



Crystal structure of (2-acetylferrocen-1-yl)boronic acid

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Received 5 December 2018

Accepted 22 January 2019

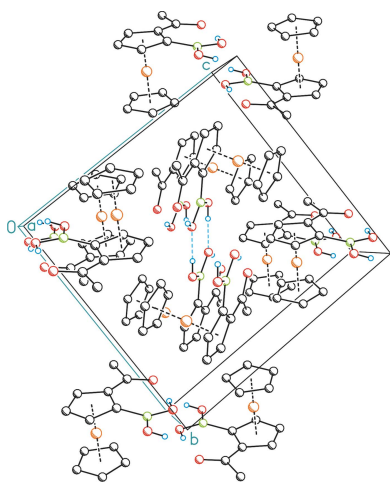
Edited by M. Weil, Vienna University of
Technology, Austria**Keywords:** crystal structure; ferrocene; planar
chirality; boronic acid; *ortho*-functionalization.**CCDC reference:** 1892711**Supporting information:** this article has
supporting information at journals.iucr.org/e

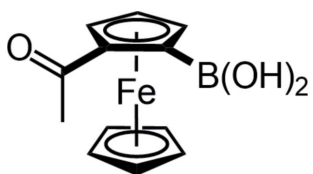
(2-Acetylferrocen-1-yl)boronic acid, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_8\text{BO}_3)]$ or 2-C(O)CH₃-1-B(OH)₂-Fc [Fc = $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$], crystallizes in the centrosymmetric space group $P2_1/n$. The boronic acid functionality interacts *via* intramolecular hydrogen bonds with the acetyl group and with the –B(OH)₂ functionality of an adjacent molecule. The resulting centrosymmetric dimer exhibits an *anti*-positioning of the ferrocenyl moieties towards the central B₂O₄ plane. Consequently, an (*R_p*,*S_p*)-, *i.e.* a *meso* configuration is present for this dimer. In the crystal, weak C–H...O hydrogen bonds consolidate the molecular packing.

1. Chemical context

The synthesis of 1,2-functionalized ferrocenes is a striking topic in ferrocene chemistry (Schaarschmidt & Lang, 2013; Korb *et al.*, 2014a) and is mostly realized *via ortho*-directed metalation and subsequent reaction with electrophiles (Schaarschmidt & Lang, 2013) or intramolecular rearrangement (Werner & Butenschön, 2013; Korb & Lang, 2014, 2016; Korb *et al.*, 2017). The resulting ferrocenes are predominantly used as ligands in *C,C* cross-coupling catalysis (Schaarschmidt *et al.*, 2014; Jensen & Johannsen, 2003; Vinci *et al.*, 2009; Debono *et al.*, 2010; Karpus *et al.*, 2016), but also the introduction of ferrocenyl substituents by catalytic conversions is of rising interest (Hildebrandt *et al.*, 2011a,b; Speck *et al.*, 2015; Korb *et al.*, 2014b). The introduction of electronically and sterically modified substrates requires the synthesis of the respective ferrocenes that bear groups suitable for oxidative additions or transmetalation reactions (Lehrich *et al.*, 2015; Speck *et al.*, 2014). In case of substrates that are sensitive towards a nucleophilic attack, *e.g.* acyl groups, the Suzuki–Miyaura instead of a Negishi reaction is commonly used, and hence requires the presence of a boronic acid functionality (Speck *et al.*, 2015). However, the acidic protons prevent a straightforward *ortho*-directed metalation, and additional reaction steps for the introduction and removal of protecting groups are required. Electrophilic aromatic substitution (*S_EAr*) reactions are also not suitable, since they usually give 1'- or 3-functionalized products (Rosenblum & Woodward, 1958).

Within our attempts to synthesize new electronically modified ferrocenes as substrates for Suzuki–Miyaura reactions, we herein present the synthesis and crystal structure of an *ortho*-functionalized ferrocenylboronic acid, obtained *via S_EAr* without using a protection group strategy for the acidic protons.





