Barium bis[tetrafluoridobromate(III)]

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Single crystals of barium bis[tetrafluoridobromate(III)], $Ba[BrF_4]_2$, were obtained in the form of tiny blocks. Crystal-structure refinement of $Ba[BrF_4]_2$ from single-crystal X-ray diffraction data confirmed the previous model obtained on the basis of powder data [Ivlev *et al.* (2014). *Eur. J. Inorg. Chem.* pp. 6261–6267], but with all atoms refined with anisotropic displacement parameters. The crystal structure consists of two symmetry-independent barium cations that are each coordinated by twelve fluorine atoms, forming edge-sharing polyhedra, and an almost square-planar $[BrF_4]^-$ anion. The compound crystallizes in the $Ba[AuF_4]_2$ structure type.

3D view
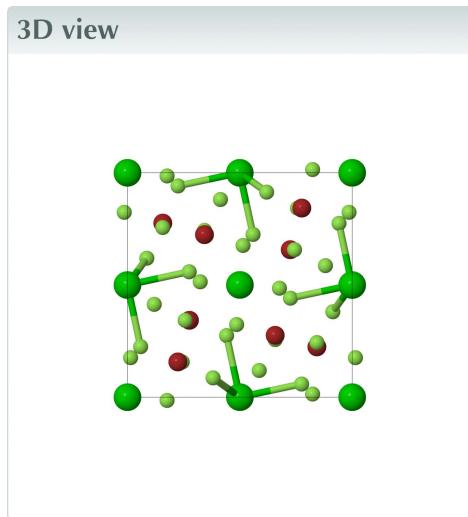
Structure description

The first synthesis of $Ba[BrF_4]_2$ was performed by Sharpe & Eméleus (1948) by treating anhydrous barium chloride or barium fluoride with bromine trifluoride. The product was, however, only characterized by means of a quantitative elemental analysis. The thermal properties of $Ba[BrF_4]_2$ were later studied by Kiselev and co-workers, who investigated the thermal decomposition of $Ba[BrF_4]_2$ to yield barium fluoride (Kiselev *et al.*, 1987). To the best of our knowledge, our report on the crystal structure of $Ba[BrF_4]_2$ determined from X-ray and neutron powder diffraction data at 300 K was the first structural investigation of the title compound (Ivlev *et al.*, 2014). We showed that $Ba[BrF_4]_2$ crystallizes in the space group $I\bar{4}$ and adopts the $Ba[AuF_4]_2$ structure type. Here we present our results on the re-refinement of the crystal structure of $Ba[BrF_4]_2$ from single-crystal X-ray diffraction data at 100 K.

As expected, the unit-cell parameters of the single-crystal study at 100 K (Table 1) are smaller than those determined during the powder study at 300 K, $a = 9.65081$ (11), $c = 8.03453$ (13) Å, $V = 748.32$ (2) Å^3 (Ivlev *et al.*, 2014). The crystal structure contains two symmetry-independent Ba^{2+} cations on special Wyckoff positions 2*a* (site symmetry $\bar{4}$..) and 2*d* ($\bar{4}$..), respectively. Each Ba site is coordinated by twelve F atoms forming edge-
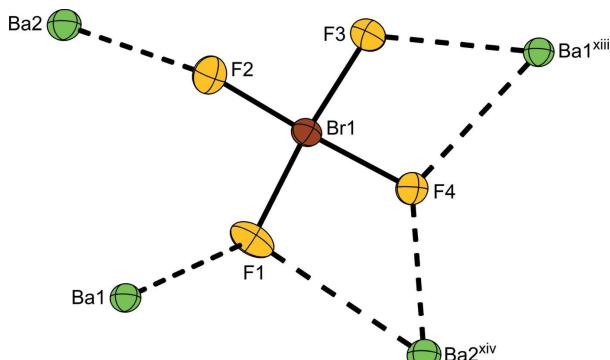
Figure 1
The closest contacts between one $[BrF_4]^-$ anion and surrounding Ba^{2+} cations. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (xiii) $x + \frac{1}{2}$, $y + \frac{1}{2}$, $z + \frac{1}{2}$; (xiv) $x + \frac{1}{2}$, $y - \frac{1}{2}$, $z + \frac{1}{2}$.]

