 (12)	0.0146 (4)
C12	-0.1484 (3)	0.06195 (9)	0.01761 (12)	0.0140 (3)
H12A	-0.2596	0.0432	-0.0148	0.017*
C13	-0.1279 (3)	0.06408 (9)	0.11011 (12)	0.0129 (3)
C14	-0.2708 (3)	0.04000 (9)	0.17213 (12)	0.0144 (3)
N3	0.0302 (2)	0.33319 (7)	0.07019 (10)	0.0133 (3)
H3N	0.0921	0.3714	0.0844	0.028 (7)*
N4	0.0433 (3)	0.30671 (8)	0.22110 (11)	0.0195 (3)
H4NA	0.0914	0.3465	0.2380	0.045 (8)*
H4NB	-0.0055	0.2836	0.2658	0.051 (9)*
N5	0.0395 (2)	0.36729 (8)	-0.07645 (10)	0.0154 (3)
H5NA	0.0937	0.4051	-0.0543	0.029 (7)*
H5NB	-0.0126	0.3660	-0.1356	0.050 (9)*
C15	-0.0200 (3)	0.29254 (9)	0.13517 (12)	0.0140 (3)
C16	-0.1329 (3)	0.23951 (9)	0.10904 (13)	0.0160 (4)
H16A	-0.1734	0.2109	0.1526	0.019*
C17	-0.1855 (3)	0.22903 (9)	0.01850 (13)	0.0164 (4)
H17A	-0.2638	0.1929	0.0006	0.020*
C18	-0.1282 (3)	0.26914 (9)	-0.04682 (13)	0.0151 (4)
H18A	-0.1615	0.2601	-0.1087	0.018*
C19	-0.01989 (16)	0.32341 (5)	-0.01954 (7)	0.0129 (3)
O1W	0.05579 (16)	0.21932 (5)	0.77225 (7)	0.0176 (3)
H1WA	0.0359	0.2525	0.7396	0.042 (8)*
H1WB	0.1458	0.2209	0.8155	0.057 (10)*
O2W	-0.3280 (2)	0.06443 (7)	-0.21595 (9)	0.0173 (3)
H2WA	-0.2977	0.0393	-0.2567	0.045 (8)*
H2WB	-0.4203	0.0440	-0.1961	0.066 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.01484 (13)	0.01232 (12)	0.00737 (11)	-0.00036 (10)	0.00172 (9)	0.00067 (9)
O1	0.0191 (7)	0.0131 (6)	0.0095 (6)	0.0017 (5)	0.0023 (5)	-0.0006 (5)
O2	0.0174 (7)	0.0130 (6)	0.0155 (6)	0.0031 (5)	0.0001 (5)	0.0004 (5)
O3	0.0197 (7)	0.0144 (6)	0.0101 (6)	0.0022 (5)	0.0022 (5)	0.0020 (5)
O4	0.0204 (7)	0.0131 (6)	0.0153 (6)	0.0033 (5)	0.0006 (5)	-0.0005 (5)
O5	0.0292 (8)	0.0171 (7)	0.0073 (6)	0.0023 (6)	0.0018 (5)	-0.0009 (5)
N1	0.0120 (7)	0.0103 (7)	0.0089 (6)	-0.0010 (5)	0.0013 (5)	-0.0004 (5)
C1	0.0124 (8)	0.0108 (8)	0.0129 (8)	-0.0026 (6)	0.0026 (6)	-0.0005 (6)
C2	0.0115 (8)	0.0097 (8)	0.0103 (8)	-0.0015 (6)	0.0016 (6)	0.0010 (6)
C3	0.0135 (8)	0.0110 (8)	0.0113 (8)	-0.0023 (6)	0.0010 (6)	0.0026 (6)