2. Structural commentary

The title compound crystallizes in the centrosymmetric space group $P2_1/n$ with one molecule in the asymmetric unit (Fig. 1). An intramolecular hydrogen bond between the oxygen atom of the acetyl group (O1) and the neighbouring hydroxy group (O2) of the boronic acid functionality of 2.650 (2) Å (Table 1) is present. Therefore, both substituents are co-planar with each other [$\text{BO}_2 \cdots \text{C}_2\text{O} = 2.9 (4)^\circ$]. The $\text{C}=\text{O}$ distance of 1.233 (2) Å is neither affected by the involvement into this hydrogen bond, nor the presence of an *ortho* substituent and is therefore similar to unsubstituted acetyl ferrocene (Sato *et al.*, 1984).

With regard to the C_5H_3 plane of the ferrocenyl backbone, both substituents reveal a slight *endo*-bending of $7.0 (3)^\circ$ ($\text{C}_5\text{H}_3 \cdots \text{C}_2\text{O}$) and $9.5 (3)^\circ$ ($\text{C}_5\text{H}_3 \cdots \text{BO}_2$). The ferrocenyl backbone exhibits an eclipsed conformation ($\text{C1}-\text{Cg}-\text{Cg}-\text{C8} = 8.21 (14)^\circ$; Cg is the centroid of the respective cyclopentadienyl ring) and a tilt angle of $179.28 (2)^\circ$. The hydrogen atom at O3 is directed away from the ferrocenyl backbone and points to an adjacent molecule.

3. Supramolecular features

In addition to the aforementioned intramolecular hydrogen bond between O1 and O2, the latter atom is also involved as an acceptor of an intermolecular hydrogen bond with the second hydroxy group (O3) of an adjacent boronic acid

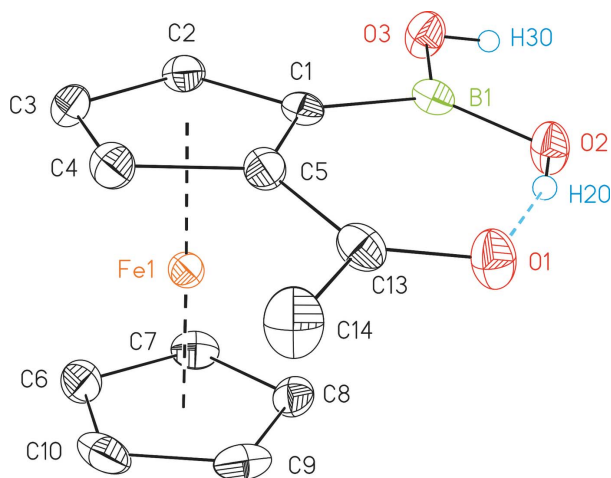


Figure 1

The molecular structure of the title compound showing the intramolecular hydrogen bond between the acetyl and the boronic acid functionalities. Displacement ellipsoids are drawn at the 50% probability level; C-bonded hydrogen atoms have been omitted for clarity.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O2}-\text{H2O} \cdots \text{O1}$	0.82	1.85	2.650 (2)	166
$\text{O3}-\text{H3O} \cdots \text{O2}^{\text{i}}$	0.82	1.94	2.744 (2)	168
$\text{C9}-\text{H9} \cdots \text{O3}^{\text{ii}}$	0.93	2.45	3.308 (3)	154
$\text{C10}-\text{H10} \cdots \text{O1}^{\text{iii}}$	0.93	2.53	3.404 (3)	156

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

functionality of 2.744 (2) Å (Fig. 2, Table 1). The resulting dimer is centrosymmetric with the inversion center located at the middle of the eight-membered ring formed by the two boronic acid functionalities. Therefore, both ferrocenyl moieties are positioned *anti* with regard to the central B_2O_4 plane. Hence, a racemic mixture of both enantiomers crystallized, giving the R_p/S_p -configured, *i.e.* *meso* diastereomer if the dimer is considered as one supramolecular entity. The respective *racem* configuration (R_p/R_p or S_p/S_p) is not present within the packing (Fig. 3).

The B—O bond lengths involving O3 [1.356 (3) Å] and O2 [1.362 (3) Å] are similar, although the latter also acts as a hydrogen-bond acceptor, in contrast to O3.

A short contact of 4.6807 (14) Å between a C_5H_3 and a C_5H_5 ring does not show a perpendicular positioning of the two groups ($\beta = 25^\circ$) and therefore does not fit the criteria for a *T*-shaped π - π interaction (Sinnokrot *et al.*, 2002). However, weak $\text{C}-\text{H} \cdots \text{O}$ interactions between aromatic H atoms and the carbonyl O1 atom and a boronic acid O atom (O3) consolidate the crystal packing (Table 1).

