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The ‘super acid’ BF_3H_2O stabilized by 1,4-dioxane: new preparative aspects and the crystal structure of $BF_3H_2O{\cdot}C_4H_8O_2$

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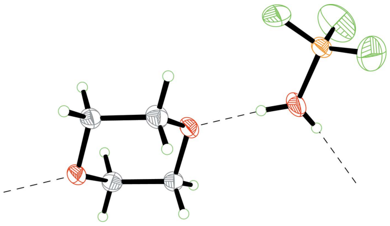
Highly Brønsted-acidic boron trifluoride monohydrate, a widely used ‘super acid-catalyst’, is a colourless fuming liquid that releases BF_3 at room temperature. Compared to the liquid components, *i.e.* boron trifluoride monohydrate and 1,4-dioxane, their 1:1 adduct, $BF_3H_2O{\cdot}C_4H_8O_2$, is a solid with pronounced thermal stability (m.p. 401–403 K). The crystal structure of the long-time-stable easy-to-handle and weighable compound is reported along with new preparative aspects and the results of ^{1}H, ^{11}B, ^{13}C and ^{19}F spectroscopic investigations, particularly documenting its high Brønsted acidity in acetonitrile solution. The remarkable stability of solid $BF_3H_2O{\cdot}C_4H_8O_2$ is attributed to the chain structure established by O—H⋯O hydrogen bonds of exceptional strength {O2⋯H1—O1 [O⋯O = 2.534 (3) Å] and O1—H1⋯O3^{i} [2.539 (3) Å] in the concatenating unit >O2⋯H1—O1—H2⋯O3^{i}<}, taking into account the molecular (non-ionic) character of the structural moieties. Indirectly, this structural feature documents the outstanding acidification of the H_2O molecule bound to BF_3 and reflects the super acid nature of BF_3H_2O. In detail, the $C_2^2(7)$ zigzag chain system of hydrogen bonding in the title structure is characterized by the double hydrogen-bond donor and double ($\kappa O,\kappa O'$) hydrogen-bond acceptor functionality of the aqua ligand and dioxane molecule, respectively, the almost equal strength of both hydrogen bonds, the approximatety linear arrangement of the dioxane O atoms and the two neighbouring water O atoms. Furthermore, the approximately planar arrangement of B, F and O atoms in sheets perpendicular to the *c* axis of the orthorhombic unit cell is a characteristic structural feature.



1. Chemical context

Solutions of boron trifluoride in water have been under investigation for more than 200 years (Gay-Lussac & Thenard, 1809; Davy, 1812; Berzelius, 1824). Meerwein (1933) was able to isolate the BF_3 dihydrate and, after addition of one further equivalent of BF_3 at low temperature, the BF_3 monohydrate also. Both hydrates were examined in detail (Klinkenberg & Ketelaar, 1935; McGrath *et al.*, 1944; Greenwood & Martin, 1951; Wamser, 1951; Pawlenko, 1959) and while the dihydrate was shown to be distillable without decomposition under reduced pressure, boron trifluoride monohydrate releases BF_3 above its melting point of 279.2 K. At room temperature, it is a colourless fuming liquid with a density of 1.8 g ml^{-1}. To examine the acidity of the monohydrate, reactions with ethers, alcohols and carboxylic acids *etc.* were performed by Meerwein & Pannwitz (1934). They obtained $BF_3H_2O{\cdot}C_4H_8O_2$, which they called the *dioxane salt of boron trifluoride monohydrate*, by adding BF_3H_2O to a solution of 1,4-dioxane in petroleum naphta. $BF_3H_2O{\cdot}C_4H_8O_2$ (**1**) precipitates as

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Table 1
Selected bond lengths (Å).

Values for $BF_3H_2O{\cdot}C_4H_8O_2$, BF_3H_2O (Mootz & Steffen, 1981*b*) and $BF_3H_2O{\cdot}H_2O$ (Mootz & Steffen, 1981*c*) in the left, middle and right columns, respectively; in square brackets are the corresponding bond valences and the valence sums calculated using the Brown formalism {r_0[B—O(F)] = 1.371 (1.281), B = 0.37; Brown & Altermatt, 1985}; in braces are the values corrected for libration (Schomaker & Trueblood, 1968).