C4	0.0130 (8)	0.0130 (8)	0.0099 (7)	-0.0021 (6)	0.0006 (6)	-0.0007 (6)
C5	0.0137 (8)	0.0106 (8)	0.0119 (8)	-0.0021 (6)	0.0032 (6)	-0.0004 (6)
C6	0.0111 (8)	0.0113 (8)	0.0107 (8)	-0.0006 (6)	0.0016 (6)	0.0010 (6)
C7	0.0131 (8)	0.0130 (8)	0.0124 (8)	-0.0009 (7)	0.0023 (6)	0.0000 (6)
O6	0.0163 (7)	0.0183 (7)	0.0099 (6)	-0.0033 (5)	0.0011 (5)	0.0001 (5)
O7	0.0185 (7)	0.0222 (7)	0.0157 (6)	-0.0068 (6)	0.0034 (5)	0.0009 (5)
O8	0.0178 (7)	0.0201 (7)	0.0099 (6)	-0.0022 (5)	0.0024 (5)	0.0018 (5)
O9	0.0177 (7)	0.0250 (8)	0.0184 (7)	-0.0080 (6)	0.0001 (5)	0.0000 (6)
O10	0.0235 (8)	0.0282 (8)	0.0083 (6)	-0.0037 (6)	0.0009 (5)	-0.0014 (5)
N2	0.0138 (7)	0.0113 (7)	0.0101 (7)	-0.0003 (6)	0.0013 (5)	0.0008 (5)
C8	0.0163 (9)	0.0120 (8)	0.0114 (8)	-0.0002 (7)	0.0006 (6)	0.0005 (6)
C9	0.0140 (8)	0.0109 (8)	0.0116 (8)	-0.0003 (6)	0.0035 (6)	0.0005 (6)
C10	0.0181 (9)	0.0140 (8)	0.0110 (8)	-0.0009 (7)	0.0041 (7)	0.0008 (6)
C11	0.0208 (9)	0.0130 (8)	0.0102 (8)	0.0013 (7)	0.0024 (7)	-0.0011 (6)
C12	0.0172 (9)	0.0127 (8)	0.0117 (8)	-0.0010 (7)	-0.0011 (7)	-0.0008 (6)
C13	0.0158 (9)	0.0107 (8)	0.0124 (8)	-0.0005 (7)	0.0022 (7)	-0.0001 (6)
C14	0.0156 (9)	0.0138 (8)	0.0137 (8)	0.0003 (7)	0.0010 (7)	0.0020 (6)
N3	0.0132 (7)	0.0133 (7)	0.0132 (7)	0.0000 (6)	0.0012 (6)	0.0014 (6)
N4	0.0245 (9)	0.0203 (9)	0.0135 (8)	-0.0020 (7)	0.0012 (6)	0.0044 (6)
N5	0.0178 (8)	0.0167 (8)	0.0114 (7)	-0.0017 (6)	0.0010 (6)	-0.0002 (6)
C15	0.0133 (9)	0.0142 (8)	0.0147 (8)	0.0019 (7)	0.0025 (7)	0.0027 (7)
C16	0.0158 (9)	0.0126 (8)	0.0201 (9)	0.0023 (7)	0.0034 (7)	0.0036 (7)
C17	0.0144 (9)	0.0114 (8)	0.0234 (10)	0.0019 (7)	0.0020 (7)	-0.0021 (7)
C18	0.0153 (9)	0.0146 (9)	0.0155 (8)	0.0020 (7)	0.0023 (7)	-0.0023 (7)
C19	0.0108 (8)	0.0153 (8)	0.0128 (8)	0.0037 (7)	0.0021 (6)	-0.0002 (6)
O1W	0.0221 (7)	0.0167 (7)	0.0134 (6)	0.0014 (6)	-0.0011 (5)	-0.0008 (5)
O2W	0.0201 (7)	0.0194 (7)	0.0129 (6)	-0.0013 (6)	0.0041 (5)	-0.0039 (5)

Geometric parameters (Å, °)

Fe1—O3	2.0101 (13)	N2—C9	1.340 (2)
Fe1—O8	2.0135 (14)	C8—C9	1.511 (3)
Fe1—N2	2.0392 (15)	C9—C10	1.372 (2)
Fe1—O6	2.0413 (13)	C10—C11	1.407 (3)
Fe1—N1	2.0478 (14)	C10—H10A	0.9500
Fe1—O1	2.0544 (13)	C11—C12	1.408 (3)
O1—C1	1.290 (2)	C12—C13	1.379 (2)
O2—C1	1.227 (2)	C12—H12A	0.9500
O3—C7	1.298 (2)	C13—C14	1.518 (3)
O4—C7	1.224 (2)	N3—C15	1.366 (2)
O5—C4	1.321 (2)	N3—C19	1.3668 (18)
O5—H5	0.8501	N3—H3N	0.9200
N1—C6	1.335 (2)	N4—C15	1.347 (2)
N1—C2	1.339 (2)	N4—H4NA	0.9200
C1—C2	1.509 (2)	N4—H4NB	0.9200
C2—C3	1.372 (2)	N5—C19	1.3475 (19)
C3—C4	1.416 (2)	N5—H5NA	0.9200
C3—H3A	0.9500	N5—H5NB	0.9199
C4—C5	1.409 (2)	C15—C16	1.388 (3)