4. Database survey

Besides ferrocenyl boronic acid (Bresner *et al.*, 2004) and acetyl ferrocene (Sato *et al.*, 1984) that are frequently used in

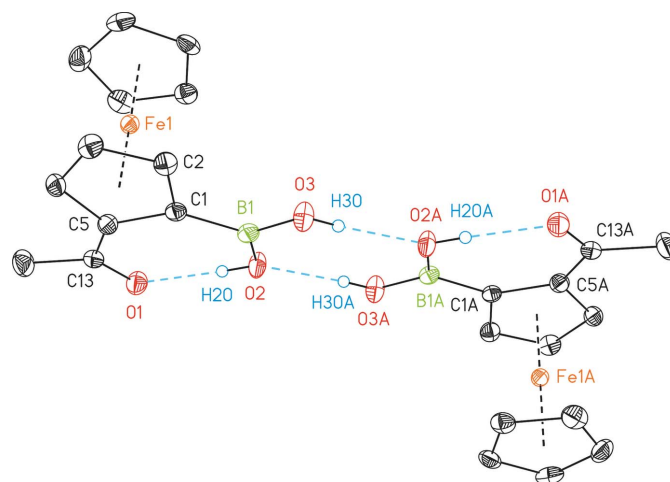
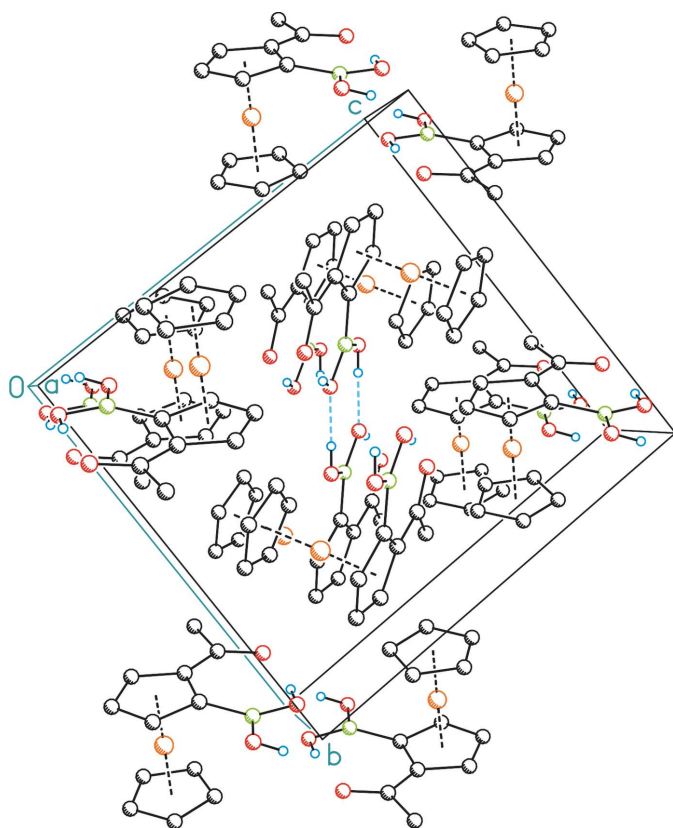


Figure 2

Intra- and intermolecular hydrogen bonds within the dimer, with displacement ellipsoids drawn at the 50% probability level. C-bonded hydrogen atoms have been omitted for clarity. [Symmetry code: (A) $1 - x, 1 - y, 1 - z$.]


Figure 3

Unit cell of the title compound in a view along [100]. Hydrogen bonds are shown as pale-blue dashed lines; displacement ellipsoids are drawn at the 50% probability level. C-bonded hydrogen atoms have been omitted for clarity.

general, other *ortho*-substituted analogues are sparsely described.

Crystal structures of acetylferrocenes bearing additional *ortho*-substituents are limited to a few examples, *e.g.* with PPh₂ (Torres *et al.*, 2011), iodine (Ferber *et al.*, 2007) and a ferrocenylmethyl group (Xie *et al.*, 2011) as the sole second substituent. In contrast, carbonyl, *i.e.* formyl or acyl groups, are more common, *e.g.* in ferrocenyl methylferrocene (Enders *et al.*, 2003).

