

# Rubidium tetrafluoridobromate(III): redetermination of the crystal structure from single-crystal X-ray diffraction data

Artem V. Malin,<sup>a</sup> Sergei I. Ivlev,<sup>b</sup> Roman V. Ostvald<sup>a</sup> and Florian Kraus<sup>b\*</sup>

<sup>a</sup>National Research Tomsk Polytechnic University, 30 Lenina Avenue, 634050 Tomsk, Russian Federation, and

<sup>b</sup>Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str. 4, 35032 Marburg, Germany. \*Correspondence e-mail: f.kraus@uni-marburg.de

Received 14 November 2019

Accepted 26 November 2019

Edited by M. Weil, Vienna University of Technology, Austria

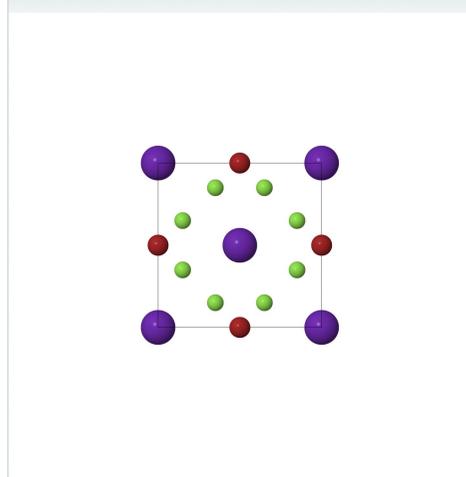
Keywords: crystal structure; rubidium; tetrafluoridobromate; redetermination.

CCDC reference: 1968250

Structural data: full structural data are available from iucrdata.iucr.org

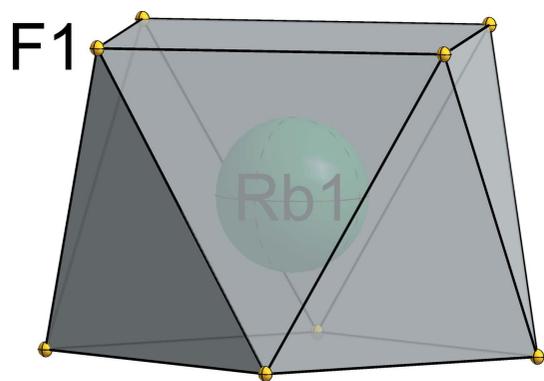
Single crystals of rubidium tetrafluoridobromate(III),  $\text{RbBrF}_4$ , were grown by melting and recrystallizing  $\text{RbBrF}_4$  from its melt. This is the first determination of the crystal structure of  $\text{RbBrF}_4$  using single-crystal X-ray diffraction data. We confirmed that the structure contains square-planar  $[\text{BrF}_4]^-$  anions and rubidium cations that are coordinated by F atoms in a square-antiprismatic manner. The compound crystallizes in the  $\text{KBrF}_4$  structure type. Atomic coordinates and bond lengths and angles were determined with higher precision than in a previous report based on powder X-ray diffraction data [Ivlev *et al.* (2015). *Z. Anorg. Allg. Chem.* **641**, 2593–2598].

## 3D view



## Structure description

The first attempt to determine the lattice parameters of rubidium tetrafluoridobromate(III) from powder X-ray diffraction data was undertaken by Popov *et al.* (1987). They reported the following tetragonal *I*-centered unit cell:  $a = 6.401(3)$ ,  $c = 11.1538(7)$  Å,  $V = 472.7(6)$  Å<sup>3</sup> at room temperature. The authors stated that the structure of  $\text{RbBrF}_4$  is isotypic to that of  $\text{KBrF}_4$  but did not provide further crystallographic details. The next report on the crystal structure of  $\text{RbBrF}_4$  was published by Seppelt and coworkers, stating that the crystal structure is not isotypic to  $\text{KBrF}_4$  (Mahjoub *et al.*, 1989). In a later study we showed that the structure model by Mahjoub *et al.* (1989) was not correct. Indeed, the crystal-structure model obtained from powder X-ray diffraction data [ $I4/mcm$ ,  $a = 6.37181(15)$ ,  $c = 11.4934(3)$  Å,  $V = 466.63(2)$  Å<sup>3</sup> at 293 K; Ivlev *et al.*, 2015] revealed isotypism to  $\text{KBrF}_4$ . On basis of the obtained powder X-ray diffraction data, only the Rb and Br atoms could be refined with anisotropic



