

Low-temperature modification of $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$

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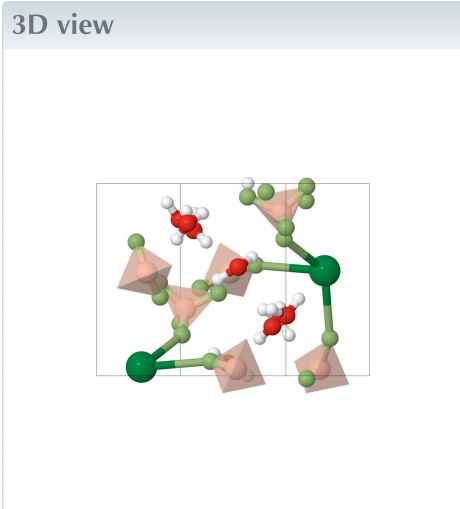
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The crystal structure of the low-temperature modification of $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$, barium bis(tetrafluoridoborate) trihydrate, was determined at 150 K. In contrast to the room-temperature modification, which crystallizes in the space group $C222_1$ [$a = 7.1763$ (6), $b = 18.052$ (2), $c = 7.1631$ (6) Å, $V = 927.93$ (15) Å³ at 300 K, $Z = 4$; Charkin *et al.* (2023). *J. Struct. Chem.* **64**, 253–261], the low-temperature phase is monoclinic, space group $P2_1$ [$a = 7.0550$ (4), $b = 7.1706$ (3), $c = 9.4182$ (6) Å, $\beta = 109.295$ (7)°, $V = 449.68$ (5) Å³, $Z = 2$]. The structure of the low-temperature modification of $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$ features O—H···F and O—H···O hydrogen bonding between water molecules and BF_4^- anions. One of the coordinating water molecules in the low-temperature modification is disordered over two sets of sites.



Structure description

Recently, the orthorhombic crystal structure of the compound $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$ was reported on the basis of room-temperature (RT) single-crystal data in space group $C222_1$ (Charkin *et al.*, 2023). The authors observed a phase transition at decreasing temperature but were unable to solve the crystal structure of the low-temperature (LT) modification. We have now succeeded in solving the crystal structure of LT- $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$.

The asymmetric unit of LT- $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$ contains one Ba^{2+} cation, two tetrahedral BF_4^- anions and three water molecules, one of which (O3) is disordered over two sets of sites with approximately equal occupancy [ratio 0.56 (2):0.44 (2)]. The Ba^{2+} cation has a coordination number of 10 and is coordinated by seven F ligands from six BF_4^- anions and by three water ligands (Fig. 1). In anhydrous $\text{Ba}(\text{BF}_4)_2$ (Bunič *et al.*, 2007), the Ba^{2+} cation is surrounded by ten BF_4^- anions. The B(1)F₄ unit in LT- $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$ is bound to four Ba^{2+} cations, while the B(2)F₄ unit is connected in a chelate mode to one Ba^{2+} cation and to another *via* a μ_2 -bridging F ligand. Each $[\text{BaF}_7\text{O}_3]$ coordination polyhedron

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1A\cdots F5^i$	0.829 (10)	2.075 (8)	2.892 (12)	168.8 (7)
$O1-H1B\cdots F7^{ii}$	0.842 (10)	2.016 (7)	2.849 (13)	170.5 (7)
$O2-H2A\cdots F4$	0.974 (9)	2.331 (9)	3.119 (13)	137.4 (5)
$O2-H2B\cdots F8^{iii}$	0.977 (9)	2.053 (11)	3.002 (15)	163.5 (7)
$O3A-H3AA\cdots O2^{iii}$	0.88 (2)	2.191 (11)	2.96 (3)	146.5 (18)
$O3A-H3AB\cdots F7^{iv}$	0.84 (2)	2.386 (8)	3.13 (2)	147.7 (17)
$O3B-H3BA\cdots F5$	0.86 (3)	2.355 (9)	3.15 (3)	153.0 (16)

