Aquatrifluoridoboron–1,3-dioxolan-2-one (1/2)

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The crystal structure of the co-crystal of aquatrifluoridoboron with two ethylene carbonate (systematic name: 1,3-dioxolan-2-one) molecules, $BF_3H_2O \cdot 2OC(OCH_2)_2$, was determined by low-temperature single-crystal X-ray diffraction. The co-crystal crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The asymmetric unit consists of an aquatrifluoridoboron molecule and two ethylene carbonate molecules, connected by O—H⋯O=C hydrogen bonds. This crystal structure is an interesting example of a superacidic BF_3H_2O species co-crystallized with an organic carbonate.

3D view

Chemical scheme
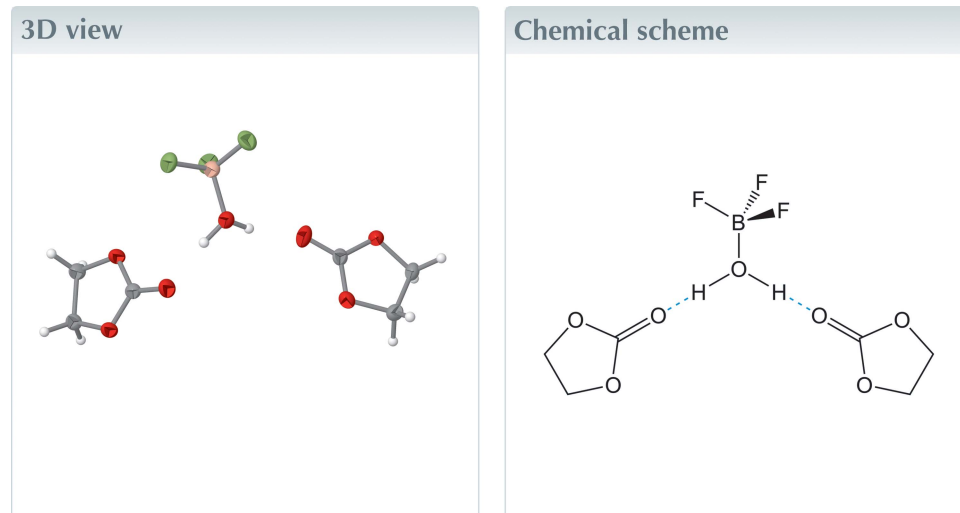
Structure description

Adducts synthesized from boron trifluoride and various organic carbonates have been reported as potential functional electrolyte additives for secondary (rechargeable) lithium-ion batteries (Eisele *et al.*, 2020), and have been shown to modify the electrode surfaces, resulting in reduced cell resistance and better capacity retention at high current rates. Recently, the use of BF_3-based additives has been extended to divalent-metal batteries, namely calcium-ion batteries (Forero-Saboya *et al.*, 2021; Bodin *et al.*, 2023), where their decomposition into boron-crosslinked polymeric matrices in the passivation layer was found to be crucial for calcium plating and stripping. Such BF_3 adducts are moisture sensitive and readily hydrolyze to form BF_3H_2O (Simonov *et al.*, 1996; Fonari *et al.*, 1997). The title co-crystal formed from the boron trifluoride–ethylene carbonate (1/1) adduct, $BF_3 \cdot OC(OCH_2)_2$, upon exposure to moisture.

The $BF_3H_2O \cdot 2OC(OCH_2)_2$ co-crystal crystallizes in the orthorhombic Sohncke space group $P2_12_12_1$ with one aquatrifluoridoboron and two ethylene carbonate molecules in the asymmetric unit (Fig. 1). The two $OC(OCH_2)_2$ molecules have an essentially identical molecular shape (slightly twisted), which also agrees well with the crystal structure determination of 1,3-dioxolan-2-one (Atterberry & Bond, 2019). The B—O and B—F
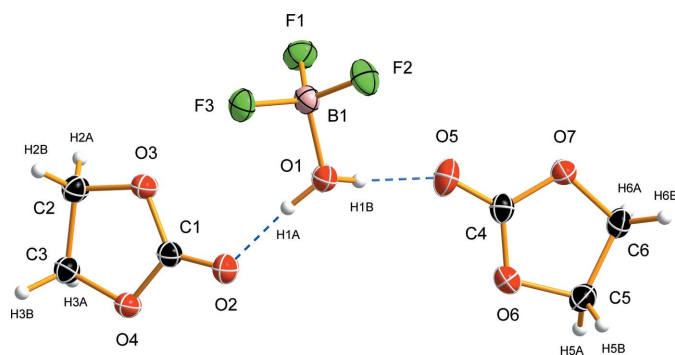
Figure 1
The asymmetric unit and the atom-labelling scheme of the BF₃H₂O·2OC(OCH₂)₂ co-crystal. Anisotropic displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are depicted as spheres of arbitrary radius, and hydrogen bonds are indicated by blue dashed lines.