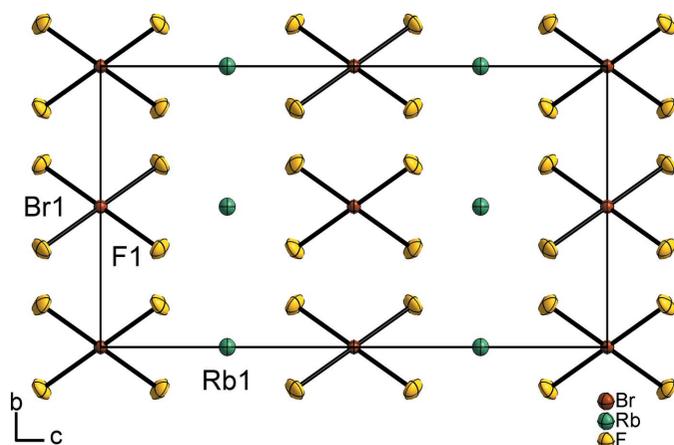
**Figure 1**  
The square-antiprismatic coordination sphere of the Rb<sup>+</sup> cation by F<sup>-</sup> anions. Atoms are shown with arbitrary radii.

displacement parameters. We were now able to grow single crystals of RbBrF<sub>4</sub> and present our results on the basis of single-crystal X-ray diffraction data at 100 K, which allowed for anisotropic refinement of all atoms and confirmed our previous model with higher precision.

The lattice parameters of RbBrF<sub>4</sub> obtained from the current single-crystal X-ray diffraction data (Table 1) are, as expected, slightly smaller than those of the room temperature powder X-ray data given above. In the structure, all atoms are located on special positions: Rb1 occupies Wyckoff position 4a (site symmetry 422), Br1 4d (*m.mm*), and F1 16l (*.m*). The rubidium cation is coordinated in a square-antiprismatic manner by fluorine atoms (Fig. 1), whereas the bromine(III) atom shows a square-planar coordination by fluorine atoms.

The resulting Br–F bond length of 1.8905 (16) Å is comparable with the value of 1.932 (8) Å obtained from powder X-ray diffraction data at 293 K, as well as with the Br–F bond lengths reported for other tetrafluoridobromates(III) (Ivlev *et al.*, 2015). The Rb–F distance amounts to 2.8447 (10) Å, likewise in good agreement with powder X-ray data (2.851 (7) Å).

A section of the crystal structure of RbBrF<sub>4</sub> is shown in Fig. 2.



**Figure 2**  
The crystal structure of the title compound in a projection along the *a* axis. Displacement ellipsoids are shown at the 70% probability level.

**Table 1**  
Experimental details.

Crystal data	RbBrF <sub>4</sub>
Chemical formula	241.38
<i>M<sub>r</sub></i>	Tetragonal, <i>I4/mcm</i>
Crystal system, space group	100
Temperature (K)	6.2991 (5), 11.4659 (10)
<i>a</i> , <i>c</i> (Å)	454.95 (8)
<i>V</i> (Å <sup>3</sup> )	4
<i>Z</i>	Mo <i>K</i> α
Radiation type	19.61
μ (mm <sup>-1</sup> )	0.19 × 0.15 × 0.03
Crystal size (mm)	
Data collection	
Diffractometer	Bruker D8 QUEST area detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.151, 0.480
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	5872, 322, 189
<i>R<sub>int</sub></i>	0.070
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.833
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.020, 0.038, 1.06
No. of reflections	322
No. of parameters	13
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.66, −0.73

Computer programs: *APEX3* (Bruker, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2018) and *publCIF* (Westrip, 2010).

