Redetermination of the crystal structure of K[BrF$_4$] from single-crystal X-ray diffraction data

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Single crystals of K[BrF$_4$], potassium tetrafluoridobromate(III), were grown from a solution of KHF$_2$ in bromine trifluoride. The current report is the first refinement of the crystal structure of K[BrF$_4$] using single-crystal X-ray diffraction data. In comparison with previous refinements from powder data, the fractional coordinates of the F atom were determined with higher precision, and anisotropic displacement parameters were refined for all atoms. The structure contains square-planar [BrF$_4$]$^-$ anions. The coordination polyhedron of the potassium cation is a square antiprism.

3D view
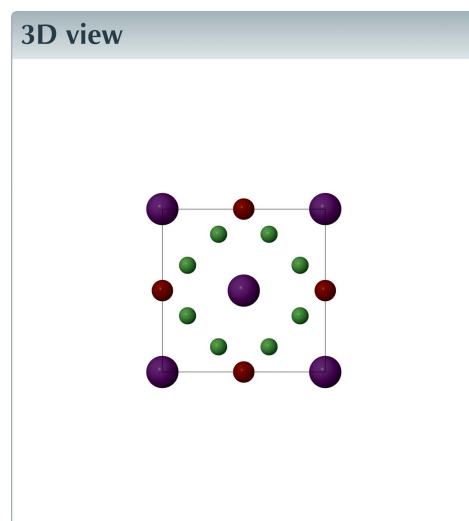
Structure description

The first attempt to elucidate the crystal structure of K[BrF$_4$] was carried out by Siegel using powder X-ray diffraction data (Siegel, 1956). He could index the powder pattern in a tetragonal cell, space group $I4/mcm$, with a = 6.162 (2), c = 11.081 (2) Å, and the [BrF$_4$]$^-$ anion having a tetrahedral configuration. Subsequently, the diffraction data of Siegel were reinterpreted by Sly & Marsh (1957). They kept the unit cell but assigned different positions to the atoms within the same group type, yielding a more reasonable square-planar [BrF$_4$]$^-$ anion. This shape of the anion was later confirmed by Edwards and Jones using powder neutron diffraction data [a = 6.17 (1), c = 11.10 (1) Å; Edwards & Jones, 1969]. Similar cell parameters were reported later by Chrétien and Bouy using powder X-ray diffraction data (a = 6.162, c = 11.081 Å, no s.u. given; Chrétien & Bouy, 1958) and by Popov *et al.* [powder X-ray diffraction data, a = 6.192 (5), c = 11.108 (7) Å; Popov *et al.*, 1987]. Although this was not reported anywhere, we assume that all measurements were performed at room temperature. Here we report our results of the crystal structure determination of K[BrF$_4$] using single-crystal X-ray diffraction data at 100 K.

The lattice parameters obtained from our diffraction data (Table 1) are in good correspondence with previously published values. The K$^+$ cation resides on Wyckoff

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Table 1
Experimental details.

Crystal data	
Chemical formula	K[BrF$_4$]
M_r	195.01
Crystal system, space group	Tetragonal, $I4/mcm$
Temperature (K)	100
a, c (Å)	6.0999 (6), 11.0509 (14)
V (Å^3)	411.19 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	10.95
Crystal size (mm)	0.23 × 0.15 × 0.13
Data collection	
Diffractometer	STOE IPDS 2T
Absorption correction	Numerical (X-$RED32$ and X-$SHAPE$; Stoe & Cie, 2017)
T_{min}, T_{max}	0.157, 0.272
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2822, 214, 198
R_{int}	0.050
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.742
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.015, 0.032, 1.24
No. of reflections	214
No. of parameters	13
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.73

Computer programs: WinXpose in *X-AREA* (Stoe & Cie, 2016), Recipe in *X-AREA* (Stoe & Cie, 2015), Integrate in *X-AREA* (Stoe & Cie, 2018), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2018) and *publCIF* (Westrip, 2010).
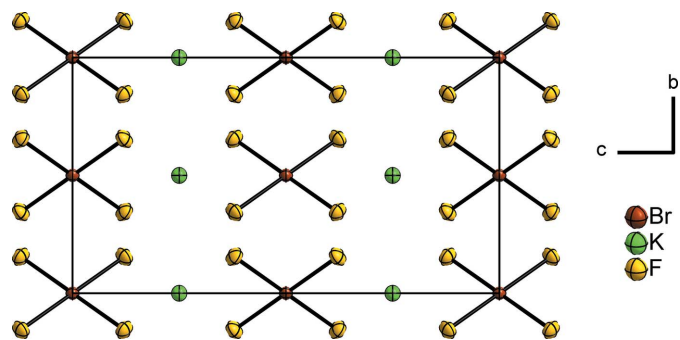

Figure 1
The crystal structure of K[BrF$_4$] in a projection along the *a* axis. Displacement ellipsoids are shown at the 70% probability level.

vessel (perfluorinated ethylene propylene copolymer) at 393 K. After complete dissolution of KHF$_2$, the resulting solution was allowed to cool down to room temperature. Within two hours, large colourless crystals were observed, which were picked directly out of liquid BrF$_3$.