bond lengths [1.5236 (18) Å and 1.3718 (18)–1.3760 (17) Å, respectively] in the BF_3H_2O molecule of the title co-crystal are similar to those found in BF_3H_2O (Mootz & Steffen, 1981a), $BF_3H_2O \cdot H_2O$ (Mootz & Steffen, 1981b), $BF_3H_2O \cdot C_4H_8O_2$ (Barthen & Frank, 2019), or adducts of BF_3 and organic carbonates (Bodin et $al.$, 2023). The F—B—F angles [110.75 (12)–112.57 (12)°] are larger than the O—B—F angles, with the angle involving F1 [109.23 (11)°] being significantly larger than the other two angles [105.47 (11)° and 106.41 (12)°]. The hydrogen atoms of the H_2O moiety in the BF_3H_2O adduct are inclined toward the F1 atom, with the angle between the B—O bond and the plane defined by the water atoms being 128 (2)°. The overall shape of the BF_3 moiety in BF_3H_2O in terms of bond lengths and angles is similar to that of the BF_4^- anion (Lozinšek, 2021).

Figure 2
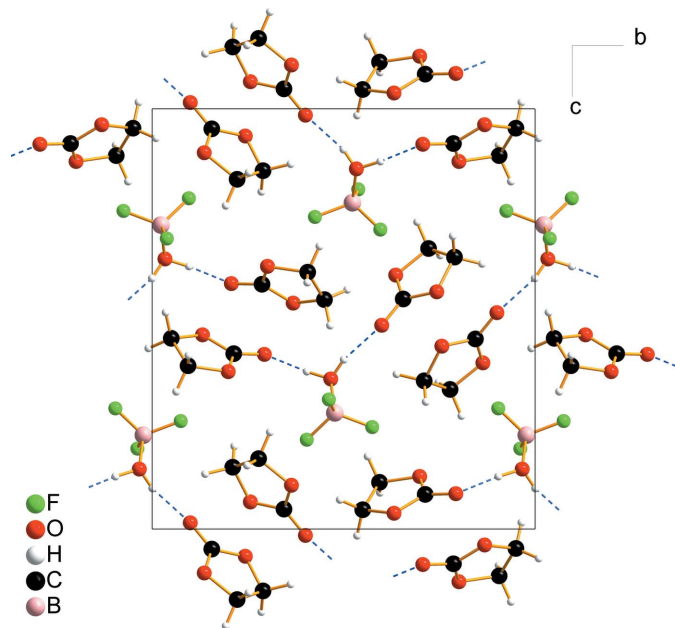Crystal packing of $BF_3H_2O \cdot 2OC(OCH_2)_2$ viewed along [100]. Hydrogen bonds are indicated by blue dashed lines.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1A⋯O2	0.90 (3)	1.67 (3)	2.5637 (15)	175 (3)
O1—H1B⋯O5	0.82 (3)	1.79 (3)	2.5985 (15)	166 (2)

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_3H_4O_3 \cdot H_2BF_3O$
M_r	261.95
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	150
a, b, c (Å)	5.44197 (4), 13.09134 (8), 14.36102 (9)
V (Å³)	1023.12 (1)
Z	4
Radiation type	Cu $K\alpha$
μ (mm⁻¹)	1.65
Crystal size (mm)	0.18 × 0.08 × 0.05
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, Eiger2 R CdTe 1M
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2022)
T_{min}, T_{max}	0.663, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34542, 2134, 2100
R_{int}	0.038
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.050, 1.04
No. of reflections	2134
No. of parameters	195
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.11, −0.13
Absolute structure	Flack x determined using 853 quotients [$(I^+)-(I^-)$]/[$(I^+)+(I^-)$] (Parsons et $al.$, 2013)
Absolute structure parameter	−0.05 (3)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *OLEX2* (Dolomanov et $al.$, 2009), *DIAMOND* (Brandenburg, 2005) and *publCIF* (Westrip, 2010).