## Synthesis and crystallization

Rubidium tetrafluoridobromate(III) was synthesized by direct reaction of bromine trifluoride with rubidium chloride. The reaction was carried out under Freon-113, which acted as a protective layer against hydrolysis and as a heat absorber. The mixture of RbCl and BrF<sub>3</sub> was kept in a closed Teflon vessel. After three days, the Freon was removed by vacuum distillation and RbBrF<sub>4</sub> was obtained as a solid white residue. The powder was melted at 523 K and subsequently cooled down to room temperature. Single crystals of RbBrF<sub>4</sub> were obtained as small plates after crushing the solid lumps.

## Refinement

Crystal data, data collection and structure refinement details are given in Table 1.

## Acknowledgements

We thank the Russian Governmental Program 'Nauka' N 4.3967.2017/PCh for support. We thank the Deutsche Forschungsgemeinschaft for generous funding.

## References

- Brandenburg, K. (2018). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2018). *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Ivlev, S., Karttunen, A. J., Ostvald, R. & Kraus, F. (2015). *Z. Anorg. Allg. Chem.* **641**, 2593–2598.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

- Mahjoub, A. R., Hoser, A., Fuchs, J. & Seppelt, K. (1989). *Angew. Chem.* **101**, 1528–1529.
- Popov, A. I., Kiselev, Y. M., Sukhoverkhov, V. F., Chumaevskii, N. A., Krasnyanskaya, O. A. & Sadikova, A. T. (1987). *Russ. J. Inorg. Chem.* **32**, 619–622.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## full crystallographic data

*IUCrData* (2019). 4, x191595 [https://doi.org/10.1107/S2414314619015955]

## Rubidium tetrafluoridobromate(III): redetermination of the crystal structure from single-crystal X-ray diffraction data

Artem V. Malin, Sergei I. Ivlev, Roman V. Ostvald and Florian Kraus

### Rubidium tetrafluoridobromate(III)

#### Crystal data

RbBrF<sub>4</sub>

$M_r = 241.38$

Tetragonal, *I4/mcm*

$a = 6.2991$  (5) Å

$c = 11.4659$  (10) Å

$V = 454.95$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 432$

$D_x = 3.524$  Mg m<sup>-3</sup>

$D_m = 3.33$  Mg m<sup>-3</sup>

$D_m$  measured by helium pycnometry

Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 285 reflections

$\theta = 4.5\text{--}31.3^\circ$

$\mu = 19.61$  mm<sup>-1</sup>

$T = 100$  K

Plate, colorless

0.19 × 0.14 × 0.03 mm

#### Data collection

Bruker D8 QUEST area detector  
diffractometer

Radiation source: microfocus sealed X-ray tube,  
Incoatec Iμs

Detector resolution: 7.9 pixels mm<sup>-1</sup>

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.151$ ,  $T_{\max} = 0.480$

5872 measured reflections

322 independent reflections

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

$R_{\text{int}} = 0.070$

$\theta_{\max} = 36.3^\circ$ ,  $\theta_{\min} = 3.6^\circ$

$h = -9 \rightarrow 10$

$k = -9 \rightarrow 10$

$l = -19 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.038$

$S = 1.06$

322 reflections

13 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

$w = 1/[\sigma^2(F_o^2) + (0.004P)^2 + 1.2951P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.66$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.73$  e Å<sup>-3</sup>