B1—O1	1.473 (4) [0.76] {1.528 (4) [0.65]}	1.532 (6) [0.64]	1.512 (2) [0.68]
B1—F1	1.361 (4) [0.81] {1.409 (4) [0.71]}	1.383 (5) [0.76]	1.377 (2) [0.77]
B1—F2	1.332 (4) [0.87] {1.396 (4) [0.73]}	1.399 (5) [0.73]	1.382 (2) [0.76]
B1—F3	1.333 (4) [0.87] {1.410 (4) [0.71]}	1.382 (5) [0.76]	1.390 (2) [0.74]
Σs(B–O,F)	[3.31] {[2.80]}	[2.89]	[2.96]

needle-shaped crystals which melt at 401–403 K with decomposition (Meerwein & Pannwitz, 1934). Unexpectedly, the experiment described in §6 resulted in the same product. The primordial idea of this experiment was to prepare an anhydrous solution of HBF_4 from HBF_4/H_2O (1:1 *w*:*w*) by distilling off water as the 1,4-dioxane/water azeotrope with coincident replacement of water by an excess of 1,4-dioxane. The dioxane adduct **1** starts to precipitate after a short period of time if a small amount of water remains in the resulting liquid. The formation of **1** in a 'HBF_4 solution' impressively illustrates how efficently BF_3 is stabilized by water and dioxane. The reactions and equilibria of HBF_4-, BF_3-, H_2O- and HF-containing systems have been examined in detail (Pawlenko, 1968; Gascard & Mascherpa, 1973; Christe *et al.*, 1975; Mootz & Steffen, 1981*a*; Yeo & Ford, 2006; Dubey *et al.*, 2007) and it remains amazing that BF_3H_2O, unlike the other boron trihalide/water mixtures, releases the strong Lewis-acid (BF_3) unhydrolysed. Investigations by Greenwood & Martin (1951) showed that BF_3H_2O is highly ionized in the liquid state and that the Hammett acidity of $H[BF_3OH]$ is $H_0 = -11.4$. By NMR spectroscopic determination of the thermodynamic acidity function from ^{13}C chemical-shift changes of the signals of unsaturated ketones at infinite dilution in the acid under investigation, Farcasui & Ghenciu (1992) found boron trifluoride monohydrate to be super acidic, with $H_0 < -14$. The applications of this super acid are numerous, *e.g.* as a highly effective catalyst for several Friedel–Craft reactions (Yoneda *et al.*, 1969; Oyama *et al.*, 1978; Liu *et al.*, 2003; Prakash *et al.*, 2016, and references therein). The long-time-stable and easy-to-handle solid **1** provides the 'super acid BF_3H_2O' in a safe and efficient way.

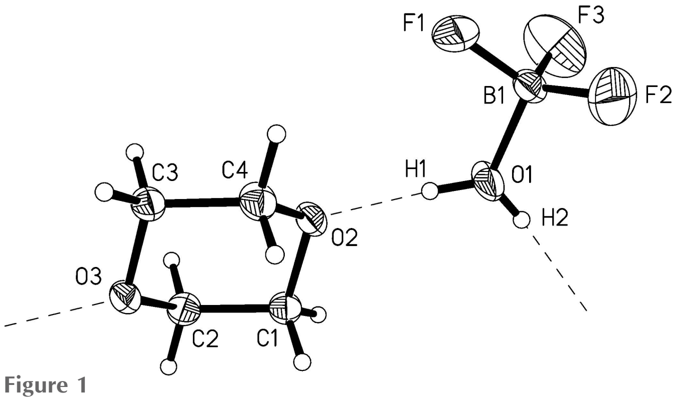
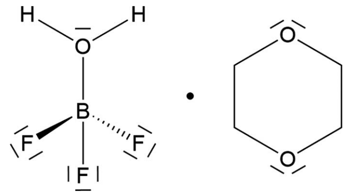


Figure 1
Diagram of the asymmetric unit of the crystal structure of compound **1**, displaying the atom-labelling scheme. Anisotropic displacement ellipsoids are drawn at the 40% probability level and the radii of H atoms are chosen arbitrarily. The direction of hydrogen bonding is given by dashed lines.