Refinement

Details of data collection and structure refinement are given in Table 1.

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position 4*a* (site symmetry 422). The centre of the [BrF$_4$]$^-$ anion is located on Wyckoff position 4*d* (*m.mm*), with the F atoms occupying Wyckoff position 16*l* (..*m*). The Br—F bond length amounts to 1.8924 (9) Å. This value is typical for the [BrF$_4$]$^-$ anion and is observed in other known tetrafluoridobromates that were investigated earlier by us (Table 2). The F—Br—F angles are 90.02 (3) and 89.98 (5)°, respectively, and are right angles within the 3σ criterion. The nearest K—F distance is 2.7112 (6) Å. The resulting coordination sphere of the potassium cation by fluorine atoms is a square antiprism. The crystal structure of K[BrF$_4$] and its unit cell is shown in Fig. 1.

Synthesis and crystallization

Potassium tetrafluoridobromate(III) was synthesized using potassium hydrogen fluoride KHF$_2$ (0.20 g, 2.6 mmol, 1 eq.) and an excess of liquid bromine trifluoride (1 ml, 2.8 g, 20.4 mmol, 8.0 eq.). The reaction was carried out in an FEP

Table 2
Interatomic distances (Å) in known *M* tetrafluoridobromates(III) (*M* = Na, K, Rb, Cs, Ba).

Compound	Br—F	*M*—F
K[BrF$_4$] (at 100 K; this work)	1.8924 (9)	2.7112 (6)
Na[BrF$_4$] (at 100 K; Ivlev *et al.*, 2016)	1.899 (1)	2.4674 (4)
Rb[BrF$_4$] (at RT; Ivlev *et al.*, 2015)	1.932 (8)	2.851 (7)
Cs[BrF$_4$] (at RT; Ivlev *et al.*, 2013)	1.94 (7) − 1.97 (4)	2.89 (3) − 3.490 (8)
Ba[BrF$_4$]$_2$ (at RT; Ivlev *et al.*, 2014)	1.801 (4)–1.935 (2)	2.696 (3)–3.376 (3)

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full crystallographic data

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Potassium tetrafluoridobromate(III)

Crystal data

$K^+ \cdot BrF_4^-$
$M_r = 195.01$
Tetragonal, $I4/mcm$
$a = 6.0999$ (6) Å
$c = 11.0509$ (14) Å
$V = 411.19$ (10) Å^3
$Z = 4$
$F(000) = 360$
$D_x = 3.150$ Mg m^{-3}

Melting point: 533 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3833 reflections
$\theta = 3.7$–32.1°
$\mu = 10.95$ mm^{-1}
$T = 100$ K
Block, colorless
$0.23 \times 0.15 \times 0.13$ mm

Data collection

STOE IPDS 2T
  diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4
  mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method, ω scans
Absorption correction: numerical
  (X-RED32 and X-SHAPE; Stoe & Cie, 2017)

$T_{min} = 0.157$, $T_{max} = 0.272$
2822 measured reflections
214 independent reflections
198 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 31.8°$, $\theta_{min} = 3.7°$
$h = -9 \rightarrow 9$
$k = -8 \rightarrow 9$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.032$
$S = 1.24$
214 reflections
13 parameters
0 restraints
Primary atom site location: structure-invariant
  direct methods

$w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 0.2331P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}
Extinction correction: SHELXL2016
  (Sheldrick, 2015b),
  $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0087 (11)

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}
Br1	0.500000	0.000000	0.500000	0.00790 (12)
K1	0.500000	0.500000	0.250000	0.01054 (16)
F1	0.65508 (11)	0.15508 (11)	0.37889 (7)	0.0138 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.00811 (14)	0.00811 (14)	0.00749 (15)	0.00046 (10)	0.000	0.000
K1	0.0108 (2)	0.0108 (2)	0.0101 (3)	0.000	0.000	0.000
F1	0.0146 (3)	0.0146 (3)	0.0122 (4)	−0.0008 (4)	0.0030 (2)	0.0030 (2)

Geometric parameters (Å, º)

