Redetermination of the crystal structure of caesium tetrafluoridobromate(III) from single-crystal X-ray diffraction data

Artem V. Malin,[a] Sergei I. Ivlev,[b] Roman V. Ostvald[a] and Florian Kraus[b]*

[a]National Research Tomsk Polytechnic University, 30 Lenina avenue, 634050 Tomsk, Russian Federation, and [b]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany. *Correspondence e-mail: f.kraus@uni-marburg.de

Caesium tetrafluoridobromate(III), $CsBrF_4$, was crystallized in form of small blocks by melting and recrystallization. The crystal structure of $CsBrF_4$ was redetermined from single-crystal X-ray diffraction data. In comparison with a previous study based on powder X-ray diffraction data [Ivlev *et al.* (2013). *Z. Anorg. Allg. Chem.* **639**, 2846–2850], bond lengths and angles were determined with higher precision, and all atoms were refined with anisotropic displacement parameters. It was confirmed that the structure of $CsBrF_4$ contains two square-planar $[BrF_4]^-$ anions each with point group symmetry *mmm*, and a caesium cation (site symmetry *mm*2) that is coordinated by twelve fluorine atoms, forming an anticuboctahedron. $CsBrF_4$ is isotypic with $CsAuF_4$.

3D view
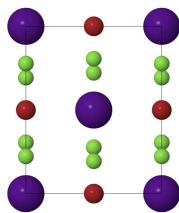
Structure description

The first report of unit-cell parameters of $CsBrF_4$ from powder X-ray diffraction data was given by Popov *et al.* (1987). They indexed the powder pattern using a primitive tetragonal unit cell with lattice parameters of $a = 9.828\ (3)$, $c = 7.166\ (5)$ Å, $V = 692.2\ (3)$ Å^3 (temperature not given). These lattice parameters are quite different compared to those of other known alkali metal tetrafluoridobromates(III) that crystallize in the $KBrF_4$ structure type [$KBrF_4$, *I*4/*mcm* (No. 140), $a = 6.174\ (2)$, $c = 11.103\ (2)$ Å, $V = 423$ Å^3; Siegel, 1956], and consequently $CsBrF_4$ is not isotypic with $KBrF_4$ on basis of the data provided by Popov *et al.* (1987). However, neither the crystal structure nor other crystallographic details of $CsBrF_4$ were given at that time.

Recently, we have determined the crystal structure of $CsBrF_4$ from powder X-ray diffraction (PXRD) data where we could only refine the F atoms isotropically (Ivlev *et al.*,
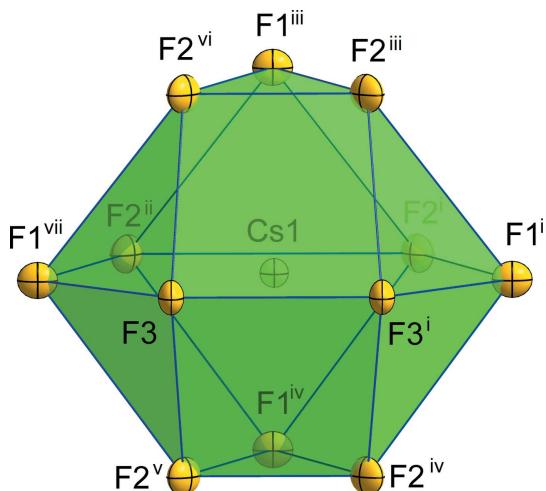
Figure 1
The anticuboctahedron around the caesium cation. Displacement ellipsoids are shown at the 70% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y, -z + 1$; (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $-x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $-x + 1, -y, -z + 1$.]

2013). We have shown that $CsBrF_4$ is isotypic with $CsAuF_4$ (Schmidt & Müller, 2004) and crystallizes in the space group *Immm* (No. 71) with lattice parameters $a = 5.6413$ (8), $b = 6.8312$ (9), $c = 12.2687$ (17) Å, $V = 472.79$ (11) Å^3, $Z = 4$ at 293 K. These lattice parameters are not related to the unit cell reported by Popov *et al.* (1987). We assume that their powder pattern probably contained impurity lines, *e.g.* from possible hydrolysis products, which led to erroneous indexing. Here we present the results of a redetermination of the crystal structure of $CsBrF_4$ from single-crystal X-ray diffraction data at 100 K, leading to bond lengths and angles with higher precision, and with all atoms refined with anisotropic displacement parameters.