Although Meerwein & Pannwitz (1934) isolated compound **1** (m.p. 401–403 K) and a solid, in which BF_3H_2O is stabilized by 1,8-cineole (m.p. 344–346 K) more than 80 years ago, the crystal structures of these compounds are still unknown and the reasons for the unexpected high thermal stability, especially of the dioxane adduct, are still unknown. Generally, there are very rare examples of crystal structures with BF_3H_2O moieties bound to O-donor molecules. The crystal structure of boron trifluoride monohydrate itself has been reported by Mootz & Steffen (1981*b*), after redetermination of the crystal structure of the dihydrate in the same year (Mootz & Steffen, 1981*c*; Bang & Carpenter, 1964). Stabilization of the mono- and dihydrate with 18-crown-6 (Bott *et al.*, 1991; Feinberg *et al.*, 1993; Simonov *et al.*, 1995) or of BF_3H_2O with dicyclohexane-18-crown-6 (Fonar *et al.*, 1997) led to three further crystal structures containing the BF_3H_2O moiety and, as the most recent example, stabilization with triphenylphosphane oxide (Chekhlov, 2005) gave a crystalline 1:2 adduct of BF_3H_2O and $(C_6H_5)_3PO$.

2. Structural commentary

Compound **1** was found to crystallize in the orthorhombic space group *Pbca* with eight formula units in the unit cell and all components in general positions. Fig. 1 shows the asymmetric unit of the crystal structure, which contains aquatrifluoridoboron and 1,4-dioxane *molecular* moieties. The dioxane moiety is free of any kind of conformational disorder often recognized in the case of saturated six-membered ring species. Bond lengths, angles and torsion angles defining the chair conformation are in excellent agreement with the expectations for a 'fully ordered' dioxane molecule, *e.g.* found in the structure of uncomplexed 1,4-dioxane at 153 K (Buschmann *et al.*, 1986). Compared to the mean equivalent isotropic displacement parameter (U_{eq}) of the C and O atoms in the 1,4-dioxane moiety [= 0.0427 (6) $Å^2$], the mean U_{eq} value of B1, O1 and F1 to F3 in the aquatrifluoridoboron moiety [0.0867 (8) $Å^2$] is dramatically higher and correction for libration is needed prior to comparison with the geometries of BF_3H_2O moieties in related compounds. In Table 1, the uncorrected and corrected (Schomaker & Trueblood, 1968; RG = 0.0241) B—O and B—F bond lengths of **1** are given in comparison to the bond lengths of BF_3H_2O (Mootz & Steffen, 1981*c*) and $BF_3H_2O{\cdot}H_2O$ (Mootz & Steffen, 1981*b*). After

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O1—H1$\cdots$O2	0.82 (5)	1.72 (5)	2.534 (3)	175 (5)
O1—H2$\cdots$O3^{i}	0.82 (5)	1.72 (5)	2.539 (3)	170 (5)

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

correction, the values of **1** agree well with those of the hydrates and those in almost undistorted BF_4^- as found in Li[BF_4] at 200 K [1.387 (3)–1.391 (3) Å; Matsumoto *et al.*, 2006] or in H_5O_2[BF_4] [1.381 (2)–1.399 (2) Å; Mootz & Steffen, 1981*a*]. The bond-valence sum of B1 is as expected taking into account the 'uncorrected' nature of the r_0 values used (Brown & Altermatt, 1985). Interestingly, for all compounds mentioned in Table 1, the B—F bond perpendicular to the plane of the aqua ligand (**1**: B1—F3; BF_3H_2O: B1—F2; $BF_3H_2O{\cdot}H_2O$: B1—F3) is slightly but significantly longer than the other two B—F bonds, probably attributable to a small destabilizing interaction with the oxygen lone pair. The F—B—O angles in all three compounds [**1**: 105.6 (3)–109.8 (3)°; BF_3H_2O: 105.9 (4)–108.1 (4)°; $BF_3H_2O{\cdot}H_2O$: 106.3 (1)–109.8 (1)°] are smaller than the F—B—F angles [**1**: 109.9 (3)–112.1 (3)°; BF_3H_2O: 111.2 (4)–113.0 (4)°; $BF_3H_2O{\cdot}H_2O$: 109.8 (1)–114.0 (1)°]. This fits to the observation (Table 1) that the B—O bond in the BF_3H_2O moiety is relatively weaker than the B—F bonds and the planar geometry of BF_3 is preserved in the aqua complex to some extent. Furthermore, for all three compounds, the O—B—F angle including the F atom that is approximately in plane with the aqua ligand [**1**: O1—B1—F1 = 105.6 (3)°; BF_3H_2O: O—B—F3 = 105.9 (4)°; $BF_3H_2O{\cdot}H_2O$: O1—B—F2 = 106.3 (1)°] is significantly smaller than the other O—B—F angles. This observation may be attributed to an attractive F$\cdots$H interaction within the moiety.