Functionalized ferrocenylboronic acids are usually reported together with their protected 1,3,2-dioxaborolane derivatives. As *ortho*-substituents, diisopropylcarbamoyl (Batsanov *et al.*, 2007) and dimethylcarbamoyl (Norrild & Søjtofte, 2001), together with their respective aminomethyl derivatives (Batsanov *et al.*, 2007; Norrild & Søjtofte, 2001) have structurally been described. Heterocycles, such as imidazolidone (Metallinos *et al.*, 2012) are also known as *ortho*-substituents for ferrocenyl derivatives.

In case of non-ferrocenyl-based aromatics, the 2-C(O)CH₃-1-B(OH)₂ substitution pattern is solely reported for the benzene core (Ganguly *et al.*, 2003). In contrast to the title compound, the boronic acid functionality is rotated out of coplanarity with the benzene core and the acetyl group by 78.2 and 77.7°, respectively.

Table 2

Experimental details.

Crystal data	
Chemical formula	[Fe(C ₅ H ₅)(C ₇ H ₈ BO ₃)]
<i>M_r</i>	271.88
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	116
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.7627 (3), 11.7335 (5), 12.7969 (5)
β (°)	98.527 (4)
<i>V</i> (Å ³)	1152.70 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.30
Crystal size (mm)	0.40 × 0.25 × 0.20
Data collection	
Diffractometer	Oxford Gemini S
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.868, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4556, 2406, 2108
<i>R</i> _{int}	0.019
(sin θ/λ) _{max} (Å ⁻¹)	0.667
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.071, 1.08
No. of reflections	2406
No. of parameters	157
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.37, -0.28

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2014), *SHELXT2013* (Sheldrick, 2015a), *SHELXL2013* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

For *ortho*-carbonyl groups in general, the involvement of the boronic acid functionality in inter- and intramolecular hydrogen bonds, similar to the title compound, is a common feature (Yan *et al.*, 2003; Luliński *et al.*, 2007; Durka *et al.*, 2014; Madura *et al.*, 2015).

5. Synthesis and crystallization

Ferroceneboronic acid (0.5 g, 2.175 mmol) was suspended in acetic anhydride (10 ml). To this suspension BF₃·OEt₂ (0.40 ml, 3.15 mmol) was added in a single portion. The reaction mixture was stirred for 30 min at ambient temperature. Afterwards, the mixture was poured into ice and was stirred for 10 minutes. A KOH solution (9 *M*, 10 ml) was added in a single portion following a neutralization with K₂CO₃ until the CO₂ evolution stopped. The mixture was extracted with dichloromethane (3 × 20 ml) and the organic phase was dried over MgSO₄. The volatiles were removed in vacuum (1 mbar). The crude material obtained was purified by flash chromatography on silica using a 4/1 (*v/v*) diethyl ether/dichloromethane mixture. The title compound was isolated as a brown solid. Yield: 75 mg (0.28 mmol, 13% based on ferroceneboronic acid).

IR data (KBr, ν/cm⁻¹): 3357 (*w*), 2925 (*m*), 2855 (*m*), 1685 (*m*), 1654 (*s*), 1647 (*m*), 1636 (*s*), 1618 (*s*), 1578 (*m*), 1559 (*m*), 1522 (*m*), 1507 (*m*), 1457 (*s*); 1419 (*s*), 1411 (*s*), 1374 (*s*), 1354 (*s*), 1345 (*s*); 1318 (*m*), 1247 (*m*), 1207 (*m*), 1134 (*m*), 1106 (*m*), 1094 (*m*), 1045 (*m*), 1001 (*w*), 924 (*w*), 873 (*w*), 862 (*w*), 785

(*w*), 668 (*m*), 642 (*w*). ^1H NMR (CDCl_3 , δ): 2.49 (*s*, 3H, CH_3), 4.23 (*s*, 5H, C_5H_5), 4.78 (*t*, $J_{\text{HH}} = 2.6$ Hz, 1H, C_5H_3), 4.92 (*dd*, $J_{\text{HH}} = 2.6$ Hz, 1.3 Hz, 1H, C_5H_3), 5.01 (*dd*, $J_{\text{HH}} = 2.6$ Hz, 1.3 Hz, 1H, C_5H_3), 7.38 (*br s*, 2H, $\text{B}(\text{OH})_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 28.1 (CH_3), 71.1 (C_5H_5), 76.1 (C_5H_3), 77.2 (C_5H_3), 80.1 (C_5H_3), 81.1 (C_5H_3), 81.8 (C_5H_3), 208.1 (CO). HRMS (ESI-TOF, *m/z*): calculated for $\text{C}_{12}\text{H}_{13}\text{BFeO}_3$ 272.0304, found 272.0320 [M] $^+$.

