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Key indicators

Single-crystal X-ray study
T = 180 K
Mean $\sigma(C-C)$ = 0.006 Å
R factor = 0.054
wR factor = 0.105
Data-to-parameter ratio = 16.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Hydrogen-bonding motifs in the solid-state structure of ferroceneboronic acid

At 180 K, the crystal structure of ferroceneboronic acid, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_6\text{BO}_2)]$, consists of centrosymmetric $[\text{FcB}(\text{OH})_2]_2$ dimers [Fc is $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$], formed by a pair of complementary $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions [$\text{O}\cdots\text{H}$ 1.97 Å and $\text{O}\cdots\text{O}$ 2.806 (3) Å]. The remaining two O-bound H atoms per $[\text{FcB}(\text{OH})_2]_2$ moiety serve to link the dimeric units to adjacent dimers in a criss-cross fashion, very similar to that between hydrogen-bonded chains in solid $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]_2$.

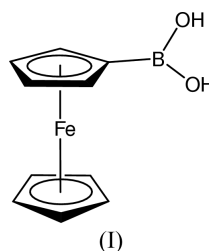
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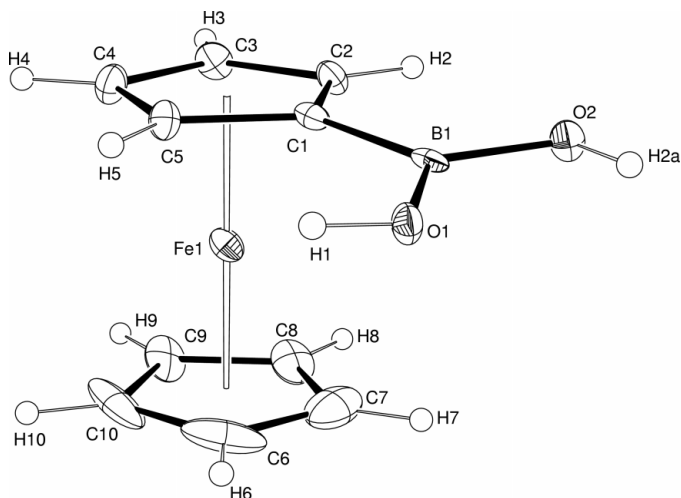
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Comment

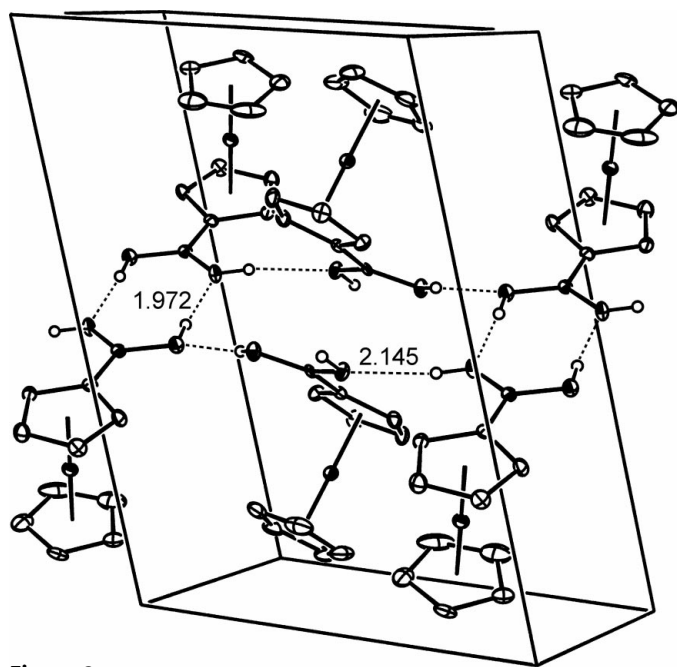
The title compound, ferroceneboronic acid, $\text{FcB}(\text{OH})_2$ [Fc is $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$], has been known since the late 1950s, having been initially synthesized by Nesmeyanov *et al.* (1959) by the reaction of lithioferrocene with $(\text{BuO})_3\text{B}$, and subsequent hydrolytic work-up. A number of alternative syntheses have been reported in the interim (Shechter & Helling, 1961; McVey *et al.*, 1967), and continued interest in this compound and related derivatives is in part due to their implication in Suzuki-type coupling reactions (Hua *et al.*, 2001) and in anion and neutral molecule sensing (Dusemund *et al.*, 1995; Ori & Shinkai, 1995). Although the solid-state structures of a number of related compounds, including the diboronic acid $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]_2$ (Braga *et al.*, 2003), the cyclic boronic anhydride $(\text{FcBO})_3$ (Bats *et al.*, 2002), boronic esters (such as $\text{FcBO}_2\text{C}_6\text{H}_4\text{-1,2}$; Aldridge & Bresner, 2003; Aldridge, Bresner & Fallis, 2004) and [5]trovacenylboronic acid, $(\eta^7\text{-C}_7\text{H}_7)\text{V}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]$ (Elschenbroich *et al.*, 2004), have been determined, to our knowledge there have been no reports to date concerning the crystal structure of $\text{FcB}(\text{OH})_2$. The title compound, (I), was isolated in this instance as the main organometallic product from the aerobic hydrolysis of $\text{FcB}(\text{OCH}_2\text{CH}_2)_2\text{S}$ in a mixed toluene–hexane solvent (Aldridge *et al.*, 2004).



The structural parameters relating to the individual $\text{FcB}(\text{OH})_2$ units of (I) are unremarkable, with the geometries at the Fe and B centres mirroring those found in related compounds (Bats *et al.*, 2002; Braga *et al.*, 2003; Aldridge *et al.*,


Figure 1

A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by spheres of arbitrary size.