sharing polyhedra. The $Ba\cdots F$ distances lie in the range of 2.680 (14)–3.324 (16) Å [powder data at RT yielded the range of 2.696 (3)–3.376 (3) Å]. The bromine atom occupies the general Wyckoff position $8g$ and is coordinated by four fluorine atoms also located on general positions in an almost square-planar shape. The resulting Br—F bond lengths are 1.829 (13), 1.861 (12), 1.934 (13), and 1.935 (13) Å, which is comparable with our previous model on basis of powder data [*cf.*: 1.800 (4), 1.856 (4), 1.902 (4), 1.935 (2) Å]. The two longer Br—F bond lengths correspond to the F atoms coordinating two barium cations each. The two other fluorine atoms coordinate only to one barium cation each and thus have shorter Br—F bond lengths. The F—Br—F *cis*-angles are 84.9 (6), 89.6 (6), 92.6 (6) and 92.9 (6)°, which corresponds with the previously published results: 85.14 (16), 90.02 (13), 91.80 (15), 93.04 (18)°. Fig. 1 shows the closest contacts between one $[BrF_4]^-$ anion and its surrounding Ba^{2+} cations, and Fig. 2 shows the packing of the cations and anions in the crystal structure.

Synthesis and crystallization

Tiny crystals of barium tetrafluoridobromate(III) were obtained by direct reaction of bromine trifluoride with barium fluoride in a closed Teflon vessel. In contrast to $Rb[BrF_4]$
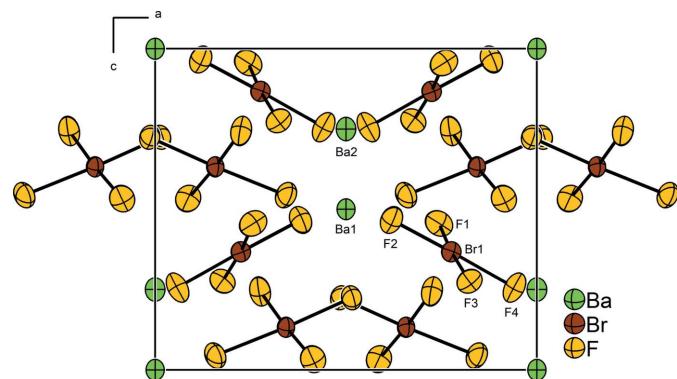

Figure 2
The crystal structure of $Ba[BrF_4]_2$ in a projection along the *b* axis. Displacement ellipsoids are shown at the 50% probability level.

Table 1
Experimental details.

Crystal data	
Chemical formula	$Ba[BrF_4]_2$
M_r	449.16
Crystal system, space group	Tetragonal, $I\bar{4}$
Temperature (K)	100
a, c (Å)	9.5823 (6), 8.0380 (11)
V (Å³)	738.05 (14)
Z	4
Radiation type	Cu $K\alpha$
μ (mm⁻¹)	55.60
Crystal size (mm)	$0.02 \times 0.02 \times 0.01$
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan [*X-AREA* (Stoe, 2020) based on Koziskova *et al.*, (2016)]
T_{min}, T_{max}	0.068, 0.362
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2012, 746, 688
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.637
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.127, 1.08
No. of reflections	746
No. of parameters	50
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	1.84, −1.05
Absolute structure	Flack x determined using 266 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.012 (17)

Computer programs: *X-AREA* (Stoe, 2020), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2020) and *publCIF* (Westrip, 2010).

(Malin *et al.*, 2019) and $Cs[BrF_4]$ (Malin *et al.*, 2020), it was not possible to improve the crystal quality by melting and recrystallization since $Ba[BrF_4]_2$ decomposes before reaching its melting point.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Because of very small size of the crystals, we had to employ a diffractometer with a Cu source to improve the reflection intensities at the cost of a more complicated absorption correction.