Br1—F1	1.8923 (9)	K1—F1^{viii}	2.7112 (6)
Br1—F1^{i}	1.8924 (9)	K1—F1^{ix}	2.7112 (6)
Br1—F1^{ii}	1.8924 (9)	K1—F1^{x}	2.7112 (6)
Br1—F1^{iii}	1.8924 (9)	K1—F1	2.7112 (6)
K1—F1^{iv}	2.7112 (6)	K1—K1^{xi}	4.3133 (6)
K1—F1^{v}	2.7112 (6)	K1—K1^{xii}	4.3133 (6)
K1—F1^{vi}	2.7112 (6)	K1—K1^{xiii}	4.3133 (6)
K1—F1^{vii}	2.7112 (6)	K1—K1^{x}	4.3133 (6)
F1—Br1—F1^{i}	90.02 (5)	F1^{viii}—K1—K1^{xi}	142.700 (14)
F1—Br1—F1^{ii}	89.98 (5)	F1^{ix}—K1—K1^{xi}	37.300 (14)
F1^{i}—Br1—F1^{ii}	180.0	F1^{x}—K1—K1^{xi}	72.421 (19)
F1—Br1—F1^{iii}	180.0	F1—K1—K1^{xi}	107.579 (19)
F1^{i}—Br1—F1^{iii}	89.98 (5)	F1^{iv}—K1—K1^{xii}	37.300 (14)
F1^{ii}—Br1—F1^{iii}	90.02 (5)	F1^{v}—K1—K1^{xii}	142.700 (14)
F1^{iv}—K1—F1^{v}	144.84 (4)	F1^{vi}—K1—K1^{xii}	107.579 (19)
F1^{iv}—K1—F1^{vi}	139.16 (4)	F1^{vii}—K1—K1^{xii}	72.421 (19)
F1^{v}—K1—F1^{vi}	73.977 (14)	F1^{viii}—K1—K1^{xii}	37.300 (14)
F1^{iv}—K1—F1^{vii}	73.977 (14)	F1^{ix}—K1—K1^{xii}	142.700 (14)
F1^{v}—K1—F1^{vii}	139.16 (3)	F1^{x}—K1—K1^{xii}	107.579 (19)
F1^{vi}—K1—F1^{vii}	74.60 (3)	F1—K1—K1^{xii}	72.421 (19)
F1^{iv}—K1—F1^{viii}	74.60 (3)	K1^{xi}—K1—K1^{xii}	180.0
F1^{v}—K1—F1^{viii}	116.61 (3)	F1^{iv}—K1—K1^{xiii}	107.579 (19)
F1^{vi}—K1—F1^{viii}	73.977 (15)	F1^{v}—K1—K1^{xiii}	107.579 (19)
F1^{vii}—K1—F1^{viii}	78.20 (4)	F1^{vi}—K1—K1^{xiii}	37.300 (14)
F1^{iv}—K1—F1^{ix}	116.61 (3)	F1^{vii}—K1—K1^{xiii}	37.300 (14)
F1^{v}—K1—F1^{ix}	74.60 (3)	F1^{viii}—K1—K1^{xiii}	72.421 (19)
F1^{vi}—K1—F1^{ix}	78.20 (4)	F1^{ix}—K1—K1^{xiii}	72.421 (19)
F1^{vii}—K1—F1^{ix}	73.977 (15)	F1^{x}—K1—K1^{xiii}	142.700 (14)
F1^{viii}—K1—F1^{ix}	144.84 (4)	F1—K1—K1^{xiii}	142.699 (15)
F1^{iv}—K1—F1^{x}	73.977 (14)	K1^{xi}—K1—K1^{xiii}	90.0
F1^{v}—K1—F1^{x}	78.20 (4)	K1^{xii}—K1—K1^{xiii}	90.0

F1^{vi}—K1—F1^x	144.84 (4)	F1^{iv}—K1—K1^x	72.421 (19)
F1^{vii}—K1—F1^x	116.61 (3)	F1^v—K1—K1^x	72.421 (19)
F1^{viii}—K1—F1^x	139.16 (3)	F1^{vi}—K1—K1^x	142.700 (14)
F1^{ix}—K1—F1^x	73.977 (15)	F1^{vii}—K1—K1^x	142.700 (14)
F1^{iv}—K1—F1	78.20 (4)	F1^{viii}—K1—K1^x	107.579 (19)
F1^v—K1—F1	73.978 (14)	F1^{ix}—K1—K1^x	107.579 (19)
F1^{vi}—K1—F1	116.61 (3)	F1^x—K1—K1^x	37.300 (14)
F1^{vii}—K1—F1	144.84 (4)	F1—K1—K1^x	37.301 (14)
F1^{viii}—K1—F1	73.977 (14)	K1^{xi}—K1—K1^x	90.0
F1^{ix}—K1—F1	139.16 (4)	K1^{xii}—K1—K1^x	90.0
F1^x—K1—F1	74.60 (3)	K1^{xiii}—K1—K1^x	180.0
F1^{iv}—K1—K1^{xi}	142.700 (14)	Br1—F1—K1^x	125.809 (18)
F1^v—K1—K1^{xi}	37.300 (14)	Br1—F1—K1	125.809 (18)
F1^{vi}—K1—K1^{xi}	72.421 (19)	K1^x—F1—K1	105.40 (3)
F1^{vii}—K1—K1^{xi}	107.579 (19)		

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