Although both BF_3H_2O and 1,4-dioxane are liquids at room temperature, adduct **1** is a solid with a remarkably high melting point (401–403 K), mainly resulting from the concatenation of the molecular components *via* O—H$\cdots$O hydrogen bonding, as shown in Fig. 2. The high stability might be correlated to the exceptional strength of both O2$\cdots$H1—O1 [O$\cdots$O = 2.534 (3) Å] and O1—H1$\cdots$O3^{i} [2.539 (3) Å] in the concatenating >O2$\cdots$H1—O1—H2$\cdots$O3^{i}< unit. Indirectly, this structural feature documents the outstanding acidification of the H_2O molecule bound to BF_3 and reflects the super acid nature of BF_3H_2O. Further details of the hydrogen bonding are given in Table 2. To the best of our knowledge, there is no example of a water ligand bonded to a nonmetal or a metal with the ligand engaged in a hydrogen bond of similar strength (O$\cdots$O < 2.60 Å) to an O atom of a dioxane molecule. In the adduct 18-crown-6·BF_3H_2O (m.p. 345 K), mentioned in §1, the aqua ligand is hydrogen bonded to two O-donor atoms and the O$\cdots$O distances are 2.76 and 2.80 Å (Feinberg *et al.*, 1993). In the structure of $BF_3H_2O{\cdot}H_2O$, the nonligating water molecule plays a similar role as bridging species as the dioxane molecule in **1**. The O$\cdots$O distances in the characteristic $\cdots$H—O—H$\cdots$O(H_2)$\cdots$H—O—H$\cdots$ unit are 2.631 and 2.643 Å (Mootz & Steffen, 1981*c*), *i.e.* as compared to the very strong Brønsted acids fluorosulfuric acid [O$\cdots$O = 2.643 (1) Å] or trifluoromethanesulfonic acid [O$\cdots$O = 2.640 (4) Å] (Bartmann & Mootz, 1990), for example, the hydrogen bonding is of the same strength in the dihydrate and much stronger in the adduct **1**.

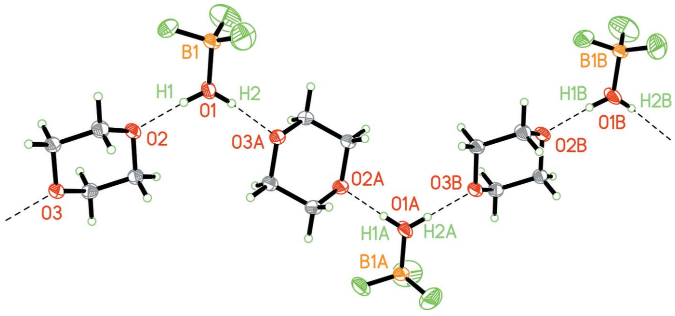


Figure 2
The zigzag chain of hydrogen-bonded moieties in the crystal of **1** [view direction [001]; 30% probability ellipsoids; symmetry codes: (A) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (B) $x, y + 1, z$]. Features indicative for the mode of concatenation of the characteristic building blocks by hydrogen bonding are: (i) double hydrogen-bond donor and double ($\kappa O,\kappa O'$) hydrogen-bond acceptor functionality of the aqua ligand and dioxane moiety, respectively; (ii) almost equal strength of both hydrogen bonds; (iii) an approximately linear arrangement of the dioxane O atoms and the two neighbouring water O atoms (*e.g.* O1, O3A, O2A and O1A); (iv) an approximately planar arrangement of B1, F1, O1, O2 and O3.