The unit-cell parameters of $CsBrF_4$ obtained from single-crystal X-ray diffraction data (Table 1) are expectedly smaller than those from the PXRD data at 293 K. The crystal structure contains two different square-planar $[BrF_4]^-$ anions, the planes of which are parallel and rotated by about 45° with respect to each other. The first anion consists of one bromi-
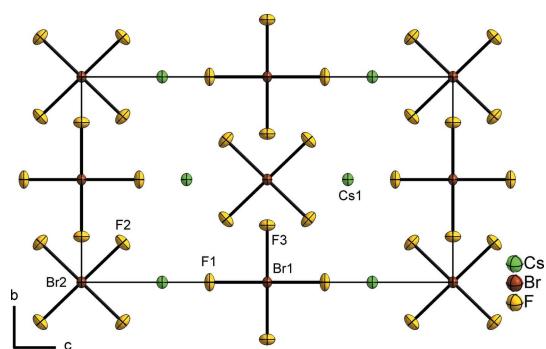
Figure 2
The crystal structure of $CsBrF_4$ in a projection along the *a* axis. Displacement ellipsoids are shown at the 70% probability level.

Table 1
Experimental details.

Crystal data	
Chemical formula	$CsBrF_4$
M_r	288.82
Crystal system, space group	Orthorhombic, *Immm*
Temperature (K)	100
a, b, c (Å)	5.5075 (3), 6.7890 (3), 12.2572 (6)
V (Å^3)	458.30 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	16.75
Crystal size (mm)	$0.11 \times 0.09 \times 0.06$
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.330, 0.558
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8570, 669, 622
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.835
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.012, 0.022, 1.12
No. of reflections	669
No. of parameters	26
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.20, −0.88

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXL* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2019) and *publCIF* (Westrip, 2010); coordinates taken from previous refinement.

ne(III) atom (Br1) on the special 2*d* (*mmm*) Wyckoff position and two fluorine atoms F1 and F3 on the special 4*j* (*mm*2) and 4*g* (*m*2*m*) Wyckoff positions, respectively. As a result of symmetry restrictions, the F—Br—F angle is exactly 90°. The Br1—F bond lengths are 1.8852 (13) and 1.9020 (15) Å [*cf.* 1.94 (4) and 1.97 (4) Å from PXRD data]. The second $[BrF_4]^-$ anion contains one bromine(III) atom (Br2) on the special 2*b* (*mmm*) Wyckoff position and one fluorine atom (F2) on the special 8*l* (*m*..) Wyckoff position. The anion is slightly distorted in-plane, resulting in an almost rectangular structure with F2—Br2—F2 angles of 87.96 (7) and 92.04 (7)° and a Br2—F2 bond length of 1.8907 (10) Å [*cf.* 87.6 (13) and 92.4 (13)°, 1.96 (3) Å from PXRD data]. In general, the bond lengths and angles of the $[BrF_4]^-$ anions in $CsBrF_4$ are in good correspondence with other known tetrafluoridobromates(III) [see Table 2 in Ivlev & Kraus (2018), and references therein]. The caesium cation occupies the special 4*i* (*mm*2) Wyckoff position and is coordinated by twelve fluorine atoms. The resulting coordination polyhedron is an anticuboctahedron (Fig. 1). The Cs···F distances are in the range 2.9615 (11) to 3.4784 (4) Å [*cf.* 3.011 (1) to 3.605 (1) from PXRD data].

The crystal structure of $CsBrF_4$ is shown in Fig. 2.

Synthesis and crystallization

Caesium tetrafluoridobromate(III) was synthesized by direct reaction of bromine trifluoride with caesium 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 CsCl and BrF_3 was kept in a closed Teflon vessel.

After three days the Freon was removed by vacuum distillation and $CsBrF_4$ was obtained as a solid white residue. The powder was melted at 483 K and cooled down to room temperature. Single crystals of $CsBrF_4$ were obtained as small blocks after crushing the solid lumps.

Refinement

Details of data collection and structure refinement are given in Table 1. Coordinates and atom labelling were taken from the previous refinement from PXRD data (Ivlev *et al.*, 2013).

