

1 Refinement of the crystal structure of barium tetrafluoridobromate(III) from 2 single-crystal X-ray diffraction data

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6 **Abstract**

7 Single-crystals of barium tetrafluoridobromate(III), Ba[BrF₄]₂, were obtained in form of tiny blocks. Crystal structure re-
8 finement of Ba[BrF₄]₂ from single-crystal X-ray diffraction data confirmed the previous model on basis of powder data
9 [Ivlev *et al.* (2014). *Eur. J. Inorg. Chem.*, pp 6261–6267], but with all atoms refined with anisotropic displacement pa-
10 rameters. The crystal structure consists of two symmetry-independent barium cations that are coordinated by twelve
11 fluorine atoms each, forming edge-sharing polyhedra, and an almost square planar [BrF₄][−] anion. The compound crystal-
12 lizes in the Ba[AuF₄]₂ structure type.

13 **Structure description**

14 The first synthesis of Ba[BrF₄]₂ was performed by Sharpe & Emeléus (1948) by treating anhydrous barium chloride or
15 barium fluoride with bromine trifluoride. The product was, however, only characterized by means of a quantitative el-
16 emental analysis. Thermal properties of Ba[BrF₄]₂ were later studied ~~later~~ by Kiselev and co-workers, who investigated
17 the thermal decomposition of Ba[BrF₄]₂ to yield barium fluoride (Kiselev *et al.*, 1987). To the best of our knowledge, our
18 report on the crystal structure of Ba[BrF₄]₂ determined from X-ray and neutron powder diffraction data at 300 K was the
19 first structural investigation of the title compound (Ivlev *et al.*, 2014). We showed that Ba[BrF₄]₂ crystallizes in the space
20 group $\bar{I}4$ and adopts the Ba[AuF₄]₂ structure type. Here we present our results on the re-refinement of the crystal structure
21 of Ba[BrF₄]₂ from single-crystal X-ray diffraction data at 100 K.

22 As expected, the ~~unit cell~~ parameters of the single-crystal study at 100 K (Table 1) are smaller than those determined
23 during the powder study at 300 K, $a = 9.65081$ (11), $c = 8.03453$ (13) Å, $V = 748.32$ (2) Å³ (Ivlev *et al.*, 2014). The crys-
24 tal structure contains two symmetry-independent Ba²⁺ cations on special Wyckoff position $2a$ (site symmetry $\bar{4}$..) and $2d$
25 ($\bar{4}$..), respectively. Each Ba site is coordinated by twelve F atoms forming edge-sharing polyhedra. The Ba···F distances
26 lie in the range of 2.680 (14)···~~3.034 (14)~~ Å (powder data at RT yielded the range of 2.696 (3)···~~2.81832 (5)~~ Å). The
27 bromine atom occupies the general Wyckoff position 8g and is coordinated by four fluorine atoms also located on general
28 positions in an almost square-planar shape. The resulting Br—F bond lengths are 1.829 (13), 1.861 (12), 1.934 (13), and
29 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),
30 1.935 (2) Å). The two longer Br—F bond lengths correspond to the F atoms coordinating two barium cations each. The
31 two other fluorine atoms coordinate only to one barium cation each and thus have shorter Br—F bond lengths. The F—
32 Br—F *cis*-angles equal 84.9 (6), 89.6 (6), 92.6 (6), and 92.9 (6)°, which corresponds to the previously published results:
33 85.14 (16), 90.02 (13), 91.80 (15), 93.04 (18)°. Fig. 1 shows the closest contacts between one [BrF₄][−] anion and its sur-
34 rounding Ba²⁺ cations, and Fig. 2 shows the packing of the cations and anions in the crystal structure.