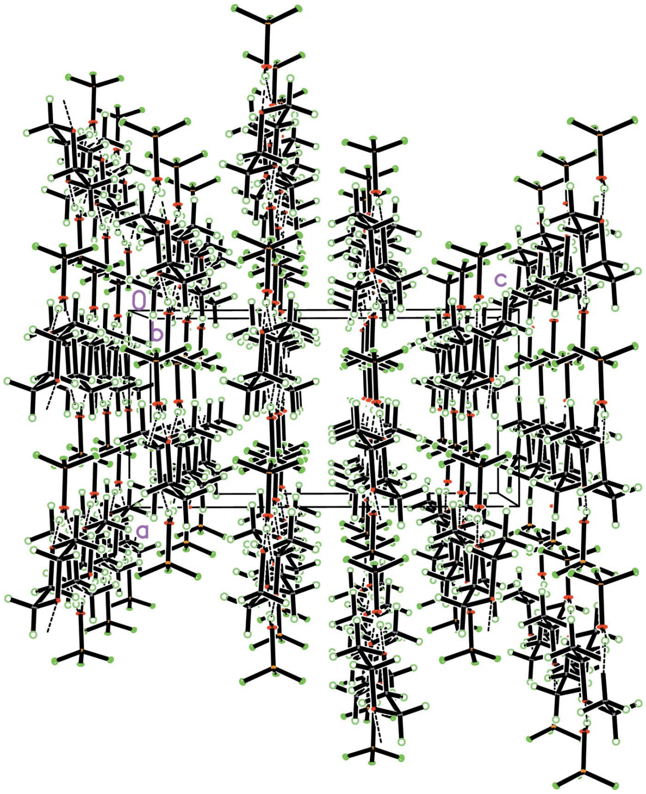


Figure 3
Packing diagram of **1** (view direction [010]) documenting the arrangement of the zigzag chains to flat sheets perpendicular to the *c* axis. Inspection of the intermolecular distances gives no evidence for interactions stronger than van der Waals forces between the chains.

3. Supramolecular features

As mentioned before, in the solid of **1** the aqua ligand of the BF_3H_2O moiety acts as a hydrogen-bond donor in two directions, establishing a $C_2^2(7)$ graph set (Etter, 1990) (Fig. 2). The propagation vector of the zigzag chain is parallel to the *b* axis of the unit cell. Note the almost equal strength of both hydrogen bonds. Fig. 3 shows the arrangement of the chains in the solid due to van der Waals interactions.

4. Database survey

A search of the Cambridge Structural Database (CSD; Version 5.40, November 2018 update; Groom *et al.*, 2016) for the BF_3H_2O moiety yielded six structures: the crown ether adducts 18-crown-6 monoaquatrifluoridoboron toluene semisolvate (CSD refcode SIXFOU; Bott *et al.* 1991), 18-crown-6 bis(monoaquatrifluoridoboron) dihydrate (LEKYIJ; Feinberg *et al.* 1993, Simonov *et al.*, 1995) and dicyclohexano-18-crown-6 bis(monoaquatrifluoridoboron) (NIYGAD; Fonar *et al.*, 1997); the phosphane oxide adduct monoaquatrifluoridoboron bis(triphenylphosphane oxide) (XATWAR; Chekhlov, 2005); two transition-metal coordination compounds [CIGVUJ10 (Van Rijn *et al.*, 1987) and UKAJIA (Orain *et al.*, 2010)], containing cocrystallized monoaquatrifluoridoboron moieties. As mentioned above, in addition to these reports on compounds having organic components, there is the report of Mootz & Steffen (1981*b*) on the inorganic parent compound BF_3H_2O and there are two reports on the dihydrate $BF_3H_2O{\cdot}H_2O$ (Mootz & Steffen, 1981*c*; Bang & Carpenter, 1964).