supplementary materials

C5—C6	1.376 (2)	C16—C17	1.383 (3)
C5—H5A	0.9500	C16—H16A	0.9500
C6—C7	1.514 (2)	C17—C18	1.380 (3)
O6—C8	1.299 (2)	C17—H17A	0.9500
O7—C8	1.225 (2)	C18—C19	1.396 (2)
O8—C14	1.294 (2)	C18—H18A	0.9500
O9—C14	1.226 (2)	O1W—H1WA	0.8499
O10—C11	1.327 (2)	O1W—H1WB	0.8500
O10—H10	0.8500	O2W—H2WA	0.8500
N2—C13	1.331 (2)	O2W—H2WB	0.8499
O3—Fe1—O8	95.80 (6)	O7—C8—O6	125.40 (17)
O3—Fe1—N2	107.52 (6)	O7—C8—C9	121.77 (16)
O8—Fe1—N2	76.88 (6)	O6—C8—C9	112.80 (15)
O3—Fe1—O6	91.49 (5)	N2—C9—C10	121.45 (17)
O8—Fe1—O6	152.40 (5)	N2—C9—C8	111.18 (15)
N2—Fe1—O6	75.54 (6)	C10—C9—C8	127.24 (16)
O3—Fe1—N1	76.40 (5)	C9—C10—C11	117.99 (17)
O8—Fe1—N1	105.50 (6)	C9—C10—H10A	121.0
N2—Fe1—N1	175.34 (6)	C11—C10—H10A	121.0
O6—Fe1—N1	102.08 (5)	O10—C11—C10	116.88 (17)
O3—Fe1—O1	151.34 (5)	O10—C11—C12	123.40 (17)
O8—Fe1—O1	94.61 (5)	C10—C11—C12	119.72 (16)
N2—Fe1—O1	100.83 (5)	C13—C12—C11	117.96 (17)
O6—Fe1—O1	91.53 (5)	C13—C12—H12A	121.0
N1—Fe1—O1	75.10 (5)	C11—C12—H12A	121.0
C1—O1—Fe1	120.35 (11)	N2—C13—C12	121.36 (17)
C7—O3—Fe1	120.33 (11)	N2—C13—C14	111.48 (15)
C4—O5—H5	104.2	C12—C13—C14	127.15 (17)
C6—N1—C2	120.86 (15)	O9—C14—O8	126.56 (17)
C6—N1—Fe1	118.84 (12)	O9—C14—C13	120.12 (16)
C2—N1—Fe1	120.19 (12)	O8—C14—C13	113.32 (16)
O2—C1—O1	124.88 (16)	C15—N3—C19	123.48 (15)
O2—C1—C2	121.58 (16)	C15—N3—H3N	121.5
O1—C1—C2	113.54 (15)	C19—N3—H3N	114.8
N1—C2—C3	121.80 (16)	C15—N4—H4NA	122.1
N1—C2—C1	110.79 (14)	C15—N4—H4NB	118.2
C3—C2—C1	127.40 (16)	H4NA—N4—H4NB	115.2
C2—C3—C4	117.97 (16)	C19—N5—H5NA	119.7
C2—C3—H3A	121.0	C19—N5—H5NB	118.4
C4—C3—H3A	121.0	H5NA—N5—H5NB	118.3
O5—C4—C5	123.70 (16)	N4—C15—N3	117.61 (17)
O5—C4—C3	116.84 (16)	N4—C15—C16	124.00 (17)
C5—C4—C3	119.46 (16)	N3—C15—C16	118.39 (17)
C6—C5—C4	117.76 (16)	C17—C16—C15	118.84 (17)
C6—C5—H5A	121.1	C17—C16—H16A	120.6
C4—C5—H5A	121.1	C15—C16—H16A	120.6
N1—C6—C5	122.10 (16)	C18—C17—C16	122.33 (18)
N1—C6—C7	111.05 (14)	C18—C17—H17A	118.8
C5—C6—C7	126.81 (16)	C16—C17—H17A	118.8

