

## Pentafluorophenylboronic acid

Peter N. Horton,<sup>a\*</sup>  
Michael B. Hursthouse,<sup>a</sup>  
Michael A. Beckett<sup>b</sup> and  
Martin P. Rugen-Hankey<sup>b</sup><sup>a</sup>School of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, England, and <sup>b</sup>Chemistry Department, University of Wales, Bangor, LL57 2UW, Wales

Correspondence e-mail: pnh@soton.ac.uk

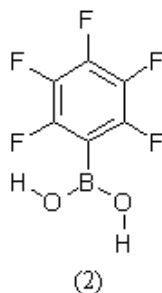
## Key indicators

Single-crystal X-ray study  
T = 120 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
R factor = 0.044  
wR factor = 0.116  
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of the title compound,  $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ , were obtained from an attempted recrystallization of  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3 \cdot \text{Et}_3\text{PO}$  from THF/hexane solution. The central B atom of the boronic acid has a trigonal planar configuration with two hydroxyl groups and one pentafluorophenyl substituent.

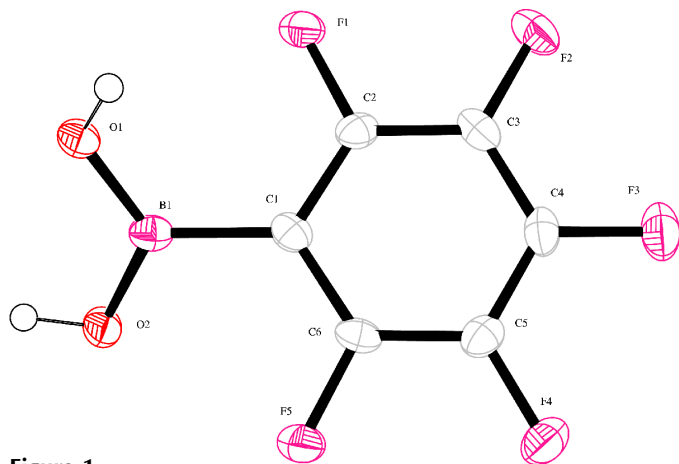
## Comment

There has been much recent interest in the chemistry of perfluoroarylboron compounds owing to their use as Lewis acid catalysts in organic transformations (Piers & Chivers, 1997; Ishihara & Yamamoto, 1999). We have recently explored the chemistry of phosphoryl donors towards  $\text{B}(\text{C}_6\text{F}_5)_3$  (Beckett *et al.*, 2000, 2001) and are now examining the related boroxine,  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$ . The adduct  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3 \cdot \text{Et}_3\text{PO}$ , (1), is readily obtained from the stoichiometric reaction of  $\text{Et}_3\text{PO}$  with  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$  in THF solution. Compound (1), a colourless solid which gave satisfactory elemental analysis data, was characterized by IR and NMR spectroscopy. The strongly Lewis acidic nature of  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$  is reflected in the  $^{31}\text{P}$  chemical shift of (1), which is considerably downfield of that of free  $\text{Et}_3\text{PO}$  (Mayer *et al.*, 1975). An attempted recrystallization of (1), by slow diffusion of hexane into a THF solution of the compound, afforded crystals of the title compound  $(\text{C}_6\text{F}_5)\text{B}(\text{OH})_2$ , (2). Presumably, (2) arose as a consequence of hydrolysis of (1), caused by  $\text{H}_2\text{O}$  in our recrystallization solvents. Compound (2) is well documented in the literature (Chambers & Chivers, 1965; Frohn *et al.*, 2002), but its crystal and molecular structure has not been previously reported.