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

shares two vertices with two other $[BaF_7O_3]$ polyhedra. The shortest $Ba\cdots Ba$ distances amounts to 5.9210 (2) Å. $Ba-F$ bond lengths range from 2.698 (7) to 3.035 (8) Å, and $Ba-O$ bond lengths from 2.777 (9) to 2.821 (8) Å (for ordered water molecules). The spread of $Ba-F$ distances in LT- $Ba(BF_4)_2(H_2O)_3$ is greater than for the RT-modification [2.729 (4) to 2.843 (17) Å; Charkin *et al.*, 2023]. The $B-F$ distances in LT- $Ba(BF_4)_2(H_2O)_3$ are in normal ranges, 1.352 (12)–1.406 (16) Å.

The packing of LT- $Ba(BF_4)_2(H_2O)_3$ is shown in Fig. 2. The two ordered water molecules form $O-H\cdots F$ hydrogen bonds, and the disordered water molecule forms both $O-H\cdots F$ and $O-H\cdots O$ hydrogen bonds (Fig. 1, Table 1).

The RT unit cell in space group $C222_1$ with $a = 7.1763$ (6) Å, $b = 18.052$ (2) Å, $c = 7.1631$ (6) Å (Charkin *et al.*, 2023) is

Table 2
Unit-cell parameters (Å, °, Å³) of $Ba(BF_4)_2(H_2O)_3$ at different temperatures (K).

T	a	b	c	β	V
100	7.0406 (5)	7.1567 (3)	9.3926 (9)	109.292 (7)	446.69 (5)
150	7.0550 (4)	7.1706 (3)	9.4182 (6)	109.295 (7)	449.68 (5)
280	7.1469 (5)	7.1775 (4)	9.5820 (7)	110.254 (6)	461.13 (5)
300	7.1763 (6)	18.052 (2)	7.1631 (6)		927.93 (15)

related to the LT mP unit cell in $P2_1$ by the transformation $-a, -c, 1/2a + 1/2b$, suggesting a *translationengleiche* symmetry relationship of index 2 (Müller, 2013). Considering the significant difference in crystal density for both modifications (2.59 g cm⁻³ for the RT modification at 300 K, 2.63 g cm⁻³ for the LT modification at 280 K, and 2.59 g cm⁻³ at 150 K), it can be assumed that the formation of a structure with more effective packing is the driving force of the observed phase transition.

We also tried to determine the temperature of the phase transition. It is noteworthy that at 280 K the LT modification remains unchanged, with significantly enlarged unit-cell parameters (Table 2). At 300 K, an orthorhombic cell was indexed with 100% of all observed reflections and with similar lattice parameters as given by Charkin *et al.* (2023). Thus, we can conclude that the ordered $oC \rightleftharpoons mP$ phase transition of $Ba(BF_4)_2(H_2O)_3$ (accompanied by twinning of the monoclinic LT phase) occurs between 280 and 300 K.

Synthesis and crystallization

Single crystals of $Ba(BF_4)_2(H_2O)_3$ were grown from an aqueous solution of $Ba(BF_4)_2$. Barium carbonate was added in

