

Crystal structure of bis(1-ethylpyridinium) dioxonium hexacyanidoferrate(II)

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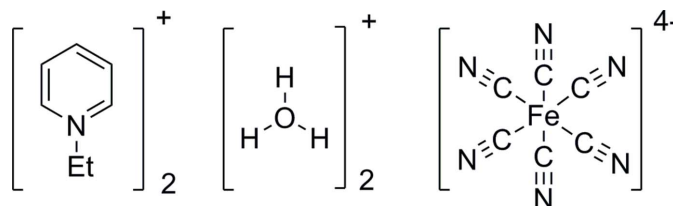
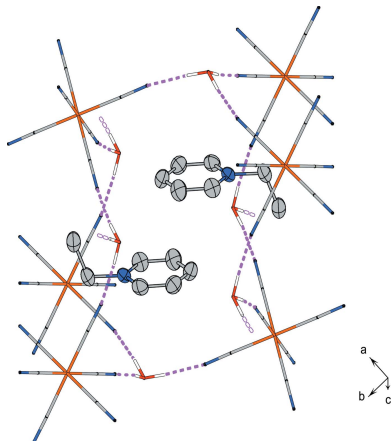
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The title compound, $(C_7H_{10}N)_2(H_3O)_2[Fe(CN)_6]$ or $(Etpy)_2(H_3O)_2[Fe(CN)_6]$ ($Etpy^+$ is 1-ethylpyridinium), crystallizes in the space group $Pnmm$. The Fe^{II} atom of the $[Fe(CN)_6]^{4-}$ anion lies on a site with site symmetry $.2/m$, and has an octahedral coordination sphere defined by six cyanido ligands. Both the $Etpy^+$ and the oxonium cations are located on a mirror plane. In the crystal, electron-donor anions of $[Fe(CN)_6]^{4-}$ and electron-acceptor cations of $Etpy^+$ are each stacked parallel to the b axis, resulting in a columnar structure with segregated moieties. The crystal packing is stabilized by a three-dimensional $O-H\cdots N$ hydrogen-bonding network between the oxonium ions and the cyanide ligands of $[Fe(CN)_6]^{4-}$.

1. Chemical context

Prussian blue is a well-known compound which displays a deep-blue colour based on an intervalence charge-transfer interaction between $[Fe^{II}(CN)_6]^{4-}$ electron-donor species and Fe^{III} electron-acceptor species. Several charge-transfer salts composed of $[Fe(CN)_6]^{4-}$ and organic acceptor cations, e.g. 1,1'-dimethyl-4,4'-bipyridinium (methyl viologen) have been reported (Nakahara & Wang, 1963; Kostina *et al.*, 2001; Kotov *et al.*, 2005; Abouelwafa *et al.*, 2010). In the majority of cases, the reported charge-transfer salts of $[Fe(CN)_6]^{4-}$ are accompanied by dicationic organic acceptor species. On the other hand, charge-transfer salts of $[Fe(CN)_6]^{4-}$ accompanied by monocationic species are rather rare (Gorelsky *et al.*, 2007).



The present X-ray crystallographic analysis of the title salt, $(Etpy)_2(H_3O)_2[Fe(CN)_6]$ ($Etpy^+$ is 1-ethylpyridinium), (I), was performed in order to elucidate the crystal packing of a charge-transfer hexacyanidoferrate(II) anion with a monocationic organic acceptor and an oxonium ion.