Extinction correction: SHELXL (Sheldrick,  
2015b),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0016 (3)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.500000	0.000000	0.500000	0.00663 (14)
Rb1	0.500000	0.500000	0.750000	0.00956 (15)
F1	0.6501 (2)	0.1501 (2)	0.61660 (13)	0.0138 (3)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.00693 (19)	0.00693 (19)	0.0060 (2)	0.0008 (2)	0.000	0.000
Rb1	0.0099 (2)	0.0099 (2)	0.0088 (2)	0.000	0.000	0.000
F1	0.0147 (5)	0.0147 (5)	0.0120 (7)	-0.0003 (8)	-0.0047 (5)	-0.0047 (5)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Br1—F1	1.8905 (16)	Rb1—F1 <sup>viii</sup>	2.8447 (10)
Br1—F1 <sup>i</sup>	1.8906 (16)	Rb1—F1 <sup>ix</sup>	2.8447 (9)
Br1—F1 <sup>ii</sup>	1.8906 (16)	Rb1—F1 <sup>x</sup>	2.8447 (9)
Br1—F1 <sup>iii</sup>	1.8906 (16)	Rb1—F1	2.8447 (9)
Rb1—F1 <sup>iv</sup>	2.8447 (10)	Rb1—Rb1 <sup>xi</sup>	4.4541 (4)
Rb1—F1 <sup>v</sup>	2.8447 (10)	Rb1—Rb1 <sup>xii</sup>	4.4541 (4)
Rb1—F1 <sup>vi</sup>	2.8447 (10)	Rb1—Rb1 <sup>xiii</sup>	4.4541 (4)
Rb1—F1 <sup>vii</sup>	2.8447 (10)	Rb1—Rb1 <sup>vi</sup>	4.4541 (4)
F1—Br1—F1 <sup>i</sup>	180.0	F1 <sup>viii</sup> —Rb1—Rb1 <sup>xi</sup>	141.53 (2)
F1—Br1—F1 <sup>ii</sup>	90.01 (10)	F1 <sup>ix</sup> —Rb1—Rb1 <sup>xi</sup>	71.76 (3)
F1 <sup>i</sup> —Br1—F1 <sup>ii</sup>	89.99 (10)	F1 <sup>x</sup> —Rb1—Rb1 <sup>xi</sup>	108.24 (3)
F1—Br1—F1 <sup>iii</sup>	89.99 (10)	F1—Rb1—Rb1 <sup>xi</sup>	71.76 (3)
F1 <sup>i</sup> —Br1—F1 <sup>iii</sup>	90.01 (10)	F1 <sup>iv</sup> —Rb1—Rb1 <sup>xii</sup>	38.47 (2)
F1 <sup>ii</sup> —Br1—F1 <sup>iii</sup>	180.0	F1 <sup>v</sup> —Rb1—Rb1 <sup>xii</sup>	141.53 (2)
F1 <sup>iv</sup> —Rb1—F1 <sup>v</sup>	143.52 (7)	F1 <sup>vi</sup> —Rb1—Rb1 <sup>xii</sup>	71.76 (3)
F1 <sup>iv</sup> —Rb1—F1 <sup>vi</sup>	73.20 (3)	F1 <sup>vii</sup> —Rb1—Rb1 <sup>xii</sup>	141.53 (2)
F1 <sup>v</sup> —Rb1—F1 <sup>vi</sup>	141.19 (6)	F1 <sup>viii</sup> —Rb1—Rb1 <sup>xii</sup>	38.47 (2)
F1 <sup>iv</sup> —Rb1—F1 <sup>vii</sup>	114.95 (5)	F1 <sup>ix</sup> —Rb1—Rb1 <sup>xii</sup>	108.24 (3)
F1 <sup>v</sup> —Rb1—F1 <sup>vii</sup>	76.95 (5)	F1 <sup>x</sup> —Rb1—Rb1 <sup>xii</sup>	71.76 (3)
F1 <sup>vi</sup> —Rb1—F1 <sup>vii</sup>	73.20 (3)	F1—Rb1—Rb1 <sup>xii</sup>	108.24 (3)
F1 <sup>iv</sup> —Rb1—F1 <sup>viii</sup>	76.95 (5)	Rb1 <sup>xi</sup> —Rb1—Rb1 <sup>xii</sup>	180.0
F1 <sup>v</sup> —Rb1—F1 <sup>viii</sup>	114.95 (5)	F1 <sup>iv</sup> —Rb1—Rb1 <sup>xiii</sup>	71.76 (3)
F1 <sup>vi</sup> —Rb1—F1 <sup>viii</sup>	78.41 (7)	F1 <sup>v</sup> —Rb1—Rb1 <sup>xiii</sup>	71.76 (3)
F1 <sup>vii</sup> —Rb1—F1 <sup>viii</sup>	143.52 (7)	F1 <sup>vi</sup> —Rb1—Rb1 <sup>xiii</sup>	141.53 (2)
F1 <sup>iv</sup> —Rb1—F1 <sup>ix</sup>	73.20 (3)	F1 <sup>vii</sup> —Rb1—Rb1 <sup>xiii</sup>	108.24 (3)