O4—C7—O3	124.87 (17)	C17—C18—C19	118.23 (16)
O4—C7—C6	121.74 (16)	C17—C18—H18A	120.9
O3—C7—C6	113.38 (15)	C19—C18—H18A	120.9
C8—O6—Fe1	120.52 (12)	N5—C19—N3	117.33 (12)
C14—O8—Fe1	119.79 (12)	N5—C19—C18	124.01 (13)
C11—O10—H10	105.5	N3—C19—C18	118.66 (13)
C13—N2—C9	121.52 (15)	H1WA—O1W—H1WB	117.8
C13—N2—Fe1	118.37 (12)	H2WA—O2W—H2WB	101.4
C9—N2—Fe1	119.87 (12)		
O3—Fe1—O1—C1	4.9 (2)	O3—Fe1—O8—C14	106.46 (14)
O8—Fe1—O1—C1	-106.13 (13)	N2—Fe1—O8—C14	-0.21 (13)
N2—Fe1—O1—C1	176.37 (13)	O6—Fe1—O8—C14	1.9 (2)
O6—Fe1—O1—C1	100.80 (13)	N1—Fe1—O8—C14	-176.08 (13)
N1—Fe1—O1—C1	-1.29 (13)	O1—Fe1—O8—C14	-100.28 (14)
O8—Fe1—O3—C7	104.38 (13)	O3—Fe1—N2—C13	-89.32 (14)
N2—Fe1—O3—C7	-177.58 (13)	O8—Fe1—N2—C13	2.70 (13)
O6—Fe1—O3—C7	-102.28 (13)	O6—Fe1—N2—C13	-176.26 (14)
N1—Fe1—O3—C7	-0.21 (13)	O1—Fe1—N2—C13	94.96 (14)
O1—Fe1—O3—C7	-6.4 (2)	O3—Fe1—N2—C9	85.10 (14)
O3—Fe1—N1—C6	0.52 (13)	O8—Fe1—N2—C9	177.12 (15)
O8—Fe1—N1—C6	-91.82 (14)	O6—Fe1—N2—C9	-1.85 (13)
O6—Fe1—N1—C6	89.12 (14)	O1—Fe1—N2—C9	-90.63 (14)
O1—Fe1—N1—C6	177.47 (14)	Fe1—O6—C8—O7	175.02 (15)
O3—Fe1—N1—C2	-175.72 (14)	Fe1—O6—C8—C9	-3.1 (2)
O8—Fe1—N1—C2	91.94 (14)	C13—N2—C9—C10	-0.9 (3)
O6—Fe1—N1—C2	-87.13 (14)	Fe1—N2—C9—C10	-175.18 (13)
O1—Fe1—N1—C2	1.22 (13)	C13—N2—C9—C8	175.08 (16)
Fe1—O1—C1—O2	-178.87 (14)	Fe1—N2—C9—C8	0.8 (2)
Fe1—O1—C1—C2	1.16 (19)	O7—C8—C9—N2	-176.81 (17)
C6—N1—C2—C3	1.7 (3)	O6—C8—C9—N2	1.4 (2)
Fe1—N1—C2—C3	177.91 (13)	O7—C8—C9—C10	-1.1 (3)
C6—N1—C2—C1	-177.17 (15)	O6—C8—C9—C10	177.16 (17)
Fe1—N1—C2—C1	-1.00 (19)	N2—C9—C10—C11	1.3 (3)
O2—C1—C2—N1	179.93 (16)	C8—C9—C10—C11	-174.01 (17)
O1—C1—C2—N1	-0.1 (2)	C9—C10—C11—C12	-1.1 (3)
O2—C1—C2—C3	1.1 (3)	O10—C11—C12—C13	-178.96 (17)
O1—C1—C2—C3	-178.93 (17)	C10—C11—C12—C13	0.5 (3)
N1—C2—C3—C4	0.3 (3)	C9—N2—C13—C12	0.3 (3)
C1—C2—C3—C4	179.06 (17)	Fe1—N2—C13—C12	174.63 (13)
C2—C3—C4—O5	178.92 (16)	C9—N2—C13—C14	-178.61 (16)
C2—C3—C4—C5	-1.8 (3)	Fe1—N2—C13—C14	-4.3 (2)
O5—C4—C5—C6	-179.53 (17)	C11—C12—C13—N2	-0.1 (3)
C3—C4—C5—C6	1.3 (3)	C11—C12—C13—C14	178.62 (17)
C2—N1—C6—C5	-2.4 (3)	Fe1—O8—C14—O9	179.03 (15)
Fe1—N1—C6—C5	-178.57 (13)	Fe1—O8—C14—C13	-1.9 (2)
C2—N1—C6—C7	175.52 (15)	N2—C13—C14—O9	-176.93 (17)
Fe1—N1—C6—C7	-0.69 (19)	C12—C13—C14—O9	4.2 (3)
C4—C5—C6—N1	0.8 (3)	N2—C13—C14—O8	3.9 (2)
C4—C5—C6—C7	-176.72 (17)	C12—C13—C14—O8	-174.90 (18)