2. Structural commentary

The structures of the molecular components of (I) are displayed in Fig. 1. The asymmetric unit of (I) contains half of an $Etpy^+$ cation and an oxonium ion (both located on a mirror plane), and one quarter of an $[Fe(CN)_6]^{4-}$ anion, the Fe^{II} atom

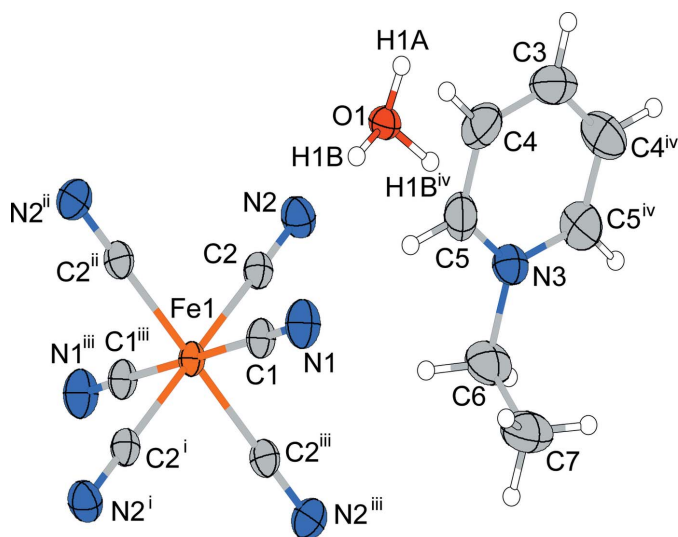


Figure 1
The structures of the molecular components of compound (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, -z$; (iii) $-x, -y, z$; (iv) $x, y, -z + 1$.]

of which is located on a site with symmetry $..2/m$. The Fe^{II} atom is coordinated by six cyanido ligands in a slightly distorted octahedral configuration [Fe–C = 1.9045 (18), 1.9068 (13) Å; C≡N = 1.157 (2), 1.1598 (17) Å; C–Fe–C_{trans} = 180.0°; C–Fe–C_{cis} = 89.60 (7)–90.40 (7)°; Fe–C–N = 178.67 (18), 179.77 (13)°]. The bond angle of the ethyl group of the Etpy⁺ ion [N3–C6–C7 = 110.77 (19) °] is similar to those of Etpy[AlCl₄] [109.2 (11)°; Zaworotko *et al.*, 1989] and poly[4-dimethylamino-1-ethylpyridin-1-ium [tri- μ -dicyanido- κ^6 N¹:N⁵-cadmium]] [111.5 (5)°; Wang *et al.*, 2015].

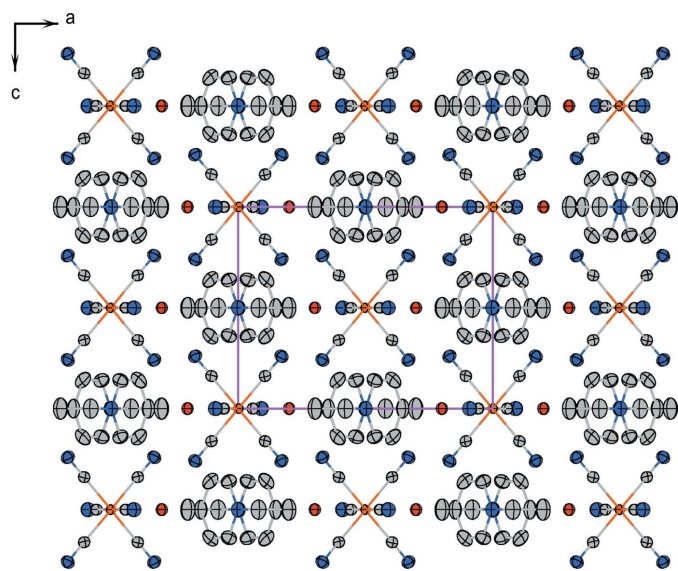


Figure 2
The crystal packing of compound (I) in a view along the *b* axis. H atoms have been omitted for clarity; the probability function is as in Fig. 1.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1A···N1 ⁱ	0.90 (3)	1.67 (3)	2.569 (2)	176 (3)
O1–H1B···N2	0.931 (18)	1.632 (19)	2.5589 (15)	173.6 (18)

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$.

3. Supramolecular features

The projection of the crystal structure of (I) along the *b* axis is shown in Fig. 2.