Aquatrifluoridoboron is stabilized in the solid state by hydrogen-bonding interactions with oxygen hydrogen-bond acceptors, such as 1,4-dioxane (Barthen & Frank, 2019) or crown ethers (Bott et $al.$, 1991; Simonov et $al.$, 1996; Fonari et $al.$, 1997; Gelmboldt et $al.$, 2012). In the present case, the BF_3H_2O molecule is hydrogen-bonded to the carbonyl oxygen atoms of the two ethylene carbonate molecules, forming a C=O⋯H—O—H⋯O=C fragment with a $D_2^2(5)$ graph-set motif (Etter, 1990) and O⋯O distances of 2.5637 (15) Å and 2.5985 (15) Å (Table 1, Figs. 1 and 2). A similar hydrogen-bonding motif was observed in the crystal structure of the $BF_3H_2O \cdot 2Ph_3PO$ co-crystal (Chekhlov, 2005).

Synthesis and crystallization

Single crystals of the $BF_3H_2O \cdot 2OC(OCH_2)_2$ co-crystal were discovered when a crystalline sample of the air-sensitive

BF$_3$·OC(OCH$_2$)$_2$ adduct was examined under a protective cold nitrogen stream at about −50 °C. The BF$_3$·OC(OCH$_2$)$_2$ compound was synthesized from dry ethylene carbonate and BF$_3$ gas under anhydrous conditions, as described previously (Bodin *et al.*, 2023). Platelet-shaped co-crystals of BF$_3$H$_2$O·2OC(OCH$_2$)$_2$ were located in a droplet at the tip of the aluminium trough (Veith & Bärnighausen, 1974) of the low-temperature crystal mounting apparatus, which likely formed by an inadvertent introduction of a small amount of moisture. Selected crystals were mounted on the diffractometer employing a previously described procedure for mounting crystals at low temperatures (Lozinšek *et al.*, 2021). The crystals melted and turned into droplets when exposed to air at room temperature.

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. Positions and isotropic thermal displacement parameters of hydrogen atoms were freely refined (Cooper *et al.*, 2010).

Funding information

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full crystallographic data

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Crystal data

$2C_3H_4O_3 \cdot H_2BF_3O$	$D_x = 1.701$ Mg m^{-3}
$M_r = 261.95$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 24984 reflections
$a = 5.44197$ (4) Å	$\theta = 4.6$–$75.5°$
$b = 13.09134$ (8) Å	$\mu = 1.65$ mm^{-1}
$c = 14.36102$ (9) Å	$T = 150$ K
$V = 1023.12$ (1) Å^3	Plate, clear colourless
$Z = 4$	$0.18 \times 0.08 \times 0.05$ mm
$F(000) = 536$	

Data collection

XtaLAB Synergy, Dualflex, Eiger2 R CdTe 1M diffractometer	$T_{min} = 0.663$, $T_{max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	34542 measured reflections
	2134 independent reflections
Mirror monochromator	2100 reflections with $I > 2\sigma(I)$
Detector resolution: 13.3333 pixels mm^{-1}	$R_{int} = 0.038$
ω scans	$\theta_{max} = 76.1°$, $\theta_{min} = 4.6°$
Absorption correction: gaussian (*CrysAlisPro*; Rigaku OD, 2022)	$h = -6 \rightarrow 6$
	$k = -15 \rightarrow 16$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.1146P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.050$	$\Delta\rho_{max} = 0.11$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.13$ e Å^{-3}
2134 reflections	Extinction correction: SHELXL (Sheldrick, 2015b), $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
195 parameters	Extinction coefficient: 0.0035 (5)
0 restraints	Absolute structure: Flack x determined using 853 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Primary atom site location: dual	
Hydrogen site location: difference Fourier map	Absolute structure parameter: -0.05 (3)
All H-atom parameters refined	