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full crystallographic data

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Barium bis[tetrafluoridobromate(III)]

Crystal data

$Ba^{2+}\cdot 2BrF_4^-$	$D_x = 4.042$ Mg m^{-3}
$M_r = 449.16$	Cu $K\alpha$ radiation, $\lambda = 1.54186$ Å
Tetragonal, $I\bar{4}$	Cell parameters from 2706 reflections
$a = 9.5823$ (6) Å	$\theta = 6.5–79.3°$
$c = 8.0380$ (11) Å	$\mu = 55.60$ mm^{-1}
$V = 738.05$ (14) Å^3	$T = 100$ K
$Z = 4$	Block, colorless
$F(000) = 792$	$0.02 \times 0.02 \times 0.01$ mm

Data collection

Stoe Stadivari diffractometer	$T_{min} = 0.068$, $T_{max} = 0.362$
Radiation source: GeniX 3D HF Cu	2012 measured reflections
Graded multilayer mirror monochromator	746 independent reflections
Detector resolution: 5.81 pixels mm^{-1}	688 reflections with $I > 2\sigma(I)$
rotation method, ω scans	$R_{int} = 0.038$
Absorption correction: multi-scan	$\theta_{max} = 79.1°$, $\theta_{min} = 6.5°$
[X-AREA (Stoe, 2020) based on Koziskova *et al.*, (2016)]	$h = -11 \rightarrow 12$
	$k = -10 \rightarrow 6$
	$l = -10 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 5.3796P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.127$	$\Delta\rho_{max} = 1.84$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -1.05$ e Å^{-3}
746 reflections	Absolute structure: Flack x determined using
50 parameters	266 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et*
0 restraints	*al.*, 2013)
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: -0.012 (17)

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}
Ba1	0.500000	0.500000	0.500000	0.0243 (6)
Br1	0.77576 (19)	0.84257 (18)	0.6325 (2)	0.0238 (5)
F1	0.7435 (16)	0.6574 (14)	0.5444 (17)	0.041 (3)
Ba2	0.500000	1.000000	0.250000	0.0293 (6)
F2	0.6192 (14)	0.9136 (15)	0.5334 (19)	0.041 (3)
F3	0.8236 (13)	1.0143 (13)	0.7242 (17)	0.036 (3)
F4	0.9413 (13)	0.7748 (13)	0.744 (2)	0.040 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0219 (7)	0.0219 (7)	0.0291 (12)	0.000	0.000	0.000
Br1	0.0251 (10)	0.0197 (9)	0.0267 (9)	−0.0021 (7)	−0.0004 (8)	0.0000 (7)
F1	0.050 (8)	0.030 (7)	0.043 (7)	−0.013 (6)	0.008 (6)	−0.008 (5)
Ba2	0.0257 (8)	0.0257 (8)	0.0364 (13)	0.000	0.000	0.000
F2	0.033 (7)	0.042 (7)	0.048 (8)	0.004 (6)	−0.009 (6)	−0.004 (6)
F3	0.042 (7)	0.027 (6)	0.038 (8)	−0.001 (5)	−0.006 (6)	−0.003 (5)
F4	0.034 (7)	0.029 (6)	0.057 (8)	0.003 (6)	−0.017 (7)	−0.006 (6)

Geometric parameters (Å, º)

Ba1—F3[i]	2.791 (13)	Br1—F2	1.829 (13)
Ba1—F3[ii]	2.791 (13)	Br1—F3	1.861 (12)
Ba1—F3[iii]	2.791 (13)	Br1—F4	1.934 (13)
Ba1—F3[iv]	2.791 (13)	Br1—F1	1.935 (13)
Ba1—F1[v]	2.801 (14)	Ba2—F2[viii]	2.680 (14)
Ba1—F1[vi]	2.801 (14)	Ba2—F2[ix]	2.680 (14)
Ba1—F1[vii]	2.801 (14)	Ba2—F2[x]	2.680 (14)
Ba1—F1	2.801 (14)	Ba2—F2	2.680 (14)
Ba1—F4[ii]	3.034 (14)	Ba2—F4[xi]	2.693 (12)
Ba1—F4[iv]	3.034 (14)	Ba2—F4[vii]	2.693 (12)
Ba1—F4[iii]	3.034 (14)	Ba2—F4[iii]	2.693 (12)
Ba1—F4[i]	3.034 (14)	Ba2—F4[xii]	2.693 (12)
F3[i]—Ba1—F3[ii]	129.1 (3)	F4[ii]—Ba1—F4[iii]	94.6 (6)
F3[i]—Ba1—F3[iii]	129.1 (3)	F4[iv]—Ba1—F4[iii]	117.4 (3)
F3[ii]—Ba1—F3[iii]	74.9 (6)	F3[i]—Ba1—F4[i]	52.0 (4)
F3[i]—Ba1—F3[iv]	74.9 (6)	F3[ii]—Ba1—F4[i]	95.7 (4)
F3[ii]—Ba1—F3[iv]	129.1 (3)	F3[iii]—Ba1—F4[i]	168.1 (4)
F3[iii]—Ba1—F3[iv]	129.1 (3)	F3[iv]—Ba1—F4[i]	62.5 (4)
F3[i]—Ba1—F1[v]	105.4 (4)	F1[v]—Ba1—F4[i]	54.6 (4)
F3[ii]—Ba1—F1[v]	67.9 (4)	F1[vi]—Ba1—F4[i]	128.6 (4)
F3[iii]—Ba1—F1[v]	125.4 (4)	F1[vii]—Ba1—F4[i]	63.2 (4)
F3[iv]—Ba1—F1[v]	62.1 (4)	F1—Ba1—F4[i]	114.0 (4)
F3[i]—Ba1—F1[vi]	125.4 (4)	F4[ii]—Ba1—F4[i]	117.4 (3)