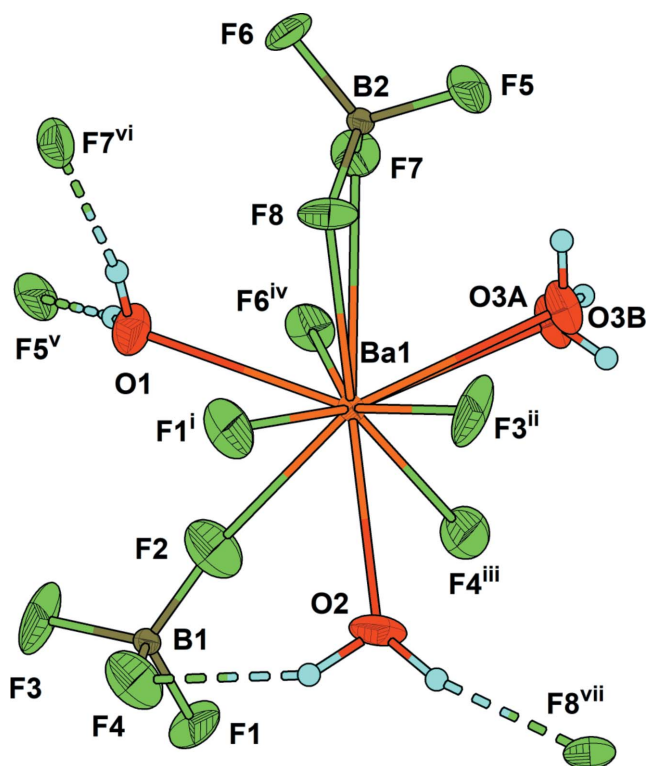


Figure 1
The environment of the Ba^{2+} cation in the crystal structure of LT- $Ba(BF_4)_2(H_2O)_3$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z$; (ii) $-x + 1, y, z$; (iii) $-x + 1, y + \frac{1}{2}, -z$; (iv) $-x + 2, y + \frac{1}{2}, -z + 1$; (v) $x - 1, y, z$; (vi) $-x + 2, y - \frac{1}{2}, -z + 1$.]

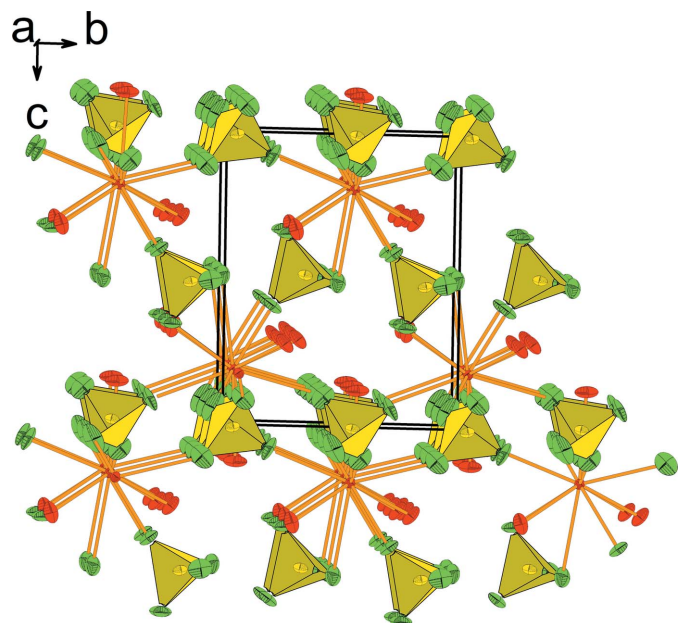


Figure 2
Crystal structure of LT- $Ba(BF_4)_2(H_2O)_3$ in a view approximately along [100]. Displacement ellipsoids are the same as in Fig. 1. Display of hydrogen-bonding interactions was omitted for clarity.

Table 3
Experimental details.

Crystal data	
Chemical formula	Ba(BF ₄) ₂ (H ₂ O) ₃
<i>M_r</i>	365.01
Crystal system, space group	Monoclinic, <i>P2</i> ₁
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0550 (4), 7.1706 (3), 9.4182 (6)
β (°)	109.295 (7)
<i>V</i> (Å ³)	449.68 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.53
Crystal size (mm)	0.36 × 0.27 × 0.07
Data collection	
Diffractometer	New Gemini, Dual, Cu at home/ near, Atlas
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T</i> _{min} , <i>T</i> _{max}	0.075, 0.472
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	2386, 2386, 2212
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.674
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.089, 1.07
No. of reflections	2386
No. of parameters	120
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.93, -1.05
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter	-0.03 (4)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *DIAMOND* (Putz *et al.*, 2023) and *OLEX2* (Dolomanov *et al.*, 2009).