35 **Synthesis and crystallization**

36 Tiny crystals of barium tetrafluoridobromate(III) were obtained by direct reaction of bromine trifluoride with barium
37 fluoride in a closed Teflon vessel. In contrast to Rb[BrF₄] (Malin *et al.*, 2019) and Cs[BrF₄] (Malin *et al.*, 2020), it was
38 not possible to improve the crystal quality by melting and recrystallization since Ba[BrF₄]₂ decomposes before reaching

39 its melting point.

40 Refinement details

41 Details of data collection and structure refinement are given in Table 1. Due to very small size of the crystals, we had to
42 employ a diffractometer with a Cu source to improve the reflection intensities at the cost of a more complicated
43 absorption correction.

44 Table 1

45 Experimental details

46	Crystal data	
47	Chemical formula	Ba ²⁺ ·(BrF ₄ ⁻) ₂
48	<i>M</i> _r	449.16
49	Crystal system, space group	Tetragonal, $\bar{I}4$
50	Temperature (K)	100
51	<i>a</i> , <i>c</i> (Å)	9.5823 (6), 8.0380 (11)
52	<i>V</i> (Å ³)	738.05 (14)
53	<i>Z</i>	4
54	Radiation type	Cu <i>K</i> α
55	μ (mm ⁻¹)	55.60
56	Crystal size (mm)	0.02 × 0.02 × 0.01
57		
58	Data collection	
59	Diffractometer	Stoe Stadivari
60	Absorption correction	Multi-scan (<i>X-AREA</i> (Stoe, 2020) based on Koziskova <i>et al.</i> , (2016))
61	<i>T</i> _{min} , <i>T</i> _{max}	0.068, 0.362
62	No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	2012, 746, 688
63	<i>R</i> _{int}	0.038
64	(sin θ/λ) _{max} (Å ⁻¹)	0.637
65		
66	Refinement	
67	<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.127, 1.08
68	No. of reflections	746
69	No. of parameters	50
70	Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.84, -1.05
71	Absolute structure	Flack <i>x</i> determined using 266 quotients [(<i>I</i> ⁺)-(<i>I</i> ⁻)]/[(<i>I</i> ⁺)+(<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013).
72	Absolute structure parameter	-0.012 (17)

73 Computer programs: *X-AREA* (Stoe, 2020), *X-AREA* (Stoe, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg,
74 2020), *publCIF* (Westrip, 2015).

75 Acknowledgements

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77 Funding information

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93 **Figure 1**

94 ~~Caption 1 (including probability level and symmetry codes)~~ ~~Caption 2~~

1 full crystallographic data

2 Refinement of the crystal structure of barium tetrafluoridobromate(III) from
3 single-crystal X-ray diffraction data

4 (I)

5 *Crystal data*

6	Ba ²⁺ ·(BrF ₄ ⁻) ₂	$D_x = 4.042 \text{ Mg m}^{-3}$
7	$M_r = 449.16$	Cu $K\alpha$ radiation, $\lambda = 1.54186 \text{ \AA}$
8	Tetragonal, $I\bar{4}$	Cell parameters from 2706 reflections
9	$a = 9.5823 (6) \text{ \AA}$	$\theta = 6.5\text{--}79.3^\circ$
10	$c = 8.0380 (11) \text{ \AA}$	$\mu = 55.60 \text{ mm}^{-1}$
11	$V = 738.05 (14) \text{ \AA}^3$	$T = 100 \text{ K}$
12	$Z = 4$	Block, colorless
13	$F(000) = 792$	$0.02 \times 0.02 \times 0.01 \text{ mm}$

14 *Data collection*

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

21 *Refinement*

22	Refinement on F^2	Primary atom site location: structure-invariant direct
23	Least-squares matrix: full	methods
24	$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 5.3796P]$
25	$wR(F^2) = 0.127$	where $P = (F_o^2 + 2F_c^2)/3$
26	$S = 1.08$	$(\Delta/\sigma)_{\max} < 0.001$
27	746 reflections	$\Delta\rho_{\max} = 1.84 \text{ e \AA}^{-3}$
28	50 parameters	$\Delta\rho_{\min} = -1.05 \text{ e \AA}^{-3}$
29	0 restraints	Absolute structure: Flack x determined using 266 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons <i>et al.</i> , 2013). Absolute structure parameter: $-0.012 (17)$

30 *Special details*

31 *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.