F3ⁱⁱ—Ba1—F1^{vi}	105.4 (4)	F4^{iv}—Ba1—F4ⁱ	94.6 (6)
F3ⁱⁱⁱ—Ba1—F1^{vi}	62.1 (4)	F4ⁱⁱⁱ—Ba1—F4ⁱ	117.4 (3)
F3^{iv}—Ba1—F1^{vi}	67.9 (4)	F2—Br1—F3	92.6 (6)
F1^v—Ba1—F1^{vi}	90.93 (7)	F2—Br1—F4	177.3 (6)
F3ⁱ—Ba1—F1^{vii}	67.9 (4)	F3—Br1—F4	84.9 (6)
F3ⁱⁱ—Ba1—F1^{vii}	62.1 (4)	F2—Br1—F1	92.9 (6)
F3ⁱⁱⁱ—Ba1—F1^{vii}	105.4 (4)	F3—Br1—F1	174.4 (6)
F3^{iv}—Ba1—F1^{vii}	125.4 (4)	F4—Br1—F1	89.6 (6)
F1^v—Ba1—F1^{vii}	90.93 (7)	Br1—F1—Ba1	132.3 (7)
F1^{vi}—Ba1—F1^{vii}	165.4 (5)	F2^{viii}—Ba2—F2^{ix}	136.3 (4)
F3ⁱ—Ba1—F1	62.1 (4)	F2^{viii}—Ba2—F2^x	63.5 (6)
F3ⁱⁱ—Ba1—F1	125.4 (4)	F2^{ix}—Ba2—F2^x	136.3 (4)
F3ⁱⁱⁱ—Ba1—F1	67.9 (4)	F2^{viii}—Ba2—F2	136.3 (4)
F3^{iv}—Ba1—F1	105.4 (4)	F2^{ix}—Ba2—F2	63.5 (6)
F1^v—Ba1—F1	165.4 (5)	F2^x—Ba2—F2	136.3 (4)
F1^{vi}—Ba1—F1	90.93 (7)	F2^{viii}—Ba2—F4^{xi}	114.0 (5)
F1^{vii}—Ba1—F1	90.93 (7)	F2^{ix}—Ba2—F4^{xi}	109.7 (5)
F3ⁱ—Ba1—F4ⁱⁱ	168.1 (4)	F2^x—Ba2—F4^{xi}	67.9 (5)
F3ⁱⁱ—Ba1—F4ⁱⁱ	52.0 (4)	F2—Ba2—F4^{xi}	68.4 (5)
F3ⁱⁱⁱ—Ba1—F4ⁱⁱ	62.5 (4)	F2^{viii}—Ba2—F4^{vii}	67.9 (5)
F3^{iv}—Ba1—F4ⁱⁱ	95.7 (4)	F2^{ix}—Ba2—F4^{vii}	68.4 (5)
F1^v—Ba1—F4ⁱⁱ	63.2 (4)	F2^x—Ba2—F4^{vii}	114.0 (5)
F1^{vi}—Ba1—F4ⁱⁱ	54.6 (4)	F2—Ba2—F4^{vii}	109.7 (5)
F1^{vii}—Ba1—F4ⁱⁱ	114.0 (4)	F4^{xi}—Ba2—F4^{vii}	178.0 (7)
F1—Ba1—F4ⁱⁱ	128.6 (4)	F2^{viii}—Ba2—F4ⁱⁱⁱ	68.4 (5)
F3ⁱ—Ba1—F4^{iv}	62.5 (4)	F2^{ix}—Ba2—F4ⁱⁱⁱ	114.0 (5)
F3ⁱⁱ—Ba1—F4^{iv}	168.1 (4)	F2^x—Ba2—F4ⁱⁱⁱ	109.7 (5)