small portions to 40%_{wt} HBF₄. After completion of the gaseous CO₂ release, the solution was decanted from residual BaCO₃. Evaporation of water at room temperature yielded small crystals of Ba(BF₄)₂(H₂O)₃. Note that an excess of HBF₄ led to the formation of crystals of anhydrous Ba(BF₄)₂ in our experiments.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The obtained crystals suffer from racemic twinning and additionally show twinning by pseudo-

merohedry at decreasing temperature. To avoid complicated refinement, many crystals were tested until a crystal with a Flack parameter (Flack, 1983) close to zero was found. The twin law corresponding to a 180° rotation around the [100] direction was determined, and the reflection array was indexed as a two-component twin with a negligible amount of non-indexed reflections. Because of the relatively small amount (BASF = 0.26) of the second domain, the final refinement was performed with a HKLF5-type file containing reflections from the first domain and overlapping reflections. Because of unstable refinement, EADP commands in *SHELXL* (Sheldrick, 2015) were applied to the pair of disordered O3 atoms and also to the pair of B atoms. Hydrogen atoms were placed on calculated positions and refined with AFIX 7 restrictions. One reflection with an error/e.s.d. ratio of 5.5 was omitted.

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full crystallographic data

IUCrData (2023). **8**, x230488 [<https://doi.org/10.1107/S2414314623004881>]

Low-temperature modification of $\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_3$

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Barium bis(tetrafluoridoborate) trihydrate

Crystal data

$\text{Ba}(\text{BF}_4)_2(\text{H}_2\text{O})_{32}(\text{BF}_4) \cdot 3(\text{H}_2\text{O}) \cdot \text{Ba}$

$M_r = 365.01$

Monoclinic, $P2_1$

$a = 7.0550$ (4) Å

$b = 7.1706$ (3) Å

$c = 9.4182$ (6) Å

$\beta = 109.295$ (7)°

$V = 449.68$ (5) Å³

$Z = 2$

$F(000) = 336$

$D_x = 2.696$ Mg m⁻³

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

Cell parameters from 5692 reflections

$\theta = 3.0$ – 28.2 °

$\mu = 4.53$ mm⁻¹

$T = 150$ K

Plate, colourless

$0.36 \times 0.27 \times 0.07$ mm

Data collection

New Gemini, Dual, Cu at home/near, Atlas diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 10.6426 pixels mm⁻¹

ω scans

Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.075$, $T_{\max} = 0.472$

2386 measured reflections

2386 independent reflections

2212 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 28.6$ °, $\theta_{\min} = 2.3$ °

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.089$

$S = 1.07$

2386 reflections

120 parameters

1 restraint

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$

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

$(\Delta/\sigma)_{\max} = 0.009$

$\Delta\rho_{\max} = 0.93$ e Å⁻³

$\Delta\rho_{\min} = -1.05$ e Å⁻³

Absolute structure: Classical Flack method

preferred over Parsons because s.u. lower

Absolute structure parameter: -0.03 (4)

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. Refined as a 2-component twin.