Crystallographic studies on compounds which contain a similar  $(\text{C}_6\text{F}_5)\text{BO}_2$  motif are limited to the cyclic pentafluorophenylboronic acid ester of 2,3-dihydroxynaphthalene,  $(\text{C}_6\text{F}_5)\text{BO}_2\text{C}_{10}\text{H}_6$  (Vagedes *et al.*, 1999) and the metallocycle  $[\text{ZrCp}_2\{\mu\text{-O}_2\text{B}(\text{C}_6\text{F}_5)\}]_2$  (Balkwill *et al.*, 2002). The motif also appears in the borate anion of the salt  $[\text{CpNi}(\text{C}_6\text{H}_6)\text{NiCp}][\text{B}_3\text{O}_3(\text{C}_6\text{F}_5)_3]$  (Priego *et al.*, 2000), in which there are B atoms with both trigonal and tetrahedral geometry. The cyclic trimeric borinic acid derivative  $[\{(\text{C}_6\text{F}_5)_2\text{B}(\text{OH})\}_3]$  contains

Received 5 August 2004  
Accepted 9 September 2004  
Online 6 November 2004



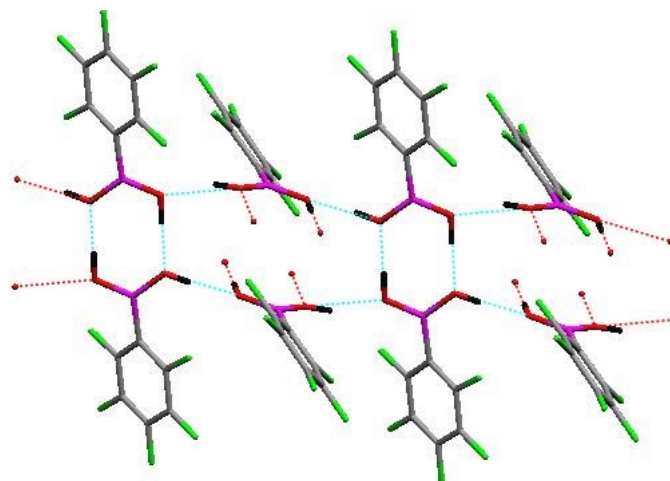
**Figure 1**  
View of the structure of  $(\text{C}_6\text{F}_5)\text{B}(\text{OH})_2$ , showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

the  $\text{C}_6\text{F}_5\text{BO}_2$  motif with tetrahedral boron (Beringhelli *et al.*, 2003).

B and C atoms are essentially trigonal planar and most of the B—O, B—C, and C—F bond lengths are unremarkable, with structural data for the  $\text{C}_6\text{F}_5\text{BO}_2$  motif similar to those previously reported. Bond angles at B and C are consistent with  $sp^2$  hybridization but with significant deviations from the expected  $120^\circ$  angles occurring in close proximity to the  $\text{B}(\text{OH})_2$  substituent on C1. Thus the angles C6—C1—C2 [ $115.31(16)^\circ$ ], F1—C2—C3 [ $116.81(17)^\circ$ ] and F5—C6—C5 [ $117.20(16)^\circ$ ] are significantly smaller than the other C—C—C and C—C—F angles respectively. The  $\text{B}(\text{OH})_2$  group is twisted by  $38.14(15)^\circ$  relative to the  $\text{C}_6\text{F}_5$  group. The B—O distances are equivalent and average  $1.359 \text{ \AA}$ , consistent with relatively strong  $\pi$ -interactions and a bond order  $>1$  (Beckett *et al.*, 1996). Conversely, the C1—B1 bond length [ $1.579(3) \text{ \AA}$ ] is slightly greater than that typically found in boroxines *e.g.*  $(4\text{-MeC}_6\text{H}_4)_3\text{B}_3\text{O}_3$ ,  $1.543(4) \text{ \AA}$  (Beckett *et al.*, 1996), indicating a weakening of this bond by the electron-withdrawing  $\text{C}_6\text{F}_5$  group. The H atoms were located and H—O—B angles and H—O distances average  $113.3^\circ$  and  $0.855 \text{ \AA}$ , respectively. Both H atoms are involved in hydrogen bonds, H2O in a hydrogen-bond dimer (equivalent to the carboxylic acid dimer) and H1O in an extended tape (see Fig. 2), which combine, giving a two-dimensional extended structure.