The [Fe(CN)₆]^{4–} electron-donor anions and the Etpy⁺ electron-acceptor cations stack separately in columns parallel to the *b* axis whereby both types of columns are alternately arranged in the *a*- and *c*-axis directions.

In the crystal of (I), the oxonium ions and [Fe(CN)₆]^{4–} ions form a three-dimensional O–H···N hydrogen-bonding network (Table 1). A pair of Etpy⁺ cations is enclosed in the hydrogen-bonding cage formed by six [Fe(CN)₆]^{4–} ions and six oxonium ions (Fig. 3). Two pyridinium rings of the Etpy⁺ cations are arranged in parallel and the ethyl groups are alternating with each other. The centroid-to-centroid distance (4.147 Å) and the face-to-face distance of the least-square planes (3.731 Å) between two pyridinium rings indicate that π – π interactions are not developed.

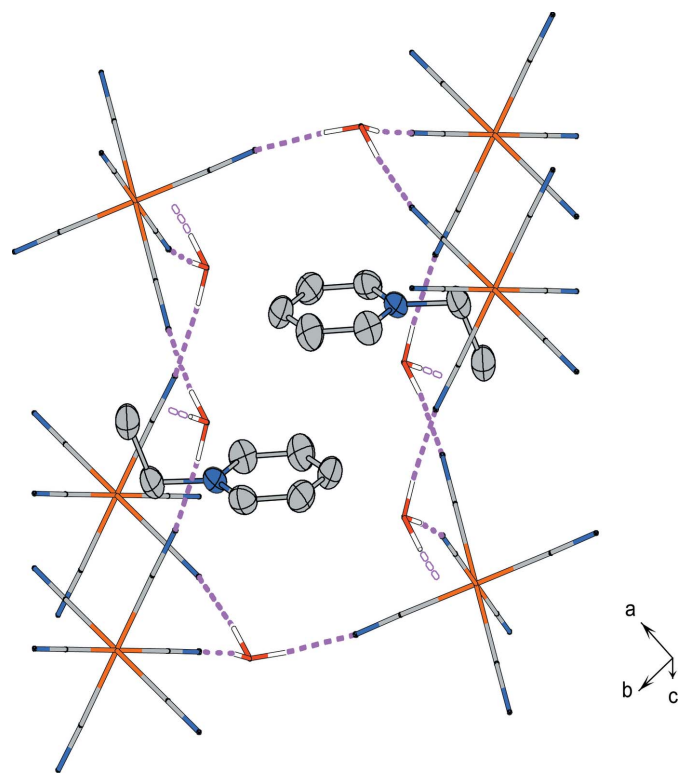


Figure 3
Hydrogen-bonding network composed of [Fe(CN)₆]^{4–} anions and oxonium cations. Magenta dashed lines represent hydrogen bonds.

4. Database survey

Several crystal structures of compounds containing the Etpy⁺ cation have been deposited in the Cambridge Structural Database (Groom *et al.* 2016), *e.g.* Etpy[AlCl₄] (Zaworotko *et al.*, 1989), Etpy[Ni(mnt)₂] (mnt = maleonitrile-1,2-dithiolate; Robertson *et al.*, 1999), or (Etpy)₂[CoCl₄] (Felloni *et al.*, 2004). A hexacyanidoferrate(II) salt, (Hpy)₂(H₃O)₂[Fe(CN)₆] (Hpy⁺ = *N*-hydropyridinium; Gorelsky *et al.*, 2007), quite similar to (I), has been also reported.