F1 <sup>v</sup> —Rb1—F1 <sup>ix</sup>	78.41 (7)	F1 <sup>viii</sup> —Rb1—Rb1 <sup>xiii</sup>	108.24 (3)
F1 <sup>vi</sup> —Rb1—F1 <sup>ix</sup>	114.95 (5)	F1 <sup>ix</sup> —Rb1—Rb1 <sup>xiii</sup>	38.47 (2)
F1 <sup>vii</sup> —Rb1—F1 <sup>ix</sup>	73.20 (3)	F1 <sup>x</sup> —Rb1—Rb1 <sup>xiii</sup>	38.47 (2)
F1 <sup>viii</sup> —Rb1—F1 <sup>ix</sup>	141.19 (6)	F1—Rb1—Rb1 <sup>xiii</sup>	141.53 (2)
F1 <sup>iv</sup> —Rb1—F1 <sup>x</sup>	78.41 (7)	Rb1 <sup>xi</sup> —Rb1—Rb1 <sup>xiii</sup>	90.0
F1 <sup>v</sup> —Rb1—F1 <sup>x</sup>	73.20 (3)	Rb1 <sup>xii</sup> —Rb1—Rb1 <sup>xiii</sup>	90.0
F1 <sup>vi</sup> —Rb1—F1 <sup>x</sup>	143.52 (7)	F1 <sup>iv</sup> —Rb1—Rb1 <sup>vi</sup>	108.24 (3)
F1 <sup>vii</sup> —Rb1—F1 <sup>x</sup>	141.19 (6)	F1 <sup>v</sup> —Rb1—Rb1 <sup>vi</sup>	108.24 (3)
F1 <sup>viii</sup> —Rb1—F1 <sup>x</sup>	73.20 (3)	F1 <sup>vi</sup> —Rb1—Rb1 <sup>vi</sup>	38.47 (2)
F1 <sup>ix</sup> —Rb1—F1 <sup>x</sup>	76.95 (5)	F1 <sup>vii</sup> —Rb1—Rb1 <sup>vi</sup>	71.76 (3)
F1 <sup>iv</sup> —Rb1—F1	141.19 (6)	F1 <sup>viii</sup> —Rb1—Rb1 <sup>vi</sup>	71.76 (3)
F1 <sup>v</sup> —Rb1—F1	73.19 (3)	F1 <sup>ix</sup> —Rb1—Rb1 <sup>vi</sup>	141.53 (2)
F1 <sup>vi</sup> —Rb1—F1	76.95 (5)	F1 <sup>x</sup> —Rb1—Rb1 <sup>vi</sup>	141.53 (2)
F1 <sup>vii</sup> —Rb1—F1	78.41 (7)	F1—Rb1—Rb1 <sup>vi</sup>	38.47 (2)
F1 <sup>viii</sup> —Rb1—F1	73.20 (3)	Rb1 <sup>xi</sup> —Rb1—Rb1 <sup>vi</sup>	90.0
F1 <sup>ix</sup> —Rb1—F1	143.52 (7)	Rb1 <sup>xii</sup> —Rb1—Rb1 <sup>vi</sup>	90.0
F1 <sup>x</sup> —Rb1—F1	114.95 (5)	Rb1 <sup>xiii</sup> —Rb1—Rb1 <sup>vi</sup>	180.0
F1 <sup>iv</sup> —Rb1—Rb1 <sup>xi</sup>	141.53 (2)	Br1—F1—Rb1 <sup>vi</sup>	126.98 (3)
F1 <sup>v</sup> —Rb1—Rb1 <sup>xi</sup>	38.47 (2)	Br1—F1—Rb1	126.98 (3)
F1 <sup>vi</sup> —Rb1—Rb1 <sup>xi</sup>	108.24 (3)	Rb1 <sup>vi</sup> —F1—Rb1	103.05 (5)
F1 <sup>vii</sup> —Rb1—Rb1 <sup>xi</sup>	38.47 (2)		

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