supplementary materials

Fe1—O3—C7—O4	178.48 (14)	C19—N3—C15—N4	178.12 (15)
Fe1—O3—C7—C6	-0.1 (2)	C19—N3—C15—C16	-2.1 (3)
N1—C6—C7—O4	-178.12 (17)	N4—C15—C16—C17	-178.46 (18)
C5—C6—C7—O4	-0.4 (3)	N3—C15—C16—C17	1.7 (3)
N1—C6—C7—O3	0.5 (2)	C15—C16—C17—C18	0.6 (3)
C5—C6—C7—O3	178.25 (17)	C16—C17—C18—C19	-2.6 (3)
O3—Fe1—O6—C8	-104.91 (13)	C15—N3—C19—N5	-179.87 (16)
O8—Fe1—O6—C8	0.6 (2)	C15—N3—C19—C18	0.0 (2)
N2—Fe1—O6—C8	2.80 (13)	C17—C18—C19—N5	-177.84 (16)
N1—Fe1—O6—C8	178.68 (13)	C17—C18—C19—N3	2.3 (2)
O1—Fe1—O6—C8	103.59 (13)		

Hydrogen-bond geometry (\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>
N3—H3N \cdots O2 ⁱ	0.92	2.00	2.8431 (19)	152
N4—H4NA \cdots O2W ⁱⁱ	0.92	2.04	2.957 (2)	173
N4—H4NB \cdots O3	0.92	2.33	3.139 (2)	147
O5—H5 \cdots O1W	0.85	1.74	2.566 (2)	164
O10—H10 \cdots O2W	0.85	1.80	2.614 (2)	159
N5—H5NA \cdots O2 ⁱ	0.92	1.98	2.800 (2)	148
N5—H5NB \cdots O6 ⁱⁱⁱ	0.92	1.96	2.832 (2)	157
O1W—H1WA \cdots O7 ^{iv}	0.85	1.98	2.826 (2)	173
O1W—H1WB \cdots O4 ⁱⁱ	0.85	2.05	2.877 (2)	166
O2W—H2WA \cdots O1 ^v	0.85	1.88	2.716 (2)	168
O2W—H2WB \cdots O9 ^{vi}	0.85	1.87	2.709 (2)	168
C16—H16A \cdots O3	0.95	2.55	3.323 (2)	139