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

33		x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
34	Ba1	0.500000	0.500000	0.500000	0.0243 (6)
35	Br1	0.77576 (19)	0.84257 (18)	0.6325 (2)	0.0238 (5)
36	F1	0.7435 (16)	0.6574 (14)	0.5444 (17)	0.041 (3)

37	Ba2	0.500000	1.000000	0.250000	0.0293 (6)
38	F2	0.6192 (14)	0.9136 (15)	0.5334 (19)	0.041 (3)
39	F3	0.8236 (13)	1.0143 (13)	0.7242 (17)	0.036 (3)
40	F4	0.9413 (13)	0.7748 (13)	0.744 (2)	0.040 (3)

41 *Atomic displacement parameters (\AA^2)*

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

50 *Geometric parameters (\AA , $^\circ$)*

51	Ba1—F3 ⁱ	2.791 (13)	Br1—F2	1.829 (13)
52	Ba1—F3 ⁱⁱ	2.791 (13)	Br1—F3	1.861 (12)
53	Ba1—F3 ⁱⁱⁱ	2.791 (13)	Br1—F4	1.934 (13)
54	Ba1—F3 ^{iv}	2.791 (13)	Br1—F1	1.935 (13)
55	Ba1—F1 ^v	2.801 (14)	Ba2—F2 ^{viii}	2.680 (14)
56	Ba1—F1 ^{vi}	2.801 (14)	Ba2—F2 ^{ix}	2.680 (14)
57	Ba1—F1 ^{vii}	2.801 (14)	Ba2—F2 ^x	2.680 (14)
58	Ba1—F1	2.801 (14)	Ba2—F2	2.680 (14)
59	Ba1—F4 ⁱⁱ	3.034 (14)	Ba2—F4 ^{xi}	2.693 (12)
60	Ba1—F4 ^{iv}	3.034 (14)	Ba2—F4 ^{vii}	2.693 (12)
61	Ba1—F4 ⁱⁱⁱ	3.034 (14)	Ba2—F4 ⁱⁱⁱ	2.693 (12)
62	Ba1—F4 ⁱ	3.034 (14)	Ba2—F4 ^{xii}	2.693 (12)
63				
64	F3 ⁱ —Ba1—F3 ⁱⁱ	129.1 (3)	F4 ⁱⁱ —Ba1—F4 ⁱⁱⁱ	94.6 (6)
65	F3 ⁱ —Ba1—F3 ⁱⁱⁱ	129.1 (3)	F4 ^{iv} —Ba1—F4 ⁱⁱⁱ	117.4 (3)
66	F3 ⁱⁱ —Ba1—F3 ⁱⁱⁱ	74.9 (6)	F3 ⁱ —Ba1—F4 ⁱ	52.0 (4)
67	F3 ⁱ —Ba1—F3 ^{iv}	74.9 (6)	F3 ⁱⁱ —Ba1—F4 ⁱ	95.7 (4)
68	F3 ⁱⁱ —Ba1—F3 ^{iv}	129.1 (3)	F3 ⁱⁱⁱ —Ba1—F4 ⁱ	168.1 (4)
69	F3 ⁱⁱⁱ —Ba1—F3 ^{iv}	129.1 (3)	F3 ^{iv} —Ba1—F4 ⁱ	62.5 (4)
70	F3 ⁱ —Ba1—F1 ^v	105.4 (4)	F1 ^v —Ba1—F4 ⁱ	54.6 (4)
71	F3 ⁱⁱ —Ba1—F1 ^v	67.9 (4)	F1 ^{vi} —Ba1—F4 ⁱ	128.6 (4)
72	F3 ⁱⁱⁱ —Ba1—F1 ^v	125.4 (4)	F1 ^{vii} —Ba1—F4 ⁱ	63.2 (4)
73	F3 ^{iv} —Ba1—F1 ^v	62.1 (4)	F1—Ba1—F4 ⁱ	114.0 (4)
74	F3 ⁱ —Ba1—F1 ^{vi}	125.4 (4)	F4 ⁱⁱ —Ba1—F4 ⁱ	117.4 (3)
75	F3 ⁱⁱ —Ba1—F1 ^{vi}	105.4 (4)	F4 ^{iv} —Ba1—F4 ⁱ	94.6 (6)
76	F3 ⁱⁱⁱ —Ba1—F1 ^{vi}	62.1 (4)	F4 ⁱⁱⁱ —Ba1—F4 ⁱ	117.4 (3)
77	F3 ^{iv} —Ba1—F1 ^{vi}	67.9 (4)	F2—Br1—F3	92.6 (6)
78	F1 ^v —Ba1—F1 ^{vi}	90.93 (7)	F2—Br1—F4	177.3 (6)
79	F3 ⁱ —Ba1—F1 ^{vii}	67.9 (4)	F3—Br1—F4	84.9 (6)
80	F3 ⁱⁱ —Ba1—F1 ^{vii}	62.1 (4)	F2—Br1—F1	92.9 (6)
81	F3 ⁱⁱⁱ —Ba1—F1 ^{vii}	105.4 (4)	F3—Br1—F1	174.4 (6)
82	F3 ^{iv} —Ba1—F1 ^{vii}	125.4 (4)	F4—Br1—F1	89.6 (6)
83	F1 ^v —Ba1—F1 ^{vii}	90.93 (7)	Br1—F1—Ba1	132.3 (7)
84	F1 ^{vi} —Ba1—F1 ^{vii}	165.4 (5)	F2 ^{viii} —Ba2—F2 ^{ix}	136.3 (4)