1. Twinned data refinement Scales: 0.738 (3) 0.262 (3) 2. Fixed Uiso At 1.5 times of: All O(H,H,H,H,H,H,H,H) groups 3. Uiso/Uanis restraints and constraints Uanis(O3B) = Uanis(O3A) Uanis(B2) = Uanis(B1) Uanis(F4) = Uanis(F2) 4. Others Sof(O3B)=Sof(H3BA)=Sof(H3BB)=1-FVAR(1) Sof(O3A)=Sof(H3AA)=Sof(H3AB)=FVAR(1) Fixed X: H1A(1.393391) H1B(1.25841) H3AA(0.82474) H3AB(0.919749) H3BA(0.70805) H3BB(0.82046) H2A(1.436299) H2B(1.27384) Fixed Y: H1A(0.843861) H1B(0.70964) H3AA(1.34448) H3AB(1.39917) H3BA(1.19412) H3BB(1.354321) H2A(0.999499) H2B(1.11445) Fixed Z: H1A(0.62203) H1B(0.62415) H3AA(0.77378) H3AB(0.663441) H3BA(0.651361) H3BB(0.66705) H2A(1.1758) H2B(1.21389)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ba1	0.84596 (6)	0.54566 (15)	0.18707 (5)	0.01069 (17)	
F1	0.1744 (12)	0.6957 (9)	-0.0772 (9)	0.0392 (19)	
F2	0.4423 (11)	0.5754 (14)	0.0977 (9)	0.0449 (16)	
F3	0.1320 (13)	0.4559 (13)	0.0610 (12)	0.050 (3)	
F4	0.2873 (13)	0.4098 (13)	-0.1086 (11)	0.0449 (16)	
F5	1.4219 (11)	0.4296 (12)	0.4972 (9)	0.0361 (18)	
F6	1.2726 (11)	0.2125 (11)	0.5958 (8)	0.0299 (16)	
F7	1.1150 (11)	0.4849 (9)	0.5097 (9)	0.0311 (18)	
F8	1.1510 (13)	0.2707 (18)	0.3442 (11)	0.035 (3)	
O1	0.6644 (13)	0.2926 (16)	0.3248 (12)	0.031 (2)	
O2	0.6901 (12)	0.565 (2)	-0.1296 (9)	0.033 (2)	
B1	0.2610 (14)	0.537 (4)	-0.0048 (10)	0.0136 (15)	
B2	1.2421 (17)	0.3491 (17)	0.4874 (13)	0.0136 (15)	
O3A	1.128 (3)	0.813 (4)	0.298 (2)	0.025 (4)	0.56 (2)
O3B	1.197 (4)	0.756 (4)	0.284 (3)	0.025 (4)	0.44 (2)
H1A	0.606609	0.343861	0.377970	0.038*	
H1B	0.741590	0.209640	0.375850	0.038*	
H3AA	1.175261	0.844480	0.226220	0.038*	0.56 (2)
H3AB	1.080250	0.899170	0.336559	0.038*	0.56 (2)
H3BA	1.291950	0.694120	0.348640	0.038*	0.44 (2)
H3BB	1.179539	0.854321	0.332950	0.038*	0.44 (2)
H2A	0.563701	0.499499	-0.175799	0.038*	
H2B	0.726160	0.614450	-0.213891	0.038*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0098 (2)	0.0107 (2)	0.0114 (3)	-0.0003 (4)	0.00317 (18)	-0.0011 (4)
F1	0.044 (5)	0.021 (3)	0.049 (5)	0.011 (3)	0.010 (4)	0.022 (3)
F2	0.029 (3)	0.052 (4)	0.052 (4)	0.000 (3)	0.011 (3)	-0.013 (3)
F3	0.043 (5)	0.048 (5)	0.082 (7)	0.010 (4)	0.051 (5)	0.030 (5)
F4	0.029 (3)	0.052 (4)	0.052 (4)	0.000 (3)	0.011 (3)	-0.013 (3)
F5	0.014 (4)	0.056 (5)	0.038 (5)	-0.005 (3)	0.008 (3)	0.003 (4)
F6	0.037 (4)	0.031 (4)	0.022 (4)	0.005 (3)	0.010 (3)	0.016 (3)
F7	0.028 (4)	0.024 (4)	0.040 (5)	0.008 (3)	0.009 (3)	0.001 (3)
F8	0.040 (6)	0.048 (6)	0.011 (4)	0.006 (4)	0.000 (3)	-0.002 (5)
O1	0.029 (5)	0.022 (5)	0.045 (7)	0.002 (3)	0.017 (5)	0.008 (4)

O2	0.026 (4)	0.055 (7)	0.013 (3)	0.006 (6)	0.000 (3)	-0.001 (6)
B1	0.010 (3)	0.021 (4)	0.010 (3)	-0.003 (4)	0.003 (3)	0.002 (4)
B2	0.010 (3)	0.021 (4)	0.010 (3)	-0.003 (4)	0.003 (3)	0.002 (4)
O3A	0.020 (10)	0.028 (11)	0.034 (8)	-0.007 (6)	0.017 (7)	-0.017 (7)
O3B	0.020 (10)	0.028 (11)	0.034 (8)	-0.007 (6)	0.017 (7)	-0.017 (7)

Geometric parameters (Å, °)