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_{iso}*/U_{eq}
F1	0.05387 (16)	0.46158 (7)	0.69151 (6)	0.0345 (2)
F2	0.31541 (19)	0.57475 (6)	0.75716 (6)	0.0347 (2)
F3	0.35784 (17)	0.40399 (6)	0.78723 (6)	0.0320 (2)
O1	0.4683 (2)	0.46651 (8)	0.64281 (7)	0.0283 (2)
H1A	0.518 (5)	0.404 (2)	0.6252 (19)	0.071 (8)*
H1B	0.432 (5)	0.5005 (19)	0.5968 (17)	0.052 (6)*
O2	0.6234 (2)	0.29312 (8)	0.58425 (7)	0.0312 (2)
O3	0.29867 (18)	0.19871 (7)	0.62526 (7)	0.0266 (2)
O4	0.59130 (18)	0.13169 (7)	0.53775 (7)	0.0255 (2)
C1	0.5104 (2)	0.21312 (10)	0.58256 (9)	0.0232 (3)
C2	0.2189 (3)	0.09379 (11)	0.61128 (10)	0.0267 (3)
H2A	0.062 (4)	0.0949 (14)	0.5867 (13)	0.033 (5)*
H2B	0.220 (3)	0.0629 (13)	0.6729 (12)	0.025 (4)*
C3	0.4125 (3)	0.04997 (10)	0.54606 (10)	0.0249 (3)
H3A	0.349 (4)	0.0354 (14)	0.4844 (13)	0.031 (4)*
H3B	0.497 (4)	−0.0097 (15)	0.5697 (12)	0.030 (5)*
B1	0.2884 (3)	0.47702 (12)	0.72354 (11)	0.0252 (3)
O5	0.3601 (2)	0.59963 (8)	0.51501 (8)	0.0359 (3)
O6	0.60783 (19)	0.63618 (7)	0.39559 (7)	0.0280 (2)
O7	0.31353 (19)	0.74337 (7)	0.43534 (6)	0.0266 (2)
C4	0.4246 (3)	0.65572 (10)	0.45246 (9)	0.0240 (3)
C5	0.6409 (3)	0.72193 (11)	0.33235 (10)	0.0305 (3)
H5B	0.793 (4)	0.7521 (16)	0.3486 (14)	0.040 (5)*
H5A	0.649 (4)	0.6923 (14)	0.2694 (14)	0.038 (5)*
C6	0.4207 (3)	0.78959 (11)	0.35281 (10)	0.0291 (3)
H6B	0.470 (3)	0.8616 (15)	0.3687 (13)	0.032 (4)*
H6A	0.296 (4)	0.7853 (15)	0.3028 (14)	0.040 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0260 (4)	0.0419 (5)	0.0356 (4)	−0.0012 (4)	−0.0027 (3)	0.0046 (4)
F2	0.0475 (5)	0.0265 (4)	0.0300 (4)	0.0037 (4)	−0.0046 (4)	−0.0043 (3)
F3	0.0379 (5)	0.0309 (4)	0.0273 (4)	0.0026 (4)	−0.0013 (4)	0.0085 (3)
O1	0.0324 (5)	0.0254 (5)	0.0271 (5)	0.0034 (4)	0.0049 (4)	0.0046 (4)
O2	0.0325 (5)	0.0237 (4)	0.0373 (5)	−0.0033 (4)	0.0051 (5)	−0.0004 (4)
O3	0.0256 (5)	0.0243 (4)	0.0299 (5)	0.0006 (4)	0.0066 (4)	−0.0026 (4)
O4	0.0236 (5)	0.0243 (4)	0.0285 (5)	0.0008 (4)	0.0043 (4)	−0.0025 (4)
C1	0.0240 (6)	0.0236 (6)	0.0220 (6)	0.0025 (5)	0.0007 (5)	0.0016 (5)
C2	0.0243 (7)	0.0258 (6)	0.0300 (7)	−0.0032 (5)	0.0023 (6)	−0.0027 (5)
C3	0.0236 (6)	0.0234 (6)	0.0275 (6)	−0.0009 (5)	−0.0003 (5)	−0.0010 (5)
B1	0.0282 (8)	0.0253 (7)	0.0220 (7)	0.0020 (6)	−0.0007 (6)	0.0015 (5)
O5	0.0459 (6)	0.0315 (5)	0.0303 (5)	−0.0073 (5)	−0.0016 (5)	0.0098 (4)
O6	0.0299 (5)	0.0225 (4)	0.0314 (5)	0.0031 (4)	0.0017 (4)	−0.0006 (4)
O7	0.0303 (5)	0.0240 (4)	0.0255 (4)	0.0035 (4)	0.0055 (4)	0.0024 (4)