5. NMR spectroscopy

NMR studies of $BF_3H_2O{\cdot}C_4H_8O_2$ have not been published so far. Ford & Richards (1956) have shown by low-temperature NMR investigations that, in the solid state, BF_3H_2O and $BF_3H_2O{\cdot}H_2O$ are not ionized. Diehl (1958) reported the ^{19}F NMR spectra of BF_3H_2O in aqueous solution. He observed separate broad resonances which he attributed to HBF_3OH, HBF_4, $HBF_2(OH)_2$ and $HBF(OH)_3$ in concentrated solutions at 243 K with coalescence of the peaks at higher temperatures. Gillespie & Hartman (1967) have shown by low-temperature (193 K) ^1H and ^{19}F NMR spetroscopy that BF_3H_2O is formed in dilute solutions in acetone containing both water and BF_3. They found two major peaks in the ^{19}F NMR spectrum and assigned the low-field peak (−146.05 ppm) to the 1:1 complex of BF_3 with acetone and the high-field peak (−146.59 ppm) to BF_3H_2O in acetone. The corresponding ^1H NMR signals were detected by Gillespie & Hartmann at 12.42 ppm as multipletts. In our experiments, in the presence of CD_3CN *and* 1,4-dioxane and at a significantly higher temperature (297 K), the protons were detected as a broad singlet at 9.41 ppm. Gottlieb *et al.* (1997) indicated that the influence of temperature on the NMR shift overcompensates the influence of the solvent if the basicity of the solvents is similar. Apart from this effect, the high acidity of the oxygen-bonded ^1H nuclei in the title compound is depicted by a shift of more than 7 ppm to higher frequencies (H_2O in CD_3CN: *s*, 2.13 ppm; Fulmer *et al.* 2010). The chemical shifts of the NMR signals belonging to 1,4-dioxane are close to those of the uncomplexed compound ($C_4H_8O_2$ in CD_3CN: ^1H: *s*, 3.60 ppm; ^{13}C: 68.5 ppm; Fulmer *et al.*, 2010). Due to the comparable donor numbers (Gutmann, 1976) of acetonitrile (NMR solvent) and 1,4-dioxane, it can be concluded that the acidity of BF_3H_2O is not critically reduced by 1,4-dioxane with respect to its application as a super acid-catalyst.

The NMR sample was investigated in a 5 mm precision glass NMR tube (Wilmad 507) at 297 K in the deuterium-locked mode on a Bruker Avance III 400 MHz spectrometer operating at 400.17, 376.54, 128.23 or 100.62 MHz for ^1H, ^{19}F, ^{11}B and ^{13}C nuclei, respectively. The ^1H NMR and ^{13}C chemical shifts were referenced with respect to tetramethylsilane yielding the chemical shift for CD_3CN (contains $CD_2\mathbf{H}CN$) as 1.96 ppm and $CD_3\mathbf{C}N$ as 118.7 ppm. The ^{19}F chemical shifts were referenced with respect to $CFCl_3$ (0 ppm) as external standard. The ^{11}B chemical shifts were referenced with respect to $BF_3{\cdot}(C_2H_5)_2O$ (0 ppm) as external standard. 68 mg of ground crystals were dissolved in 0.5 ml CD_3CN to prepare the NMR sample: ^1H NMR: 3.71 (*s*, 8H, $C_4\mathbf{H}_8O_2$), 9.41 (*s*, 2H, $\mathbf{H}_2O$). ^{19}F NMR: −148.10 (*s*, $^{11}B\mathbf{F}_3$), −148.04 (*s*, $^{10}B\mathbf{F}_3$). ^{11}B NMR: −0.1 (*s*, $^{11}\mathbf{B}F_3$). ^{13}C NMR: 68.0 [*t*, $^1J_{(C,H)}$ = 189 Hz, $\mathbf{C}_4H_8O_2$].

6. Synthesis and crystallization

All preparations and sample manipulations were carried out in tetrafluoroethylene hexafluoropropylene block copolymer (FEP) vessels. Tetrafluoroboric acid solution (50 wt% in water; Fluka Chemicals) was probed for its content of $[BF_3OH]^-$ by ^{19}F NMR spectroscopy. Depending on the quantity of these anions, hydrofluoric acid (48 wt% in water, Sigma–Aldrich) was added. In a typical experiment, to 131.4 g (1.24 mol) of HBF_4/H_2O, 4.53 g (0.11 mol) HF/H_2O was added at 273 K. The mixture was stirred for 15 min, before 430 g of 1,4-dioxane was added at the same temperature. Subsequently, the reaction mixture was heated and the 1,4-dioxane–water azeotrope was distilled off under normal pressure until the boiling point (361 K) began to change. 368 g of azeotrope was removed by the distillation and the residue was a pale-brown solution. This solution was stored in a sealed FEP flask under an atmosphere of dry argon (Argon 5.0). After 1 h, the formation of colourless crystals of **1** started and was allowed to continue for 9 d. The crystals were isolated under an argon atmosphere and washed with hexane/1,4-dioxane (10:1 *v*/*v*) three times using Schlenk techniques. 40.7 g (0.23 mol) were collected after drying the almost hexagonal colourless crystals in an argon stream (40 min). Compound **1** is stable at room temperature and shows a poor solubility in 1,4-dioxane, but a good solubility in acetonitrile.