5. Synthesis and crystallization

H₄[Fe(CN)₆] (106 mg) and *L*-ascorbic acid (60 mg) were dissolved in water (17 ml). The mixture was added to an aqueous solution of 1-ethylpyridinium bromide (177 mg/17 ml). After standing at 277 K for a day, yellow platelet-shaped crystals suitable for X-ray analysis were obtained. Elemental analysis: found: C, 51.52; H, 5.878; N, 24.06%; calculated for C₂₀H₂₆FeN₈O₂: C, 51.51; H, 5.63; N, 24.03%. Thermogravimetry was measured from 296 to 476 K at a rate of 5 K min⁻¹ under N₂ gas flow (100 ml min⁻¹) on a Rigaku TG-DTA Thermo Plus EVO2 TG8121. Found: 7.85% mass loss; calculated: 7.73%. The mass loss of (I) took place at around 373 to 393 K and corresponds to two water molecules per chemical formula. The result suggests that the water molecules are released from the oxonium ions. Most probably, protons, H⁺, remain in the crystal as counter-cations. The IR spectrum of compound (I) is shown in Fig. 4. Selected IR bands (KBr pellet, cm⁻¹): 3135–2941 (*s*, C–H, *str*), 2640 (*br*, O–H, *str*), 2075 (*s*, C≡N, *str*).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. In the final refinement of the title compound, three reflections, *viz.* (0 17 1), (2 16 0) and (5 15 2),

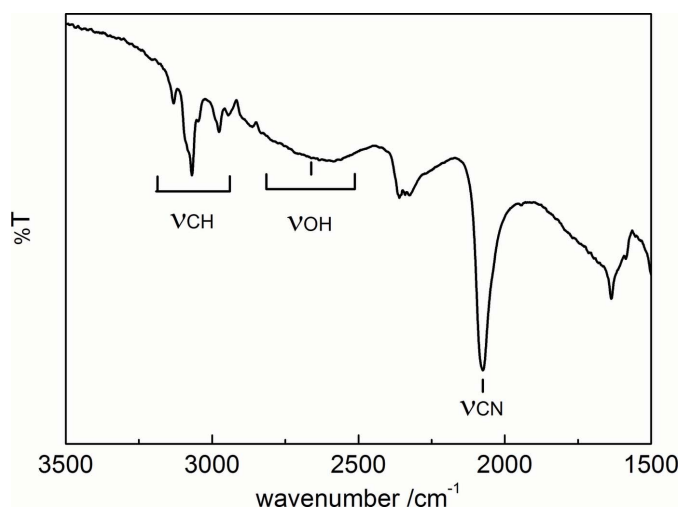


Figure 4
The IR spectrum of compound (I).

Table 2

Experimental details.

Crystal data	
Chemical formula	(C ₇ H ₁₀ N) ₂ (H ₃ O) ₂ [Fe(CN) ₆]
<i>M_r</i>	466.34
Crystal system, space group	Orthorhombic, <i>Pnmm</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.8807 (4), 12.1279 (7), 8.3962 (2)
<i>V</i> (Å ³)	1209.79 (9)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.65
Crystal size (mm)	0.28 × 0.13 × 0.08
Data collection	
Diffractometer	Rigaku R-Axis RAPID imaging-plate
Absorption correction	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)
<i>T_{min}</i> , <i>T_{max}</i>	0.907, 0.952
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	25575, 2216, 1840
<i>R_{int}</i>	0.034
(sin θ/ <i>λ</i>) _{max} (Å ⁻¹)	0.746
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.093, 1.11
No. of reflections	2213
No. of parameters	88
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.50, -0.70

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2016) and *publCIF* (Westrip, 2010).

were omitted owing to poor agreements between observed and calculated intensities. H atoms of the Etpy⁺ cation were, at first, located in a difference Fourier map, but finally placed in geometrically calculated positions and refined as riding, with C(methylene)–H = 0.92 Å, C(methyl)–H = 0.98 Å and C(aromatic)–H = 0.95 Å, all with *U*_{iso}(H) = 1.5*U*_{eq}(C). H atoms of the oxonium ion were located in a difference Fourier map and their positions refined with *U*_{iso}(H) = 1.5*U*_{eq}(O). The maximum and minimum electron density peaks are located 1.00 Å from atom C1 and 0.71 Å from atom Fe1, respectively.