F3ⁱⁱⁱ—Ba1—F4^{iv}	95.7 (4)	F2—Ba2—F4ⁱⁱⁱ	67.9 (5)
F3^{iv}—Ba1—F4^{iv}	52.0 (4)	F4^{xi}—Ba2—F4ⁱⁱⁱ	90.018 (16)
F1^v—Ba1—F4^{iv}	114.0 (4)	F4^{vii}—Ba2—F4ⁱⁱⁱ	90.018 (15)
F1^{vi}—Ba1—F4^{iv}	63.2 (4)	F2^{viii}—Ba2—F4^{xii}	109.7 (5)
F1^{vii}—Ba1—F4^{iv}	128.6 (4)	F2^{ix}—Ba2—F4^{xii}	67.9 (5)
F1—Ba1—F4^{iv}	54.6 (4)	F2^x—Ba2—F4^{xii}	68.4 (5)
F4ⁱⁱ—Ba1—F4^{iv}	117.4 (3)	F2—Ba2—F4^{xii}	114.0 (5)
F3ⁱ—Ba1—F4ⁱⁱⁱ	95.7 (4)	F4^{xi}—Ba2—F4^{xii}	90.018 (15)
F3ⁱⁱ—Ba1—F4ⁱⁱⁱ	62.5 (4)	F4^{vii}—Ba2—F4^{xii}	90.018 (15)
F3ⁱⁱⁱ—Ba1—F4ⁱⁱⁱ	52.0 (4)	F4ⁱⁱⁱ—Ba2—F4^{xii}	178.0 (7)
F3^{iv}—Ba1—F4ⁱⁱⁱ	168.1 (4)	Br1—F2—Ba2	146.6 (8)
F1^v—Ba1—F4ⁱⁱⁱ	128.6 (4)	Br1—F3—Ba1^{xiii}	114.9 (6)
F1^{vi}—Ba1—F4ⁱⁱⁱ	114.0 (4)	Br1—F4—Ba2^{xiv}	120.5 (6)
F1^{vii}—Ba1—F4ⁱⁱⁱ	54.6 (4)	Br1—F4—Ba1^{xiii}	103.2 (5)
F1—Ba1—F4ⁱⁱⁱ	63.2 (4)	Ba2^{xiv}—F4—Ba1^{xiii}	130.1 (5)
F3—Br1—F2—Ba2	103.8 (13)	F2—Br1—F3—Ba1^{xiii}	158.2 (7)
F1—Br1—F2—Ba2	−75.4 (13)	F4—Br1—F3—Ba1^{xiii}	−20.9 (7)

Symmetry codes: (i) $y-1/2$, $-x+3/2$, $-z+3/2$; (ii) $x-1/2$, $y-1/2$, $z-1/2$; (iii) $-x+3/2$, $-y+3/2$, $z-1/2$; (iv) $-y+3/2$, $x-1/2$, $-z+3/2$; (v) $-x+1$, $-y+1$, z; (vi) y, $-x+1$, $-z+1$; (vii) $-y+1$, x, $-z+1$; (viii) $y-1/2$, $-x+3/2$, $-z+1/2$; (ix) $-x+1$, $-y+2$, z; (x) $-y+3/2$, $x+1/2$, $-z+1/2$; (xi) y, $-x+2$, $-z+1$; (xii) $x-1/2$, $y+1/2$, $z-1/2$; (xiii) $x+1/2$, $y+1/2$, $z+1/2$; (xiv) $x+1/2$, $y-1/2$, $z+1/2$.