C4	0.0278 (7)	0.0212 (6)	0.0229 (6)	−0.0023 (5)	−0.0024 (5)	0.0002 (5)
C5	0.0343 (8)	0.0271 (7)	0.0302 (7)	−0.0041 (6)	0.0083 (6)	0.0000 (6)
C6	0.0355 (8)	0.0244 (7)	0.0273 (6)	0.0000 (6)	0.0034 (6)	0.0069 (5)

Geometric parameters (Å, º)

F1—B1	1.3718 (18)	C2—C3	1.522 (2)
F2—B1	1.3753 (17)	C3—H3A	0.969 (19)
F3—B1	1.3760 (17)	C3—H3B	0.97 (2)
O1—H1A	0.90 (3)	O5—C4	1.2122 (17)
O1—H1B	0.82 (3)	O6—C4	1.3139 (18)
O1—B1	1.5236 (18)	O6—C5	1.4550 (17)
O2—C1	1.2147 (17)	O7—C4	1.3200 (16)
O3—C1	1.3187 (16)	O7—C6	1.4530 (17)
O3—C2	1.4545 (16)	C5—H5B	0.95 (2)
O4—C1	1.3208 (16)	C5—H5A	0.98 (2)
O4—C3	1.4512 (17)	C5—C6	1.519 (2)
C2—H2A	0.92 (2)	C6—H6B	1.01 (2)
C2—H2B	0.972 (18)	C6—H6A	0.99 (2)
H1A—O1—H1B	110 (2)	F1—B1—O1	109.23 (11)
B1—O1—H1A	119.4 (18)	F2—B1—F3	112.57 (12)
B1—O1—H1B	114.2 (17)	F2—B1—O1	106.41 (12)
C1—O3—C2	109.38 (10)	F3—B1—O1	105.47 (11)
C1—O4—C3	109.35 (10)	C4—O6—C5	109.37 (11)
O2—C1—O3	123.81 (12)	C4—O7—C6	109.27 (11)
O2—C1—O4	122.46 (12)	O5—C4—O6	124.23 (13)
O3—C1—O4	113.73 (12)	O5—C4—O7	122.13 (14)
O3—C2—H2A	108.3 (12)	O6—C4—O7	113.64 (11)
O3—C2—H2B	105.4 (10)	O6—C5—H5B	106.1 (13)
O3—C2—C3	103.55 (11)	O6—C5—H5A	105.9 (11)
H2A—C2—H2B	110.9 (16)	O6—C5—C6	103.38 (11)
C3—C2—H2A	114.2 (12)	H5B—C5—H5A	110.5 (17)
C3—C2—H2B	113.6 (11)	C6—C5—H5B	113.6 (13)
O4—C3—C2	103.71 (11)	C6—C5—H5A	116.3 (12)
O4—C3—H3A	108.0 (11)	O7—C6—C5	103.40 (11)
O4—C3—H3B	107.7 (11)	O7—C6—H6B	108.2 (11)
C2—C3—H3A	112.9 (12)	O7—C6—H6A	107.1 (12)
C2—C3—H3B	114.7 (11)	C5—C6—H6B	112.2 (11)
H3A—C3—H3B	109.3 (16)	C5—C6—H6A	111.6 (11)
F1—B1—F2	110.75 (12)	H6B—C6—H6A	113.6 (15)
F1—B1—F3	112.08 (13)		
O3—C2—C3—O4	5.22 (14)	O6—C5—C6—O7	9.38 (14)
C1—O3—C2—C3	−4.14 (14)	C4—O6—C5—C6	−7.83 (15)
C1—O4—C3—C2	−4.81 (14)	C4—O7—C6—C5	−8.29 (15)
C2—O3—C1—O2	−178.23 (13)	C5—O6—C4—O5	−177.25 (14)
C2—O3—C1—O4	1.26 (15)	C5—O6—C4—O7	2.92 (16)

| C3—O4—C1—O2 | −178.06 (13) | C6—O7—C4—O5 | −176.09 (13) |
| C3—O4—C1—O3 | 2.44 (15) | C6—O7—C4—O6 | 3.74 (16) |

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*A*···O2	0.90 (3)	1.67 (3)	2.5637 (15)	175 (3)
O1—H1*B*···O5	0.82 (3)	1.79 (3)	2.5985 (15)	166 (2)
C3—H3*B*···F3$^{\text{i}}$	0.97 (2)	2.474 (19)	3.3085 (16)	144.2 (14)
C6—H6*B*···F1$^{\text{ii}}$	1.01 (2)	2.51 (2)	3.3974 (17)	146.4 (14)

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