Acknowledgements

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full crystallographic data

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Caesium tetrafluoridobromate(III)

Crystal data

CsBrF$_4$
$M_r = 288.82$
Orthorhombic, *Immm*
$a = 5.5075\ (3)$ Å
$b = 6.7890\ (3)$ Å
$c = 12.2572\ (6)$ Å
$V = 458.30\ (4)$ Å^3
$Z = 4$
$F(000) = 504$

$D_x = 4.186$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2913 reflections
$\theta = 3.3$–$36.8°$
$\mu = 16.75$ mm^{-1}
$T = 100$ K
Block, colorless
$0.11 \times 0.09 \times 0.06$ mm

Data collection

Bruker D8 QUEST
    diffractometer
Radiation source: microfocus X-ray tube
ω and φ scans
Absorption correction: multi-scan
    (*SADABS*; Krause *et al.*, 2015)
$T_{min} = 0.330$, $T_{max} = 0.558$
8570 measured reflections

669 independent reflections
622 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 36.4°$, $\theta_{min} = 3.3°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.012$
$wR(F^2) = 0.022$
$S = 1.12$
669 reflections
26 parameters
0 restraints
Primary atom site location: structure-invariant
    direct methods

$w = 1/[\sigma^2(F_o^2) + (0.0065P)^2 + 0.5686P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.20$ e Å^{-3}
$\Delta\rho_{min} = -0.88$ e Å^{-3}
Extinction correction: SHELXL-2018/3
    (Sheldrick 2015),
    Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.00232 (16)

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}
Cs1	0.500000	0.500000	0.71714 (2)	0.01008 (4)
Br1	0.500000	0.000000	0.500000	0.00720 (6)
Br2	0.500000	0.000000	0.000000	0.00760 (6)
F1	0.500000	0.000000	0.34482 (12)	0.0155 (3)
F2	0.500000	0.19339 (16)	0.11100 (9)	0.0169 (2)
F3	0.500000	0.2777 (2)	0.500000	0.0141 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.01130 (6)	0.01075 (6)	0.00821 (7)	0.000	0.000	0.000
Br1	0.00756 (12)	0.00827 (11)	0.00578 (13)	0.000	0.000	0.000
Br2	0.00816 (12)	0.00841 (11)	0.00624 (13)	0.000	0.000	0.000
F1	0.0179 (7)	0.0216 (7)	0.0069 (6)	0.000	0.000	0.000
F2	0.0201 (5)	0.0160 (4)	0.0146 (5)	0.000	0.000	−0.0073 (4)
F3	0.0164 (6)	0.0087 (6)	0.0172 (7)	0.000	0.000	0.000

Geometric parameters (Å, º)

Cs1—F2[i]	2.9615 (11)	Cs1—F1[vii]	3.4784 (4)
Cs1—F2[ii]	2.9615 (11)	Cs1—F1[i]	3.4784 (4)
Cs1—F3[i]	3.0597 (7)	Br1—F3	1.8852 (13)
Cs1—F3	3.0597 (7)	Br1—F3[vii]	1.8853 (13)
Cs1—F1[iii]	3.1674 (8)	Br1—F1[vii]	1.9020 (15)
Cs1—F1[iv]	3.1674 (8)	Br1—F1	1.9020 (15)
Cs1—F2[v]	3.3166 (7)	Br2—F2[viii]	1.8907 (10)
Cs1—F2[iii]	3.3166 (7)	Br2—F2[ix]	1.8907 (10)
Cs1—F2[iv]	3.3166 (7)	Br2—F2[x]	1.8907 (10)
Cs1—F2[vi]	3.3166 (7)	Br2—F2	1.8907 (10)
F2[i]—Cs1—F2[ii]	89.32 (4)	F1[iv]—Cs1—F1[i]	96.194 (16)
F2[i]—Cs1—F3[i]	105.79 (3)	F2[v]—Cs1—F1[i]	107.50 (2)
F2[ii]—Cs1—F3[i]	164.90 (3)	F2[iii]—Cs1—F1[i]	61.838 (19)
F2[i]—Cs1—F3	164.90 (3)	F2[iv]—Cs1—F1[i]	61.838 (19)
F2[ii]—Cs1—F3	105.79 (3)	F2[vi]—Cs1—F1[i]	107.50 (2)
F3[i]—Cs1—F3	59.11 (4)	F1[vii]—Cs1—F1[i]	154.77 (5)
F2[i]—Cs1—F1[iii]	69.423 (18)	F3—Br1—F3[vii]	180.0
F2[ii]—Cs1—F1[iii]	69.423 (18)	F3—Br1—F1[vii]	90.0
F3[i]—Cs1—F1[iii]	115.46 (2)	F3[vii]—Br1—F1[vii]	90.0
F3—Cs1—F1[iii]	115.46 (2)	F3—Br1—F1	90.0
F2[i]—Cs1—F1[iv]	69.423 (18)	F3[vii]—Br1—F1	90.0
F2[ii]—Cs1—F1[iv]	69.423 (18)	F1[vii]—Br1—F1	180.0
F3[i]—Cs1—F1[iv]	115.46 (2)	F2[viii]—Br2—F2[ix]	87.96 (7)
F3—Cs1—F1[iv]	115.46 (2)	F2[viii]—Br2—F2[x]	92.04 (7)
F1[iii]—Cs1—F1[iv]	120.78 (5)	F2[ix]—Br2—F2[x]	180.00 (6)