Crystals suitable for X-ray crystallography were obtained from evaporation of a saturated dichloromethane solution at ambient temperature.

6. Refinement

Crystal data, data collection and structure refinement detail are summarized in Table 2. C-bound H atoms were placed in calculated positions and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and a C–H distance of 0.93 Å for aromatic and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and a C–H distance of 0.96 Å for methyl H atoms, with their torsion angle derived from the residual electron density. The hydroxy hydrogen atoms were located from difference-Fourier maps but were treated with idealized geometry with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, an O–H distance of 0.82 Å and a torsion angle derived from the residual electron density.

Funding information

We are grateful to the Federal Cluster of Excellence EXC 1075 "MERGE Technologies for Multifunctional Lightweight Structures". This project has received funding from the European Social Fund (ESF). The publication costs of this article were funded by the German Research Foundation/DFG-392676956 and the Technische Universität Chemnitz in the funding program Open Access Publishing.

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supporting information

Acta Cryst. (2019). E75, 268-271 [https://doi.org/10.1107/S2056989019001178]

Crystal structure of (2-acetylferrocen-1-yl)boronic acid

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Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2014); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2014); data reduction: *CrysAlis RED* (Oxford Diffraction, 2014); program(s) used to solve structure: SHELXT2013 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

(2-Acetylferrocen-1-yl)boronic acid

Crystal data

[Fe(C₅H₅)(C₇H₈BO₃)]

$M_r = 271.88$

Monoclinic, $P2_1/n$

$a = 7.7627$ (3) Å

$b = 11.7335$ (5) Å

$c = 12.7969$ (5) Å

$\beta = 98.527$ (4)°

$V = 1152.70$ (8) Å³

$Z = 4$

$F(000) = 560$

$D_x = 1.567$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2357 reflections

$\theta = 3.7$ – 28.0 °

$\mu = 1.30$ mm⁻¹

$T = 116$ K

Block, orange

$0.40 \times 0.25 \times 0.20$ mm

Data collection

Oxford Gemini S
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Rigaku OD, 2015)

$T_{\min} = 0.868$, $T_{\max} = 1.000$

4556 measured reflections

2406 independent reflections

2108 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 3.2$ °

$h = -9 \rightarrow 10$

$k = -13 \rightarrow 15$

$l = -16 \rightarrow 16$

2 standard reflections every 50 reflections

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.071$

$S = 1.08$

2406 reflections

157 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.4245P]$

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

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.28$ 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.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2362 (2)	0.71679 (17)	0.35395 (14)	0.0159 (4)
C2	0.2734 (3)	0.75344 (17)	0.25306 (15)	0.0189 (4)
H2	0.3701	0.7314	0.2229	0.023*
C3	0.1414 (3)	0.82799 (17)	0.20593 (16)	0.0202 (4)
H3	0.1361	0.8621	0.1399	0.024*
C4	0.0188 (3)	0.84184 (17)	0.27622 (15)	0.0193 (4)
H4	-0.0804	0.8872	0.2649	0.023*
C5	0.0743 (3)	0.77358 (17)	0.36840 (14)	0.0174 (4)
C6	-0.0701 (3)	0.60243 (19)	0.09838 (15)	0.0243 (5)
H6	-0.0624	0.6319	0.0318	0.029*
C7	0.0489 (3)	0.52589 (18)	0.15604 (15)	0.0211 (4)
H7	0.1485	0.4961	0.1339	0.025*
C8	-0.0103 (3)	0.50261 (18)	0.25363 (15)	0.0208 (4)
H8	0.0434	0.4547	0.3066	0.025*
C9	-0.1650 (3)	0.56502 (19)	0.25598 (17)	0.0249 (5)
H9	-0.2307	0.5658	0.3111	0.030*
C10	-0.2028 (3)	0.6261 (2)	0.16011 (17)	0.0271 (5)
H10	-0.2982	0.6736	0.1410	0.033*
C13	-0.0314 (3)	0.75364 (18)	0.45290 (15)	0.0191 (4)
C14	-0.1979 (3)	0.8197 (2)	0.44975 (17)	0.0286 (5)
H14A	-0.2495	0.8027	0.5117	0.043*
H14B	-0.2771	0.7988	0.3878	0.043*
H14C	-0.1735	0.8998	0.4478	0.043*
B1	0.3493 (3)	0.6251 (2)	0.42048 (17)	0.0180 (5)
O1	0.01228 (19)	0.68590 (13)	0.52571 (11)	0.0242 (3)
O2	0.30364 (18)	0.57462 (13)	0.50825 (10)	0.0224 (3)
H2O	0.2091	0.5995	0.5190	0.034*
O3	0.50175 (17)	0.59706 (13)	0.38717 (11)	0.0237 (3)
H3O	0.5472	0.5439	0.4227	0.036*
Fe1	0.03493 (3)	0.67352 (2)	0.23909 (2)	0.01438 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0146 (9)	0.0161 (10)	0.0164 (9)	-0.0020 (8)	0.0000 (7)	-0.0028 (8)
C2	0.0174 (10)	0.0184 (10)	0.0211 (10)	-0.0030 (9)	0.0032 (8)	0.0000 (9)