Figure 2

A packing diagram, showing the hydrogen-bonding motifs both within and between the dimeric $[\text{FcB}(\text{OH})_2]_2$ units in solid (I). Distances are in Å.

2004). In particular, the small degree of bending of the boronic acid moiety out of the plane of the cyclopentadienyl ligand [Cp centroid—C1—B1 $176.4(2)^\circ$] mirrors that observed in related ferrocenes containing weakly Lewis acidic boryl (BX_2) substituents [e.g. $178.5(3)^\circ$ for $\text{FcBO}_2\text{C}_2\text{H}_2\text{Ph}_2$; Aldridge *et al.*, 2004], but contrasts with that found in the much more electron-deficient FcBBr_2 (*ca* 162° for both crystallographically independent molecules; Appel *et al.*, 1996; Aldridge & Bresner, 2003).

In the solid state, the molecular units of (I) aggregate into centrosymmetric dimers, $[\text{FcB}(\text{OH})_2]_2$, formed by a pair of complementary $\text{O—H}\cdots\text{O}$ hydrogen-bonding interactions characterized by $\text{O}\cdots\text{H}$ distances of 1.97 \AA and $\text{O—H}\cdots\text{O}$ angles of 172° . The eight-membered ring thus formed is very similar to that seen in the crystal structures of $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]_2$ and $\text{PhB}(\text{OH})_2$ (Braga *et al.*, 2003; Rettig & Trotter, 1977). Indeed, the $\text{O}\cdots\text{O}$ separations between the two components of the dimer [$2.806(3)\text{ \AA}$] are essentially identical to those found in $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]_2$ [$2.81(1)\text{ \AA}$]. The remaining two O-bound H atoms per $[\text{FcB}(\text{OH})_2]_2$ moiety serve to link the dimeric units to adjacent dimers in a criss-cross fashion, very similar to the linking between hydrogen-bonded chains in solid $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]_2$ (Braga *et al.*, 2003). The 16-membered ring thus formed (Fig. 2) incorporates two $[\text{FcB}(\text{OH})_2]_2$ dimers from within the same layer, bridged by two $\text{FcB}(\text{OH})_2$ moieties from different dimeric units of the intervening stack. The $\text{O}\cdots\text{H}$ and $\text{O}\cdots\text{O}$ distances [2.14 and $2.930(3)\text{ \AA}$, respectively] are somewhat longer than those found within each dimeric unit, but are consistent with the $\text{O}\cdots\text{O}$ distance found for the very similar structural motif present in $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{OH})_2]_2$ [$\text{O}\cdots\text{O}$ $2.89(1)\text{ \AA}$].

Experimental

The title compound was isolated as the main organometallic product from the aerobic hydrolysis of $\text{FcB}(\text{OCH}_2\text{CH}_2)_2\text{S}$ (Aldridge *et al.*, 2004). Attempted recrystallization of $\text{FcB}(\text{OCH}_2\text{CH}_2)_2\text{S}$ in air by hexane diffusion into a toluene solution led to the isolation of $\text{FcB}(\text{OH})_2$, (I), as single yellow–orange crystals suitable for X-ray diffraction. Spectroscopic data obtained (^{11}B , ^1H and ^{13}C NMR, and mass spectrometry) were in agreement with those reported previously (Shechter & Helling, 1961; McVey *et al.*, 1967).

Crystal data

$[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_6\text{BO}_2)]$
 $M_r = 229.85$
 Monoclinic, $P2_1/a$
 $a = 10.0680(7)\text{ \AA}$
 $b = 7.0080(5)\text{ \AA}$
 $c = 14.0300(13)\text{ \AA}$
 $\beta = 106.320(3)^\circ$
 $V = 950.02(13)\text{ \AA}^3$
 $Z = 4$

$D_x = 1.607\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1453 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 1.55\text{ mm}^{-1}$
 $T = 180(2)\text{ K}$
 Triangular plate, yellow
 $0.13 \times 0.10 \times 0.03\text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.824$, $T_{\max} = 0.955$
 6820 measured reflections

2130 independent reflections
 1398 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.092$
 $\theta_{\max} = 27.4^\circ$
 $h = -12 \rightarrow 12$
 $k = -9 \rightarrow 9$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.105$
 $S = 1.03$
 2130 reflections
 129 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 0.3652P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.49\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.57\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Fe1—C6	2.020 (4)	Fe1—C1	2.054 (3)
Fe1—C10	2.032 (4)	Fe1—C8	2.056 (4)
Fe1—C7	2.039 (4)	C1—B1	1.551 (5)
Fe1—C5	2.043 (3)	B1—O2	1.375 (4)
Fe1—C4	2.047 (4)	B1—O1	1.376 (4)
Fe1—C3	2.048 (3)	O1—H1	0.84
Fe1—C2	2.049 (3)	O2—H2A	0.84
Fe1—C9	2.053 (3)		
O2—B1—O1	118.0 (3)	O1—B1—C1	123.9 (3)
O2—B1—C1	118.1 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O2 ⁱ	0.84	2.14	2.930 (3)	156
O2—H2A \cdots O1 ⁱⁱ	0.84	1.97	2.806 (3)	172

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

Aromatic H atoms were constrained as riding atoms, with C—H distances of 0.95 Å. Hydroxyl H atoms were located in a difference Fourier map and refined as a rigid rotor, with O—H distances of 0.84 Å. The $U_{\text{iso}}(\text{H})$ values were fixed at 1.2 times $U_{\text{eq}}(\text{C})$ or 1.5 times $U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *DIRDIF99* (Beurskens et al., 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997);

software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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