## Experimental

To a stirred solution of  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3$  (0.50 g, 0.86 mmol) in THF ( $25 \text{ cm}^3$ ) was added  $\text{Et}_3\text{PO}$  (0.12 g; 0.89 mmol). The reaction mixture was stirred at room temperature for 1 h. Removal of volatiles *in vacuo* afforded the adduct  $(\text{C}_6\text{F}_5)_3\text{B}_3\text{O}_3 \cdot \text{Et}_3\text{PO}$ , (1), a colourless solid (0.58 g; 94%). NMR ( $\delta/\text{p.p.m.}$ ;  $\text{C}_6\text{D}_6/\text{RT}$ ):  $^1\text{H}$  (500.1 MHz): 1.4 (*q*, 6H,  $^3J$  6.6 Hz), 0.7 (*t*, 9H,  $^3J$  6.6 Hz);  $^{31}\text{P}$  (202.4 MHz): +80.0; [ $\Delta\delta = 39.0$  p.p.m., AN (acceptor number) = 86 (Mayer *et al.*, 1975)]. IR (KBr disc,  $\eta_{\text{max}} \text{ cm}^{-1}$ ): 3385 (*m*), 2984 (*m*), 1649 (*s*), 1486 (*s*), 1340 (*s*), 1244 (*s*), 1100 (*s*), 976 (*s*), 935 (*m*), 781 (*m*). Elemental analysis (%) required for  $\text{C}_{24}\text{H}_{15}\text{B}_3\text{F}_{15}\text{PO}_4$ : C 40.3, H 2.1; Found: C, 40.2, H 2.0%. A few crystals of  $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ , (2), suitable for X-ray diffrac-



**Figure 2**  
View showing hydrogen bonding (dashed lines).

tion, were grown by slow (14 days) diffusion of hexane into a THF solution of (1).

### Crystal data

$\text{C}_6\text{H}_5\text{BF}_5\text{O}_2$   
 $M_r = 211.89$   
Monoclinic,  $P2_1/c$   
 $a = 12.6214(6) \text{ \AA}$   
 $b = 6.2949(2) \text{ \AA}$   
 $c = 9.3973(4) \text{ \AA}$   
 $\beta = 98.254(2)^\circ$   
 $V = 738.89(5) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.905 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 1621 reflections  
 $\theta = 2.9\text{--}27.5^\circ$   
 $\mu = 0.22 \text{ mm}^{-1}$   
 $T = 120(2) \text{ K}$   
Plate, colourless  
 $0.15 \times 0.08 \times 0.02 \text{ mm}$

### Data collection

Nonius Kappa CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan (SORTAV; Blessing, 1997)  
 $T_{\text{min}} = 0.968$ ,  $T_{\text{max}} = 0.996$   
5560 measured reflections

1692 independent reflections  
1186 reflections with  $>2\sigma(I)$   
 $R_{\text{int}} = 0.070$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -16 \rightarrow 14$   
 $k = -8 \rightarrow 6$   
 $l = -10 \rightarrow 12$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.116$   
 $S = 1.03$   
1692 reflections  
135 parameters

All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{--H}\cdots A$	$D\text{--H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{--H}\cdots A$
$\text{O2--H2O}\cdots\text{O1}^{\text{i}}$	0.92 (3)	1.81 (3)	2.7326 (18)	176 (2)
$\text{O1--H1O}\cdots\text{O2}^{\text{ii}}$	0.82 (3)	1.99 (3)	2.7653 (19)	160 (2)

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

Data collection: COLLECT (Hoof, 1998) and DENZO (Otwinowski & Minor, 1997); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

The authors thank the EPSRC for funding the crystallographic facilities.