C3	0.0238 (11)	0.0167 (10)	0.0198 (10)	-0.0035 (9)	0.0022 (8)	0.0045 (9)
C4	0.0216 (10)	0.0140 (10)	0.0218 (10)	0.0025 (8)	0.0010 (8)	-0.0010 (9)
C5	0.0191 (10)	0.0151 (10)	0.0173 (9)	0.0011 (8)	0.0006 (8)	-0.0004 (8)
C6	0.0308 (12)	0.0261 (12)	0.0140 (9)	-0.0074 (10)	-0.0029 (8)	-0.0015 (9)
C7	0.0218 (10)	0.0192 (11)	0.0228 (10)	-0.0017 (9)	0.0053 (8)	-0.0094 (9)
C8	0.0256 (11)	0.0151 (10)	0.0214 (10)	-0.0030 (9)	0.0020 (9)	0.0002 (9)
C9	0.0201 (11)	0.0265 (12)	0.0297 (11)	-0.0095 (9)	0.0096 (9)	-0.0062 (10)
C10	0.0176 (10)	0.0245 (12)	0.0358 (12)	-0.0013 (10)	-0.0074 (9)	-0.0046 (10)
C13	0.0192 (10)	0.0200 (11)	0.0174 (9)	0.0015 (9)	0.0006 (8)	-0.0052 (9)
C14	0.0276 (12)	0.0328 (13)	0.0270 (11)	0.0116 (10)	0.0096 (10)	0.0015 (10)
B1	0.0160 (11)	0.0185 (11)	0.0186 (10)	-0.0014 (10)	-0.0001 (9)	-0.0027 (10)
O1	0.0239 (8)	0.0309 (9)	0.0184 (7)	0.0073 (7)	0.0048 (6)	0.0034 (7)
O2	0.0183 (7)	0.0286 (9)	0.0208 (7)	0.0084 (7)	0.0048 (6)	0.0071 (7)
O3	0.0190 (7)	0.0253 (9)	0.0276 (8)	0.0054 (7)	0.0059 (6)	0.0084 (7)
Fe1	0.01391 (16)	0.01475 (16)	0.01429 (15)	0.00022 (11)	0.00151 (11)	0.00008 (11)

Geometric parameters (Å, °)