F2ⁱ—Cs1—F2ᵛ	123.869 (16)	F2ᵛⁱⁱⁱ—Br2—F2	180.0
F2ⁱⁱ—Cs1—F2ᵛ	90.05 (2)	F2ⁱˣ—Br2—F2	92.04 (7)
F3ⁱ—Cs1—F2ᵛ	81.61 (2)	F2ˣ—Br2—F2	87.96 (7)
F3—Cs1—F2ᵛ	57.553 (17)	F2ᵛⁱⁱⁱ—Br2—Cs1ˣⁱ	120.01 (2)
F1ⁱⁱⁱ—Cs1—F2ᵛ	156.305 (19)	F2ⁱˣ—Br2—Cs1ˣⁱ	120.005 (19)
F1ⁱᵛ—Cs1—F2ᵛ	58.13 (3)	F2ˣ—Br2—Cs1ˣⁱ	59.995 (19)
F2ⁱ—Cs1—F2ⁱⁱⁱ	90.05 (2)	F2—Br2—Cs1ˣⁱ	59.99 (2)
F2ⁱⁱ—Cs1—F2ⁱⁱⁱ	123.868 (16)	F2ᵛⁱⁱⁱ—Br2—Cs1ˣⁱⁱ	59.99 (2)
F3ⁱ—Cs1—F2ⁱⁱⁱ	57.553 (17)	F2ⁱˣ—Br2—Cs1ˣⁱⁱ	59.995 (19)
F3—Cs1—F2ⁱⁱⁱ	81.61 (2)	F2ˣ—Br2—Cs1ˣⁱⁱ	120.005 (19)
F1ⁱⁱⁱ—Cs1—F2ⁱⁱⁱ	58.13 (3)	F2—Br2—Cs1ˣⁱⁱ	120.01 (2)
F1ⁱᵛ—Cs1—F2ⁱⁱⁱ	156.305 (19)	Cs1ˣⁱ—Br2—Cs1ˣⁱⁱ	180.0
F2ᵛ—Cs1—F2ⁱⁱⁱ	133.81 (3)	F2ᵛⁱⁱⁱ—Br2—Cs1ˣⁱⁱⁱ	120.01 (2)
F2ⁱ—Cs1—F2ⁱᵛ	90.05 (2)	F2ⁱˣ—Br2—Cs1ˣⁱⁱⁱ	120.005 (19)
F2ⁱⁱ—Cs1—F2ⁱᵛ	123.868 (17)	F2ˣ—Br2—Cs1ˣⁱⁱⁱ	59.995 (19)
F3ⁱ—Cs1—F2ⁱᵛ	57.553 (17)	F2—Br2—Cs1ˣⁱⁱⁱ	59.99 (2)
F3—Cs1—F2ⁱᵛ	81.61 (2)	Cs1ˣⁱ—Br2—Cs1ˣⁱⁱⁱ	91.951 (5)
F1ⁱⁱⁱ—Cs1—F2ⁱᵛ	156.305 (19)	Cs1ˣⁱⁱ—Br2—Cs1ˣⁱⁱⁱ	88.049 (5)
F1ⁱᵛ—Cs1—F2ⁱᵛ	58.13 (3)	F2ᵛⁱⁱⁱ—Br2—Cs1ˣⁱᵛ	59.99 (2)
F2ᵛ—Cs1—F2ⁱᵛ	46.64 (4)	F2ⁱˣ—Br2—Cs1ˣⁱᵛ	59.995 (19)
F2ⁱⁱⁱ—Cs1—F2ⁱᵛ	112.26 (3)	F2ˣ—Br2—Cs1ˣⁱᵛ	120.005 (19)
F2ⁱ—Cs1—F2ᵛⁱ	123.868 (17)	F2—Br2—Cs1ˣⁱᵛ	120.01 (2)
F2ⁱⁱ—Cs1—F2ᵛⁱ	90.05 (2)	Cs1ˣⁱ—Br2—Cs1ˣⁱᵛ	88.049 (5)