## References

- Balkwill, J. E., Cole, S. C., Coles, M. P. & Hitchcock, P. B. (2002) *Inorg. Chem.* **41**, 3548–3552.
- Beckett, M. A., Brassington, D. S., Coles, S. J. & Hursthouse, M. B. (2000) *Inorg. Chem. Commun.* **3**, 530–533.
- Beckett, M. A., Brassington, D. S., Light, M. E. & Hursthouse, M. B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1768–1772.
- Beckett, M. A., Strickland, G. C., Varma, K. S., Hibbs, D. E., Hursthouse, M. B. & Malik, K. M. A (1996). *J. Organomet. Chem.* **535**, 33–41.
- Beringhelli, T., D'Alfonso, G., Donghi, D., Maggioni, D., Mercandelli, P. & Sironi, A. (2003) *Organometallics*, **22**, 1588–1590.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Chambers, R. N. & Chivers, T. (1965). *J. Chem. Soc.* pp. 3933–3939.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Frohn, H.-J., Adonin, N. Y., Bardin, V. V. & Starichenko, V. F. (2002). *Z. Anorg. Allg. Chem.* **628**, 2827–2833.
- Hoof, R. (1998). COLLECT. Nonius BV, The Netherlands.
- Ishihara, K. & Yamamoto, H. (1999). *Eur. J. Org. Chem.* pp. 527–538.
- Mayer, U., Gutmann, V. & Gerger, W. (1975). *Monatsh. Chem.* **106**, 1275–1277.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Piers, W. E. & Chivers, T. (1997). *Chem. Soc. Rev.* **26**, 345–354.
- Priego, J. L., Doerrer, L. H., Rees, L. H. & Green, M. L. H. (2000) *Chem. Commun.* pp. 779–780.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Vagedes, D., Frohlich, R. & Erker, G. (1999). *Angew. Chem. Int. Ed. Engl.* **38**, 3362–3365.

## supporting information

*Acta Cryst.* (2004). E60, o2204–o2206 [https://doi.org/10.1107/S1600536804022408]

## Pentafluorophenylboronic acid

Peter N. Horton, Michael B. Hursthouse, Michael A. Beckett and Martin P. Rügen-Hankey

## Pentafluoroboronic acid

*Crystal data*

$C_6H_2BF_5O_2$

$M_r = 211.89$

Monoclinic,  $P2_1/c$

$a = 12.6214$  (6) Å

$b = 6.2949$  (2) Å

$c = 9.3973$  (4) Å

$\beta = 98.254$  (2)°

$V = 738.89$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 416$

$D_x = 1.905$  Mg m<sup>-3</sup>

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

Cell parameters from 1621 reflections

$\theta = 2.9$ – $27.5$ °

$\mu = 0.22$  mm<sup>-1</sup>

$T = 120$  K

Plate, colourless

$0.15 \times 0.08 \times 0.02$  mm

*Data collection*

Nonius KappaCCD Area Detector  
diffractometer

Radiation source: Nonius FR591 rotating anode  
Graphite monochromator

Detector resolution: 9.091 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans to fill Ewald Sphere

Absorption correction: multi-scan  
(SORTAV; Blessing 1997)

$T_{\min} = 0.968$ ,  $T_{\max} = 0.996$

5560 measured reflections

1692 independent reflections

1186 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.3$ °

$h = -16 \rightarrow 14$

$k = -8 \rightarrow 6$

$l = -10 \rightarrow 12$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.116$

$S = 1.03$

1692 reflections

135 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$

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

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

$\Delta\rho_{\max} = 0.27$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>

*Special details*

**Experimental.** PLEASE NOTE cell\_measurement\_fields are not relevant to area detector data, the entire data set is used to refine the cell, which is indexed from all observed reflections in a 10 degree phi range.