Ba1—F1 ⁱ	2.700 (6)	F4—B1	1.39 (2)
Ba1—F2	2.698 (7)	F5—B2	1.369 (13)
Ba1—F3 ⁱⁱ	2.735 (7)	F6—B2	1.379 (14)
Ba1—F4 ⁱⁱⁱ	2.791 (9)	F7—B2	1.385 (14)
Ba1—F6 ^{iv}	2.728 (7)	F8—B2	1.406 (16)
Ba1—F7	3.035 (8)	O1—H1A	0.83
Ba1—F8	2.933 (10)	O1—H1B	0.84
Ba1—O1	2.777 (9)	O2—H2A	0.97
Ba1—O2	2.821 (8)	O2—H2B	0.98
Ba1—O3A	2.71 (2)	O3A—H3AA	0.88
Ba1—O3B	2.78 (2)	O3A—H3AB	0.84
F1—B1	1.36 (2)	O3B—H3BA	0.86
F2—B1	1.352 (12)	O3B—H3BB	0.88
F3—B1	1.387 (15)		
F1 ⁱ —Ba1—F3 ⁱⁱ	64.4 (3)	O2—Ba1—F7	164.1 (2)
F1 ⁱ —Ba1—F4 ⁱⁱⁱ	142.9 (3)	O2—Ba1—F8	122.1 (3)
F1 ⁱ —Ba1—F6 ^{iv}	134.8 (2)	O3A—Ba1—F3 ⁱⁱ	77.3 (5)
F1 ⁱ —Ba1—F7	100.8 (2)	O3A—Ba1—F4 ⁱⁱⁱ	65.1 (6)
F1 ⁱ —Ba1—F8	60.4 (3)	O3A—Ba1—F6 ^{iv}	76.6 (4)
F1 ⁱ —Ba1—O1	66.3 (3)	O3A—Ba1—F7	65.2 (6)
F1 ⁱ —Ba1—O2	71.8 (3)	O3A—Ba1—F8	87.7 (5)
F1 ⁱ —Ba1—O3A	138.1 (5)	O3A—Ba1—O1	132.5 (5)
F1 ⁱ —Ba1—O3B	123.8 (6)	O3A—Ba1—O2	110.6 (6)
F2—Ba1—F1 ⁱ	92.1 (3)	O3B—Ba1—F7	63.6 (6)
F2—Ba1—F3 ⁱⁱ	137.5 (3)	O3B—Ba1—F8	76.9 (6)
F2—Ba1—F4 ⁱⁱⁱ	67.4 (3)	O3B—Ba1—O2	108.2 (6)
F2—Ba1—F6 ^{iv}	69.2 (2)	B1—F1—Ba1 ⁱⁱⁱ	157.8 (7)
F2—Ba1—F7	124.8 (2)	B1—F2—Ba1	149.2 (8)
F2—Ba1—F8	137.2 (3)	B1—F3—Ba1 ^v	141.5 (12)
F2—Ba1—O1	66.1 (3)	B1—F4—Ba1 ⁱ	133.4 (10)
F2—Ba1—O2	70.4 (2)	B2—F6—Ba1 ^{vi}	148.7 (7)
F2—Ba1—O3A	128.9 (6)	B2—F7—Ba1	99.9 (6)
F2—Ba1—O3B	142.5 (6)	B2—F8—Ba1	104.0 (8)
F3 ⁱⁱ —Ba1—F4 ⁱⁱⁱ	109.7 (3)	Ba1—O1—H1A	113.0
F3 ⁱⁱ —Ba1—F7	95.4 (3)	Ba1—O1—H1B	115.0
F3 ⁱⁱ —Ba1—F8	62.4 (3)	H1A—O1—H1B	109.0
F3 ⁱⁱ —Ba1—O1	124.7 (3)	Ba1—O2—H2A	115.0
F3 ⁱⁱ —Ba1—O2	68.8 (3)	F1—B1—F3	108.8 (10)
F3 ⁱⁱ —Ba1—O3B	64.1 (6)	F1—B1—F4	109.7 (8)