Acknowledgements

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Crystal structure of bis(1-ethylpyridinium) dioxonium hexacyanidoferrate(II)

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Computing details

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO* (Rigaku, 2006); data reduction: *RAPID-AUTO* (Rigaku, 2006); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2016); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(1-ethylpyridinium) dioxonium hexacyanidoferrate(II)

Crystal data

$(C_7H_{10}N)_2(H_3O)_2[Fe(CN)_6]$

$M_r = 466.34$

Orthorhombic, *Pnmm*

$a = 11.8807$ (4) Å

$b = 12.1279$ (7) Å

$c = 8.3962$ (2) Å

$V = 1209.79$ (9) Å³

$Z = 2$

$F(000) = 488$

$D_x = 1.280$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å

Cell parameters from 8639 reflections

$\theta = 3.4\text{--}32.0^\circ$

$\mu = 0.65$ mm⁻¹

$T = 173$ K

Block, pale-yellow

$0.28 \times 0.13 \times 0.08$ mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer

Radiation source: X-ray sealed tube

Graphite monochromator

Detector resolution: 10.00 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.907$, $T_{\max} = 0.952$

25575 measured reflections

2216 independent reflections

1840 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 32.0^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -17 \rightarrow 17$

$k = -18 \rightarrow 18$

$l = -12 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.093$

$S = 1.11$

2213 reflections

88 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.6061P]$

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

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

$\Delta\rho_{\max} = 0.50$ e Å⁻³

$\Delta\rho_{\min} = -0.70$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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	0.0000	0.0000	0.0000	0.02095 (10)
C1	−0.05743 (16)	0.14661 (15)	0.0000	0.0257 (3)
C2	0.10536 (11)	0.04026 (10)	0.16115 (15)	0.0255 (2)
N1	−0.09019 (17)	0.23642 (15)	0.0000	0.0371 (4)
N2	0.16963 (11)	0.06441 (11)	0.25910 (15)	0.0352 (3)
N3	0.00181 (15)	0.25836 (14)	0.5000	0.0333 (3)
C3	0.1469 (2)	0.4327 (2)	0.5000	0.0485 (6)
H3	0.1978	0.4930	0.5000	0.073*
C4	0.10987 (15)	0.38888 (16)	0.3591 (2)	0.0498 (4)
H4	0.1344	0.4192	0.2607	0.075*
C5	0.03717 (15)	0.30083 (14)	0.3608 (2)	0.0431 (4)
H5	0.0118	0.2698	0.2633	0.065*
C6	−0.0794 (2)	0.16567 (19)	0.5000	0.0485 (6)
H6A	−0.0670	0.1193	0.5954	0.073*
C7	−0.1981 (2)	0.2077 (2)	0.5000	0.0570 (7)
H7A	−0.2503	0.1452	0.5000	0.086*