85	F3 ⁱ —Ba1—F1	62.1 (4)	F2 ^{viii} —Ba2—F2 ^x	63.5 (6)
86	F3 ⁱⁱ —Ba1—F1	125.4 (4)	F2 ^{ix} —Ba2—F2 ^x	136.3 (4)
87	F3 ⁱⁱⁱ —Ba1—F1	67.9 (4)	F2 ^{viii} —Ba2—F2	136.3 (4)
88	F3 ^{iv} —Ba1—F1	105.4 (4)	F2 ^{ix} —Ba2—F2	63.5 (6)
89	F1 ^v —Ba1—F1	165.4 (5)	F2 ^x —Ba2—F2	136.3 (4)
90	F1 ^{vi} —Ba1—F1	90.93 (7)	F2 ^{viii} —Ba2—F4 ^{xi}	114.0 (5)
91	F1 ^{vii} —Ba1—F1	90.93 (7)	F2 ^{ix} —Ba2—F4 ^{xi}	109.7 (5)
92	F3 ⁱ —Ba1—F4 ⁱⁱ	168.1 (4)	F2 ^x —Ba2—F4 ^{xi}	67.9 (5)
93	F3 ⁱⁱ —Ba1—F4 ⁱⁱ	52.0 (4)	F2—Ba2—F4 ^{xi}	68.4 (5)
94	F3 ⁱⁱⁱ —Ba1—F4 ⁱⁱ	62.5 (4)	F2 ^{viii} —Ba2—F4 ^{vii}	67.9 (5)
95	F3 ^{iv} —Ba1—F4 ⁱⁱ	95.7 (4)	F2 ^{ix} —Ba2—F4 ^{vii}	68.4 (5)
96	F1 ^v —Ba1—F4 ⁱⁱ	63.2 (4)	F2 ^x —Ba2—F4 ^{vii}	114.0 (5)
97	F1 ^{vi} —Ba1—F4 ⁱⁱ	54.6 (4)	F2—Ba2—F4 ^{vii}	109.7 (5)
98	F1 ^{vii} —Ba1—F4 ⁱⁱ	114.0 (4)	F4 ^{xi} —Ba2—F4 ^{vii}	178.0 (7)
99	F1—Ba1—F4 ⁱⁱ	128.6 (4)	F2 ^{viii} —Ba2—F4 ⁱⁱⁱ	68.4 (5)
100	F3 ⁱ —Ba1—F4 ^{iv}	62.5 (4)	F2 ^{ix} —Ba2—F4 ⁱⁱⁱ	114.0 (5)
101	F3 ⁱⁱ —Ba1—F4 ^{iv}	168.1 (4)	F2 ^x —Ba2—F4 ⁱⁱⁱ	109.7 (5)
102	F3 ⁱⁱⁱ —Ba1—F4 ^{iv}	95.7 (4)	F2—Ba2—F4 ⁱⁱⁱ	67.9 (5)
103	F3 ^{iv} —Ba1—F4 ^{iv}	52.0 (4)	F4 ^{xi} —Ba2—F4 ⁱⁱⁱ	90.018 (16)