F4 ⁱⁱⁱ —Ba1—F7	116.4 (2)	F2—B1—F1	110.5 (17)
F4 ⁱⁱⁱ —Ba1—F8	152.8 (3)	F2—B1—F3	111.8 (9)
F4 ⁱⁱⁱ —Ba1—O2	72.2 (4)	F2—B1—F4	108.7 (10)
F6 ^{iv} —Ba1—F3 ⁱⁱ	151.8 (3)	F3—B1—F4	107.3 (17)
F6 ^{iv} —Ba1—F4 ⁱⁱⁱ	68.2 (3)	F5—B2—F6	109.6 (9)
F6 ^{iv} —Ba1—F7	63.8 (2)	F5—B2—F7	109.0 (10)
F6 ^{iv} —Ba1—F8	105.8 (3)	F5—B2—F8	110.6 (10)
F6 ^{iv} —Ba1—O1	68.5 (3)	F6—B2—F7	109.8 (9)
F6 ^{iv} —Ba1—O2	131.5 (3)	F6—B2—F8	109.7 (10)
F6 ^{iv} —Ba1—O3B	88.8 (5)	F7—B2—F8	108.2 (10)
F8—Ba1—F7	44.5 (2)	Ba1—O3A—H3AA	108.0
O1—Ba1—F4 ⁱⁱⁱ	124.6 (3)	Ba1—O3A—H3AB	110.0
O1—Ba1—F7	70.8 (3)	H3AA—O3A—H3AB	117.0
O1—Ba1—F8	72.5 (3)	Ba1—O3B—H3BA	111.0
O1—Ba1—O2	116.6 (3)	Ba1—O3B—H3BB	110.0
O1—Ba1—O3B	134.4 (6)	H3BA—O3B—H3BB	104.0
Ba1 ⁱⁱⁱ —F1—B1—F2	25 (2)	Ba1 ⁱ —F4—B1—F3	-3.8 (15)
Ba1 ⁱⁱⁱ —F1—B1—F3	148.0 (14)	Ba1 ^{vi} —F6—B2—F5	136.5 (11)
Ba1 ⁱⁱⁱ —F1—B1—F4	-95 (2)	Ba1 ^{vi} —F6—B2—F7	16.9 (19)
Ba1—F2—B1—F1	-111 (2)	Ba1 ^{vi} —F6—B2—F8	-101.9 (14)
Ba1—F2—B1—F3	127.5 (12)	Ba1—F7—B2—F5	103.0 (8)
Ba1—F2—B1—F4	9 (3)	Ba1—F7—B2—F6	-137.0 (8)
Ba1 ^v —F3—B1—F1	-31.2 (17)	Ba1—F7—B2—F8	-17.3 (9)
Ba1 ^v —F3—B1—F2	91.1 (18)	Ba1—F8—B2—F5	-101.1 (9)
Ba1 ^v —F3—B1—F4	-149.9 (11)	Ba1—F8—B2—F6	138.0 (7)
Ba1 ⁱ —F4—B1—F1	-121.8 (12)	Ba1—F8—B2—F7	18.2 (10)
Ba1 ⁱ —F4—B1—F2	117.3 (11)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots F5 ^v	0.829 (10)	2.075 (8)	2.892 (12)	168.8 (7)
O1—H1B \cdots F7 ^{vi}	0.842 (10)	2.016 (7)	2.849 (13)	170.5 (7)
O2—H2A \cdots F4	0.974 (9)	2.331 (9)	3.119 (13)	137.4 (5)
O2—H2B \cdots F8 ^{vii}	0.977 (9)	2.053 (11)	3.002 (15)	163.5 (7)
O3A—H3AA \cdots O2 ^{vii}	0.88 (2)	2.191 (11)	2.96 (3)	146.5 (18)
O3A—H3AB \cdots F7 ^{iv}	0.84 (2)	2.386 (8)	3.13 (2)	147.7 (17)
O3B—H3BA \cdots F5	0.86 (3)	2.355 (9)	3.15 (3)	153.0 (16)

Symmetry codes: (iv) $-x+2, y+1/2, -z+1$; (v) $x-1, y, z$; (vi) $-x+2, y-1/2, -z+1$; (vii) $-x+2, y+1/2, -z$.

Transformation matrix $oC-mP$ ($HT-LT$ phase transition of $Ba(BF_4)_2(H_3O)_3$)

-1	0	0
0	0	-1
1/2	-1/2	0