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

Fig. 1

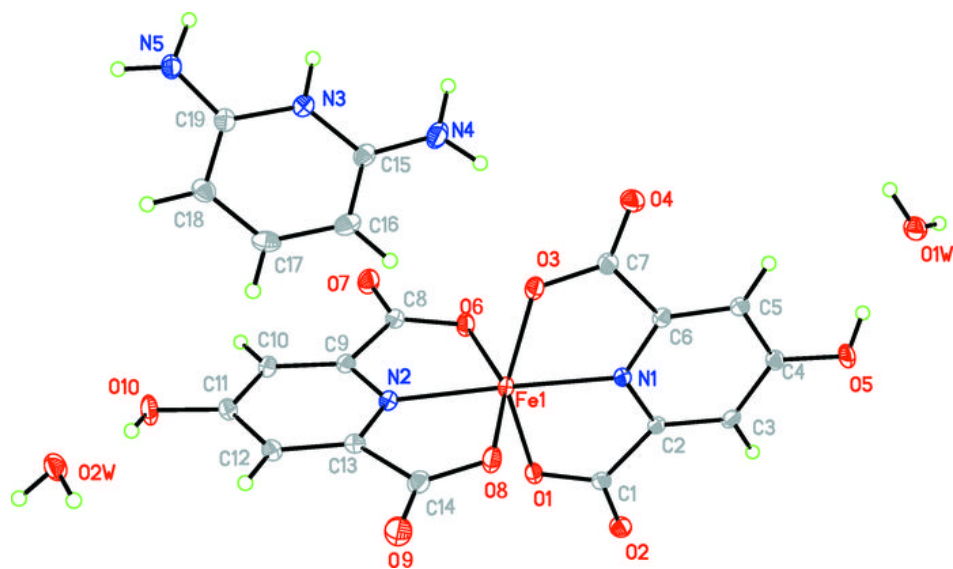


Fig. 2

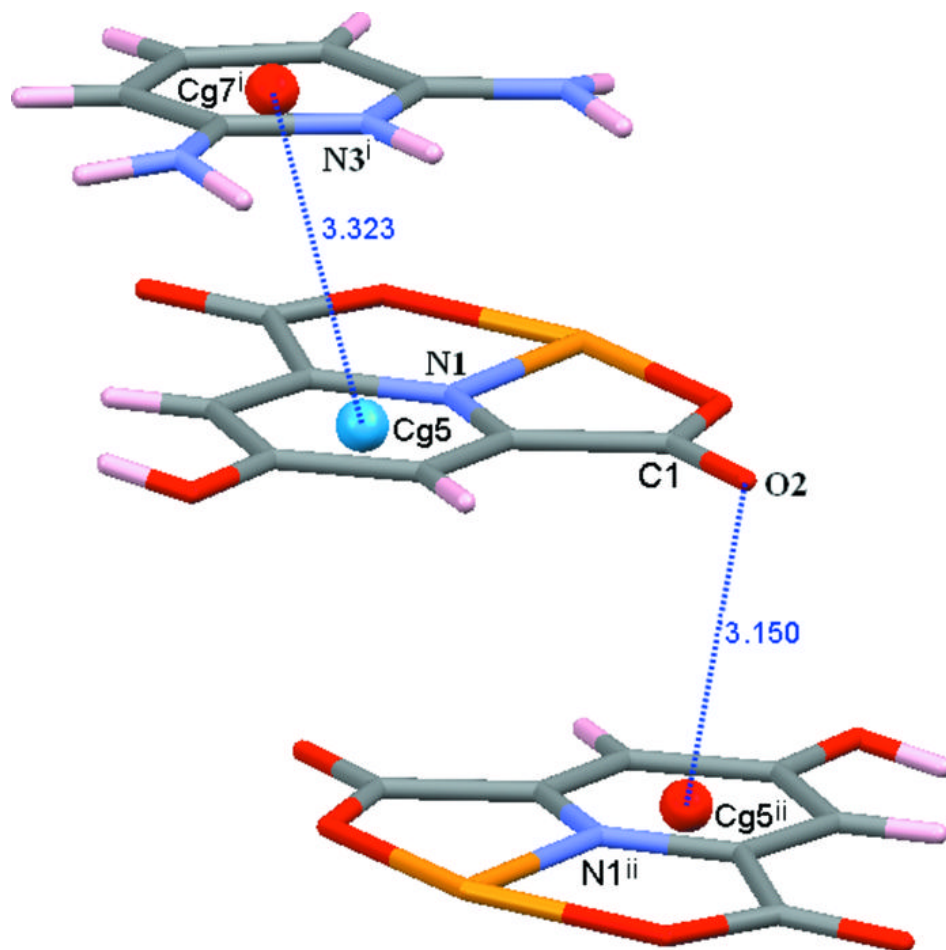


Fig. 3