F3ⁱ—Cs1—F2ᵛⁱ	81.61 (2)	Cs1ˣⁱⁱ—Br2—Cs1ˣⁱᵛ	91.951 (5)
F3—Cs1—F2ᵛⁱ	57.553 (17)	Cs1ˣⁱⁱⁱ—Br2—Cs1ˣⁱᵛ	180.0
F1ⁱⁱⁱ—Cs1—F2ᵛⁱ	58.13 (3)	Br1—F1—Cs1ˣⁱⁱⁱ	119.61 (2)
F1ⁱᵛ—Cs1—F2ᵛⁱ	156.305 (19)	Br1—F1—Cs1ˣⁱ	119.61 (2)
F2ᵛ—Cs1—F2ᵛⁱ	112.26 (3)	Cs1ˣⁱⁱⁱ—F1—Cs1ˣⁱ	120.78 (5)
F2ⁱⁱⁱ—Cs1—F2ᵛⁱ	46.64 (4)	Br1—F1—Cs1ᵛⁱⁱ	102.61 (2)
F2ⁱᵛ—Cs1—F2ᵛⁱ	133.81 (3)	Cs1ˣⁱⁱⁱ—F1—Cs1ᵛⁱⁱ	83.807 (16)
F2ⁱ—Cs1—F1ᵛⁱⁱ	147.27 (3)	Cs1ˣⁱ—F1—Cs1ᵛⁱⁱ	83.807 (16)
F2ⁱⁱ—Cs1—F1ᵛⁱⁱ	57.95 (3)	Br1—F1—Cs1ⁱ	102.61 (2)
F3ⁱ—Cs1—F1ᵛⁱⁱ	106.94 (3)	Cs1ˣⁱⁱⁱ—F1—Cs1ⁱ	83.807 (16)
F3—Cs1—F1ᵛⁱⁱ	47.83 (3)	Cs1ˣⁱ—F1—Cs1ⁱ	83.807 (16)
F1ⁱⁱⁱ—Cs1—F1ᵛⁱⁱ	96.194 (16)	Cs1ᵛⁱⁱ—F1—Cs1ⁱ	154.78 (5)
F1ⁱᵛ—Cs1—F1ᵛⁱⁱ	96.194 (16)	Br2—F2—Cs1ⁱ	179.32 (6)
F2ᵛ—Cs1—F1ᵛⁱⁱ	61.838 (19)	Br2—F2—Cs1ˣⁱⁱⁱ	90.42 (3)
F2ⁱⁱⁱ—Cs1—F1ᵛⁱⁱ	107.50 (2)	Cs1ⁱ—F2—Cs1ˣⁱⁱⁱ	89.95 (2)
F2ⁱᵛ—Cs1—F1ᵛⁱⁱ	107.50 (2)	Br2—F2—Cs1ˣⁱ	90.42 (3)
F2ᵛⁱ—Cs1—F1ᵛⁱⁱ	61.838 (19)	Cs1ⁱ—F2—Cs1ˣⁱ	89.95 (2)
F2ⁱ—Cs1—F1ⁱ	57.95 (3)	Cs1ˣⁱⁱⁱ—F2—Cs1ˣⁱ	112.26 (3)
F2ⁱⁱ—Cs1—F1ⁱ	147.27 (3)	Br1—F3—Cs1ⁱ	119.56 (2)
F3ⁱ—Cs1—F1ⁱ	47.83 (3)	Br1—F3—Cs1	119.56 (2)
F3—Cs1—F1ⁱ	106.94 (3)	Cs1ⁱ—F3—Cs1	120.89 (4)
F1ⁱⁱⁱ—Cs1—F1ⁱ	96.194 (16)		

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