An elemental analysis was performed with a HEKATECH EA 3000 elemental analyser using *Callidus 2E3* software. 1.7 mg of freshly ground crystals were used and a modifier was added to suppress the influence of the high fluorine content.

Table 3
Experimental details.

Crystal data	
Chemical formula	$H_2BF_3O{\cdot}C_4H_8O_2$
M_r	173.93
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	223
a, b, c (Å)	7.6835 (5), 12.929 (1), 15.2326 (13)
V (Å^3)	1513.2 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.16
Crystal size (mm)	0.69 × 0.48 × 0.42
Data collection	
Diffractometer	Stoe IPDS
Absorption correction	Multi-scan (Blessing, 1989)
$T_{\min}$, $T_{\max}$	0.673, 0.920
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19913, 1481, 932
$R_{\rm int}$	0.085
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.138, 1.38
No. of reflections	1481
No. of parameters	108
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.60, −0.42

Computer programs: *X-AREA* (Stoe & Cie, 2009), *SHELXS* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Analysis calculated (%) for $C_4H_{10}BF_3O_3$: 27.62 C, 5.80 H; found: 27.84 C, 5.87 H.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The positions of all H atoms were identified *via* subsequent ΔF syntheses. In the refinement, a riding model was applied, using idealized C—H bond lengths, as well as H—C—H and C—C—H angles. The $U_{\rm iso}$ values were set at $1.2U_{\rm eq}$(C) for methylene H atoms. For the H atoms of the aqua ligand, positional parameters and $U_{\rm iso}$ values were refined.

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supporting information

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The `super acid' BF_3H_2O stabilized by 1,4-dioxane: new preparative aspects and the crystal structure of $BF_3H_2O·C_4H_8O_2$

Peter Barthen and Walter Frank

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-AREA* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Aquatrifluoridoboron–1,4-dioxane (1/1)

Crystal data

$H_2BF_3O·C_4H_8O_2$
$M_r = 173.93$
Orthorhombic, *Pbca*
$a = 7.6835$ (5) Å
$b = 12.929$ (1) Å
$c = 15.2326$ (13) Å
$V = 1513.2$ (2) Å^3
$Z = 8$
$F(000) = 720$
$D_x = 1.527$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7579 reflections
$\theta = 2.7–25.9°$
$\mu = 0.16$ mm^{-1}
$T = 223$ K
Prisms, colourless
0.69 × 0.48 × 0.42 mm

Data collection

Stoe IPDS diffractometer
Radiation source: sealed tube
φ–scan
Absorption correction: multi-scan (Blessing, 1989)
$T_{min} = 0.673$, $T_{max} = 0.920$
19913 measured reflections
1481 independent reflections
932 reflections with $I > 2\sigma(I)$
$R_{int} = 0.085$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.7°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.138$
$S = 1.38$
1481 reflections
108 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
$w = 1/[\sigma^2(F_o^2) + 1.3744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ 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 (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
F1	0.2228 (2)	0.10315 (15)	0.11881 (16)	0.0760 (7)
F2	0.2173 (4)	−0.0515 (2)	0.05362 (17)	0.1020 (9)
F3	0.2125 (4)	−0.0419 (2)	0.19661 (18)	0.1177 (11)
O1	0.4628 (3)	0.0027 (2)	0.1262 (3)	0.0968 (14)
H1	0.516 (6)	0.057 (4)	0.133 (3)	0.108 (17)*
H2	0.515 (6)	−0.053 (4)	0.128 (3)	0.109 (17)*
O2	0.6367 (2)	0.16850 (14)	0.13995 (14)	0.0435 (5)
O3	0.8588 (2)	0.33805 (14)	0.11459 (14)	0.0425 (5)
C1	0.8229 (3)	0.1569 (2)	0.1462 (2)	0.0409 (7)
H11	0.8705	0.1372	0.0889	0.049*
H12	0.8511	0.1021	0.1883	0.049*
C2	0.9021 (4)	0.2567 (2)	0.1756 (2)	0.0435 (8)
H21	0.8585	0.2745	0.2341	0.052*
H22	1.0288	0.2493	0.1792	0.052*
C3	0.6730 (3)	0.3498 (2)	0.1084 (2)	0.0410 (7)
H31	0.6449	0.4046	0.0663	0.049*
H32	0.6256	0.3696	0.1657	0.049*
C4	0.5934 (4)	0.2498 (2)	0.0791 (2)	0.0448 (8)
H41	0.4666	0.2573	0.0756	0.054*
H42	0.6366	0.2319	0.0205	0.054*
B1	0.2712 (4)	0.0021 (3)	0.1232 (3)	0.0412 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0439 (11)	0.0559 (12)	0.128 (2)	0.0169 (9)	0.0004 (13)	0.0007 (12)
F2	0.0930 (18)	0.113 (2)	0.1005 (19)	−0.0035 (16)	−0.0243 (16)	−0.0500 (16)
F3	0.118 (2)	0.141 (2)	0.0942 (19)	−0.035 (2)	0.0120 (17)	0.0528 (18)
O1	0.0264 (12)	0.0294 (13)	0.234 (4)	0.0014 (11)	−0.008 (2)	−0.0130 (18)
O2	0.0295 (10)	0.0357 (10)	0.0652 (14)	−0.0044 (8)	−0.0025 (9)	0.0052 (10)
O3	0.0292 (10)	0.0355 (10)	0.0629 (14)	−0.0033 (8)	0.0010 (10)	0.0012 (10)
C1	0.0308 (16)	0.0374 (15)	0.0544 (18)	0.0027 (12)	−0.0045 (13)	0.0001 (14)
C2	0.0314 (14)	0.0430 (17)	0.056 (2)	0.0027 (13)	−0.0078 (14)	−0.0035 (14)
C3	0.0318 (15)	0.0367 (15)	0.0544 (19)	0.0014 (12)	−0.0022 (13)	0.0054 (14)
C4	0.0348 (15)	0.0442 (17)	0.055 (2)	−0.0003 (13)	−0.0100 (15)	0.0025 (14)
B1	0.0299 (16)	0.0422 (18)	0.052 (2)	−0.0037 (15)	−0.0039 (18)	0.0006 (15)