C1—C2	1.430 (3)	C7—Fe1	2.043 (2)
C1—C5	1.459 (3)	C7—H7	0.9300
C1—B1	1.560 (3)	C8—C9	1.411 (3)
C1—Fe1	2.0443 (18)	C8—Fe1	2.049 (2)
C2—C3	1.413 (3)	C8—H8	0.9300
C2—Fe1	2.059 (2)	C9—C10	1.414 (3)
C2—H2	0.9300	C9—Fe1	2.043 (2)
C3—C4	1.412 (3)	C9—H9	0.9300
C3—Fe1	2.062 (2)	C10—Fe1	2.045 (2)
C3—H3	0.9300	C10—H10	0.9300
C4—C5	1.438 (3)	C13—O1	1.233 (2)
C4—Fe1	2.040 (2)	C13—C14	1.503 (3)
C4—H4	0.9300	C14—H14A	0.9600
C5—C13	1.470 (3)	C14—H14B	0.9600
C5—Fe1	2.0150 (19)	C14—H14C	0.9600
C6—C7	1.415 (3)	B1—O3	1.356 (3)
C6—C10	1.416 (3)	B1—O2	1.362 (3)
C6—Fe1	2.0414 (19)	O2—H2O	0.8200
C6—H6	0.9300	O3—H3O	0.8200
C7—C8	1.420 (3)		
C2—C1—C5	105.66 (17)	O1—C13—C5	122.50 (18)
C2—C1—B1	121.86 (17)	O1—C13—C14	119.45 (18)
C5—C1—B1	132.22 (17)	C5—C13—C14	118.04 (17)
C2—C1—Fe1	70.16 (11)	C13—C14—H14A	109.5
C5—C1—Fe1	67.87 (10)	C13—C14—H14B	109.5
B1—C1—Fe1	121.98 (14)	H14A—C14—H14B	109.5
C3—C2—C1	109.94 (18)	C13—C14—H14C	109.5
C3—C2—Fe1	70.07 (11)	H14A—C14—H14C	109.5
C1—C2—Fe1	69.05 (11)	H14B—C14—H14C	109.5

C3—C2—H2	125.0	O3—B1—O2	119.99 (19)
C1—C2—H2	125.0	O3—B1—C1	116.25 (18)
Fe1—C2—H2	127.5	O2—B1—C1	123.75 (18)
C4—C3—C2	108.30 (18)	B1—O2—H2O	109.5
C4—C3—Fe1	69.01 (12)	B1—O3—H3O	109.5
C2—C3—Fe1	69.84 (11)	C5—Fe1—C4	41.54 (8)
C4—C3—H3	125.9	C5—Fe1—C6	162.67 (9)
C2—C3—H3	125.9	C4—Fe1—C6	124.81 (9)
Fe1—C3—H3	126.9	C5—Fe1—C7	155.19 (8)
C3—C4—C5	108.07 (18)	C4—Fe1—C7	162.14 (8)
C3—C4—Fe1	70.72 (12)	C6—Fe1—C7	40.53 (8)
C5—C4—Fe1	68.32 (11)	C5—Fe1—C9	107.54 (8)
C3—C4—H4	126.0	C4—Fe1—C9	120.33 (9)
C5—C4—H4	126.0	C6—Fe1—C9	68.20 (9)
Fe1—C4—H4	126.6	C7—Fe1—C9	68.08 (8)
C4—C5—C1	108.02 (17)	C5—Fe1—C1	42.11 (8)
C4—C5—C13	124.06 (18)	C4—Fe1—C1	70.05 (8)
C1—C5—C13	127.32 (17)	C6—Fe1—C1	153.94 (9)
C4—C5—Fe1	70.14 (11)	C7—Fe1—C1	119.38 (8)
C1—C5—Fe1	70.02 (11)	C9—Fe1—C1	126.18 (8)
C13—C5—Fe1	118.56 (14)	C5—Fe1—C10	125.46 (9)
C7—C6—C10	107.85 (18)	C4—Fe1—C10	107.24 (9)
C7—C6—Fe1	69.81 (11)	C6—Fe1—C10	40.54 (9)
C10—C6—Fe1	69.88 (11)	C7—Fe1—C10	68.05 (9)
C7—C6—H6	126.1	C9—Fe1—C10	40.46 (9)
C10—C6—H6	126.1	C1—Fe1—C10	163.81 (9)
Fe1—C6—H6	125.8	C5—Fe1—C8	120.19 (8)
C6—C7—C8	108.03 (18)	C4—Fe1—C8	155.41 (8)
C6—C7—Fe1	69.65 (12)	C6—Fe1—C8	68.21 (8)
C8—C7—Fe1	69.91 (11)	C7—Fe1—C8	40.60 (8)
C6—C7—H7	126.0	C9—Fe1—C8	40.32 (8)
C8—C7—H7	126.0	C1—Fe1—C8	107.50 (8)
Fe1—C7—H7	126.0	C10—Fe1—C8	67.96 (9)
C9—C8—C7	107.85 (18)	C5—Fe1—C2	68.80 (8)
C9—C8—Fe1	69.61 (12)	C4—Fe1—C2	67.92 (8)
C7—C8—Fe1	69.49 (12)	C6—Fe1—C2	119.92 (8)
C9—C8—H8	126.1	C7—Fe1—C2	108.35 (8)
C7—C8—H8	126.1	C9—Fe1—C2	164.08 (8)
Fe1—C8—H8	126.4	C1—Fe1—C2	40.79 (7)
C8—C9—C10	108.23 (19)	C10—Fe1—C2	154.21 (9)
C8—C9—Fe1	70.06 (12)	C8—Fe1—C2	126.99 (8)
C10—C9—Fe1	69.85 (12)	C5—Fe1—C3	68.91 (8)
C8—C9—H9	125.9	C4—Fe1—C3	40.27 (8)
C10—C9—H9	125.9	C6—Fe1—C3	107.30 (8)
Fe1—C9—H9	125.8	C7—Fe1—C3	125.75 (8)
C9—C10—C6	108.05 (19)	C9—Fe1—C3	154.59 (9)
C9—C10—Fe1	69.69 (12)	C1—Fe1—C3	69.07 (8)
C6—C10—Fe1	69.58 (12)	C10—Fe1—C3	119.80 (9)