**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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.20469 (15)	-0.1065 (3)	-0.0334 (2)	0.0205 (4)
C2	0.28746 (15)	-0.1513 (3)	-0.1108 (2)	0.0215 (4)
C3	0.37112 (14)	-0.0124 (3)	-0.12031 (19)	0.0233 (4)
C4	0.37121 (15)	0.1827 (3)	-0.0553 (2)	0.0244 (5)
C5	0.28903 (15)	0.2369 (3)	0.0197 (2)	0.0232 (4)
C6	0.20904 (15)	0.0925 (3)	0.03115 (19)	0.0212 (4)
B1	0.11484 (17)	-0.2747 (3)	-0.0150 (2)	0.0208 (5)
O1	0.07353 (11)	-0.4073 (2)	-0.12348 (16)	0.0236 (3)
O2	0.07956 (11)	-0.2880 (2)	0.11424 (13)	0.0248 (3)
F1	0.29011 (9)	-0.33900 (16)	-0.17951 (12)	0.0257 (3)
F2	0.45090 (9)	-0.06577 (18)	-0.19359 (13)	0.0314 (3)
F3	0.45065 (10)	0.31949 (18)	-0.06461 (13)	0.0352 (3)
F4	0.28823 (10)	0.42794 (16)	0.08323 (12)	0.0308 (3)
F5	0.13194 (9)	0.15083 (17)	0.10926 (12)	0.0276 (3)
H1O	0.086 (2)	-0.374 (4)	-0.204 (3)	0.041 (7)*
H2O	0.029 (2)	-0.394 (4)	0.115 (3)	0.044 (7)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0227 (10)	0.0246 (9)	0.0144 (9)	0.0001 (7)	0.0036 (8)	0.0033 (7)
C2	0.0292 (11)	0.0193 (9)	0.0160 (9)	0.0005 (7)	0.0036 (8)	0.0003 (7)
C3	0.0185 (10)	0.0335 (10)	0.0185 (10)	0.0014 (7)	0.0043 (8)	0.0041 (8)
C4	0.0245 (11)	0.0272 (10)	0.0208 (10)	-0.0083 (8)	0.0010 (8)	0.0045 (8)
C5	0.0307 (11)	0.0208 (9)	0.0175 (9)	-0.0017 (7)	0.0009 (8)	0.0000 (7)
C6	0.0248 (10)	0.0255 (9)	0.0141 (10)	0.0035 (7)	0.0059 (8)	0.0001 (7)
B1	0.0243 (12)	0.0214 (10)	0.0172 (11)	0.0021 (8)	0.0046 (9)	-0.0007 (8)
O1	0.0282 (8)	0.0288 (7)	0.0150 (8)	-0.0054 (5)	0.0071 (6)	-0.0002 (6)
O2	0.0281 (8)	0.0303 (8)	0.0170 (7)	-0.0084 (6)	0.0071 (6)	-0.0024 (5)
F1	0.0301 (7)	0.0247 (6)	0.0236 (6)	0.0011 (4)	0.0087 (5)	-0.0038 (4)
F2	0.0232 (6)	0.0430 (7)	0.0304 (7)	0.0010 (5)	0.0119 (5)	0.0006 (5)
F3	0.0327 (7)	0.0363 (7)	0.0370 (7)	-0.0142 (5)	0.0063 (5)	0.0037 (5)
F4	0.0447 (7)	0.0217 (6)	0.0257 (7)	-0.0057 (5)	0.0041 (6)	-0.0034 (4)
F5	0.0328 (7)	0.0261 (6)	0.0263 (7)	0.0005 (5)	0.0123 (5)	-0.0040 (4)

Geometric parameters (Å, °)

C1—C2	1.385 (3)	C4—C5	1.378 (3)
C1—C6	1.389 (3)	C5—F4	1.343 (2)
C1—B1	1.579 (3)	C5—C6	1.374 (3)
C2—F1	1.349 (2)	C6—F5	1.351 (2)
C2—C3	1.384 (3)	B1—O2	1.355 (3)
C3—F2	1.342 (2)	B1—O1	1.362 (2)
C3—C4	1.372 (3)	O1—H1O	0.82 (3)
C4—F3	1.334 (2)	O2—H2O	0.92 (3)
C2—C1—C6	115.31 (16)	F4—C5—C6	120.34 (17)
C2—C1—B1	121.92 (16)	F4—C5—C4	120.20 (16)
C6—C1—B1	122.73 (17)	C6—C5—C4	119.45 (17)
F1—C2—C3	116.81 (17)	F5—C6—C5	117.20 (16)
F1—C2—C1	120.14 (16)	F5—C6—C1	119.74 (16)
C3—C2—C1	123.04 (17)	C5—C6—C1	123.07 (17)
F2—C3—C4	120.00 (17)	O2—B1—O1	119.55 (18)
F2—C3—C2	120.72 (17)	O2—B1—C1	118.24 (17)
C4—C3—C2	119.28 (17)	O1—B1—C1	122.20 (18)
F3—C4—C3	120.10 (17)	B1—O1—H1O	115.6 (18)
F3—C4—C5	120.11 (16)	B1—O2—H2O	111.4 (16)
C3—C4—C5	119.79 (16)		

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>
O2—H2O...O1 <sup>i</sup>	0.92 (3)	1.81 (3)	2.7326 (18)	176 (2)
O1—H1O...O2 <sup>ii</sup>	0.82 (3)	1.99 (3)	2.7653 (19)	160 (2)

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