Geometric parameters (Å, º)

F1—B1	1.361 (4)	C1—C2	1.495 (4)
F2—B1	1.332 (4)	C1—H11	0.9800
F3—B1	1.333 (4)	C1—H12	0.9800
O1—B1	1.473 (4)	C2—H21	0.9800
O1—H1	0.82 (5)	C2—H22	0.9800
O1—H2	0.82 (5)	C3—C4	1.499 (4)
O2—C4	1.440 (3)	C3—H31	0.9800
O2—C1	1.442 (3)	C3—H32	0.9800
O3—C3	1.439 (3)	C4—H41	0.9800
O3—C2	1.442 (3)	C4—H42	0.9800
B1—O1—H1	121 (3)	O3—C3—H31	109.8
B1—O1—H2	119 (3)	C4—C3—H31	109.8
H1—O1—H2	120 (4)	O3—C3—H32	109.8
C4—O2—C1	110.4 (2)	C4—C3—H32	109.8
C3—O3—C2	110.4 (2)	H31—C3—H32	108.2
O2—C1—C2	109.5 (2)	O2—C4—C3	110.1 (2)
O2—C1—H11	109.8	O2—C4—H41	109.6
C2—C1—H11	109.8	C3—C4—H41	109.6
O2—C1—H12	109.8	O2—C4—H42	109.6
C2—C1—H12	109.8	C3—C4—H42	109.6
H11—C1—H12	108.2	H41—C4—H42	108.2
O3—C2—C1	110.1 (2)	F3—B1—F2	109.9 (3)
O3—C2—H21	109.6	F3—B1—F1	111.0 (3)
C1—C2—H21	109.6	F2—B1—F1	112.1 (3)
O3—C2—H22	109.6	F3—B1—O1	108.3 (3)
C1—C2—H22	109.6	F2—B1—O1	109.8 (3)
H21—C2—H22	108.2	F1—B1—O1	105.6 (3)
O3—C3—C4	109.5 (2)		
C4—O2—C1—C2	58.7 (3)	C2—O3—C3—C4	−58.7 (3)
C3—O3—C2—C1	59.2 (3)	C1—O2—C4—C3	−58.9 (3)
O2—C1—C2—O3	−58.6 (3)	O3—C3—C4—O2	58.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82 (5)	1.72 (5)	2.534 (3)	175 (5)
O1—H2···O3^{i}	0.82 (5)	1.72 (5)	2.539 (3)	170 (5)

Symmetry code: (i) −*x*+3/2, *y*−1/2, *z*.