H7B	−0.2108	0.2527	0.5953	0.086*
O1	0.30049 (12)	0.08078 (12)	0.5000	0.0279 (3)
H1A	0.342 (2)	0.143 (2)	0.5000	0.042*
H1B	0.2513 (15)	0.0800 (15)	0.414 (2)	0.042*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.02418 (17)	0.02126 (16)	0.01740 (15)	0.00227 (12)	0.000	0.000
C1	0.0302 (8)	0.0250 (8)	0.0218 (7)	0.0048 (6)	0.000	0.000
C2	0.0299 (6)	0.0246 (5)	0.0220 (5)	0.0015 (4)	0.0015 (5)	−0.0001 (4)
N1	0.0454 (10)	0.0307 (8)	0.0353 (9)	0.0104 (7)	0.000	0.000
N2	0.0383 (6)	0.0393 (6)	0.0280 (5)	−0.0029 (5)	−0.0044 (5)	−0.0030 (5)
N3	0.0364 (8)	0.0254 (7)	0.0380 (9)	0.0019 (6)	0.000	0.000
C3	0.0341 (11)	0.0473 (13)	0.0641 (16)	−0.0065 (10)	0.000	0.000
C4	0.0518 (9)	0.0524 (9)	0.0451 (9)	−0.0064 (8)	0.0172 (8)	0.0013 (8)
C5	0.0522 (9)	0.0434 (8)	0.0336 (7)	−0.0007 (7)	0.0058 (7)	−0.0083 (7)
C6	0.0506 (13)	0.0276 (10)	0.0674 (17)	−0.0047 (9)	0.000	0.000
C7	0.0469 (14)	0.0416 (13)	0.083 (2)	−0.0110 (11)	0.000	0.000
O1	0.0292 (6)	0.0287 (6)	0.0257 (6)	−0.0063 (5)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Fe1—C1 ⁱ	1.9045 (18)	C3—C4 ^{iv}	1.369 (2)
Fe1—C1	1.9045 (18)	C3—H3	0.9500
Fe1—C2 ⁱ	1.9068 (13)	C4—C5	1.373 (2)
Fe1—C2 ⁱⁱ	1.9068 (13)	C4—H4	0.9500
Fe1—C2 ⁱⁱⁱ	1.9068 (13)	C5—H5	0.9500
Fe1—C2	1.9069 (13)	C6—C7	1.499 (4)
C1—N1	1.157 (2)	C6—H6A	0.9900
C2—N2	1.1598 (17)	C7—H7A	0.9800
N3—C5 ^{iv}	1.3447 (19)	C7—H7B	0.9800
N3—C5	1.3447 (19)	O1—H1A	0.90 (3)
N3—C6	1.482 (3)	O1—H1B	0.931 (18)
C3—C4	1.369 (2)	O1—H1B ^{iv}	0.931 (18)
C1 ⁱ —Fe1—C1	180.0	C5—N3—C6	119.61 (10)
C1 ⁱ —Fe1—C2 ⁱ	89.78 (5)	C4—C3—C4 ^{iv}	119.5 (2)
C1—Fe1—C2 ⁱ	90.22 (5)	C4—C3—H3	120.2
C1 ⁱ —Fe1—C2 ⁱⁱ	90.22 (5)	C4 ^{iv} —C3—H3	120.2
C1—Fe1—C2 ⁱⁱ	89.78 (5)	C3—C4—C5	119.65 (17)
C2 ⁱ —Fe1—C2 ⁱⁱ	89.60 (7)	C3—C4—H4	120.2
C1 ⁱ —Fe1—C2 ⁱⁱⁱ	89.78 (5)	C5—C4—H4	120.2
C1—Fe1—C2 ⁱⁱⁱ	90.22 (5)	N3—C5—C4	120.20 (16)
C2 ⁱ —Fe1—C2 ⁱⁱⁱ	90.40 (7)	N3—C5—H5	119.9
C2 ⁱⁱ —Fe1—C2 ⁱⁱⁱ	180.00 (11)	C4—C5—H5	119.9
C1 ⁱ —Fe1—C2	90.22 (5)	N3—C6—C7	110.77 (19)
C1—Fe1—C2	89.78 (5)	N3—C6—H6A	109.5
C2 ⁱ —Fe1—C2	180.0	C7—C6—H6A	109.5
C2 ⁱⁱ —Fe1—C2	90.40 (7)	C6—C7—H7A	109.4
C2 ⁱⁱⁱ —Fe1—C2	89.60 (7)	C6—C7—H7B	109.5
N1—C1—Fe1	178.67 (18)	H7A—C7—H7B	109.5
N2—C2—Fe1	179.77 (13)	H1A—O1—H1B	110.5 (14)
C5 ^{iv} —N3—C5	120.8 (2)	H1A—O1—H1B ^{iv}	110.5 (14)
C5 ^{iv} —N3—C6	119.61 (10)	H1B—O1—H1B ^{iv}	102 (2)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots N1 ^v	0.90 (3)	1.67 (3)	2.569 (2)	176 (3)
O1—H1B \cdots N2	0.931 (18)	1.632 (19)	2.5589 (15)	173.6 (18)

Symmetry code: (v) $x+1/2, -y+1/2, -z+1/2$.