C9—C10—H10	126.0	C8—Fe1—C3	163.37 (8)
C6—C10—H10	126.0	C2—Fe1—C3	40.09 (8)
Fe1—C10—H10	126.3		
C5—C1—C2—C3	-0.7 (2)	C10—C6—C7—Fe1	-59.77 (15)
B1—C1—C2—C3	174.20 (18)	C6—C7—C8—C9	-0.2 (2)
Fe1—C1—C2—C3	58.18 (14)	Fe1—C7—C8—C9	59.26 (14)
C5—C1—C2—Fe1	-58.86 (13)	C6—C7—C8—Fe1	-59.45 (14)
B1—C1—C2—Fe1	116.02 (18)	C7—C8—C9—C10	0.5 (2)
C1—C2—C3—C4	0.9 (2)	Fe1—C8—C9—C10	59.65 (15)
Fe1—C2—C3—C4	58.44 (14)	C7—C8—C9—Fe1	-59.18 (14)
C1—C2—C3—Fe1	-57.58 (14)	C8—C9—C10—C6	-0.6 (2)
C2—C3—C4—C5	-0.7 (2)	Fe1—C9—C10—C6	59.21 (15)
Fe1—C3—C4—C5	58.27 (14)	C8—C9—C10—Fe1	-59.78 (15)
C2—C3—C4—Fe1	-58.96 (14)	C7—C6—C10—C9	0.5 (2)
C3—C4—C5—C1	0.3 (2)	Fe1—C6—C10—C9	-59.28 (15)
Fe1—C4—C5—C1	60.03 (14)	C7—C6—C10—Fe1	59.73 (14)
C3—C4—C5—C13	-171.44 (18)	C4—C5—C13—O1	172.7 (2)
Fe1—C4—C5—C13	-111.68 (19)	C1—C5—C13—O1	2.7 (3)
C3—C4—C5—Fe1	-59.77 (14)	Fe1—C5—C13—O1	88.4 (2)
C2—C1—C5—C4	0.3 (2)	C4—C5—C13—C14	-7.8 (3)
B1—C1—C5—C4	-173.9 (2)	C1—C5—C13—C14	-177.86 (19)
Fe1—C1—C5—C4	-60.11 (14)	Fe1—C5—C13—C14	-92.1 (2)
C2—C1—C5—C13	171.61 (19)	C2—C1—B1—O3	11.5 (3)
B1—C1—C5—C13	-2.5 (4)	C5—C1—B1—O3	-175.2 (2)
Fe1—C1—C5—C13	111.3 (2)	Fe1—C1—B1—O3	96.7 (2)
C2—C1—C5—Fe1	60.36 (13)	C2—C1—B1—O2	-169.19 (19)
B1—C1—C5—Fe1	-113.8 (2)	C5—C1—B1—O2	4.1 (4)
C10—C6—C7—C8	-0.2 (2)	Fe1—C1—B1—O2	-84.0 (2)
Fe1—C6—C7—C8	59.61 (14)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2O \cdots O1	0.82	1.85	2.650 (2)	166
O3—H3O \cdots O2 ⁱ	0.82	1.94	2.744 (2)	168
C9—H9 \cdots O3 ⁱⁱ	0.93	2.45	3.308 (3)	154
C10—H10 \cdots O1 ⁱⁱⁱ	0.93	2.53	3.404 (3)	156

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