104	F1 ^v —Ba1—F4 ^{iv}	114.0 (4)	F4 ^{vii} —Ba2—F4 ⁱⁱⁱ	90.018 (15)
105	F1 ^{vi} —Ba1—F4 ^{iv}	63.2 (4)	F2 ^{viii} —Ba2—F4 ^{xii}	109.7 (5)
106	F1 ^{vii} —Ba1—F4 ^{iv}	128.6 (4)	F2 ^{ix} —Ba2—F4 ^{xii}	67.9 (5)
107	F1—Ba1—F4 ^{iv}	54.6 (4)	F2 ^x —Ba2—F4 ^{xii}	68.4 (5)
108	F4 ⁱⁱ —Ba1—F4 ^{iv}	117.4 (3)	F2—Ba2—F4 ^{xii}	114.0 (5)
109	F3 ⁱ —Ba1—F4 ⁱⁱⁱ	95.7 (4)	F4 ^{xi} —Ba2—F4 ^{xii}	90.018 (15)
110	F3 ⁱⁱ —Ba1—F4 ⁱⁱⁱ	62.5 (4)	F4 ^{vii} —Ba2—F4 ^{xii}	90.018 (15)
111	F3 ⁱⁱⁱ —Ba1—F4 ⁱⁱⁱ	52.0 (4)	F4 ⁱⁱⁱ —Ba2—F4 ^{xii}	178.0 (7)
112	F3 ^{iv} —Ba1—F4 ⁱⁱⁱ	168.1 (4)	Br1—F2—Ba2	146.6 (8)
113	F1 ^v —Ba1—F4 ⁱⁱⁱ	128.6 (4)	Br1—F3—Ba1 ^{xiii}	114.9 (6)
114	F1 ^{vi} —Ba1—F4 ⁱⁱⁱ	114.0 (4)	Br1—F4—Ba2 ^{xiv}	120.5 (6)
115	F1 ^{vii} —Ba1—F4 ⁱⁱⁱ	54.6 (4)	Br1—F4—Ba1 ^{xiii}	103.2 (5)
116	F1—Ba1—F4 ⁱⁱⁱ	63.2 (4)	Ba2 ^{xiv} —F4—Ba1 ^{xiii}	130.1 (5)
117				
118	F3—Br1—F2—Ba2	103.8 (13)	F2—Br1—F3—Ba1 ^{xiii}	158.2 (7)
119	F1—Br1—F2—Ba2	-75.4 (13)	F4—Br1—F3—Ba1 ^{xiii}	-20.9 (7)

120 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) $x-1/2, y+1/2, z-1/2$;
121 (xiii) $x+1/2, y+1/2, z+1/2$; (xiv) $x+1/2, y-1/2, z+1/2$.