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**RbCl and CsCl react with BrF<sub>3</sub> yielding the corresponding decafluoridotribromates(III), MBr<sub>3</sub>F<sub>10</sub> (M = Rb, Cs), which were structurally characterized for the first time. The Br<sub>3</sub>F<sub>10</sub><sup>−</sup> anion is surprisingly not linear but contains a μ<sub>3</sub>-bridging fluorine atom and seems to be the first example of μ<sup>3</sup>-F bridging of Br atoms. The compounds are highly reactive and cannot be handled in glassware. As for the tetrafluoridobromates themselves, they are powerful oxidizers and thus suitable for the dry-chemical recycling of precious metals and additionally feature a significantly higher BrF<sub>3</sub> content.**

Under appropriate conditions fluorine is able to react with almost any element and a rich diversity of compounds result. In fluorine-containing molecules and molecular ions, the fluorine atom clearly prefers terminal positions, although many coordination compounds incorporate fluorine atoms as bridging ligands.<sup>1</sup> The most common type of F-bridging is the μ<sub>2</sub>-connection (either straight mono(μ-F), or bent di(μ-F)).<sup>2–13</sup> The highly strained tri(μ-F)-bridges between various elements<sup>1</sup> are scarce with only some examples in the literature.<sup>2–13</sup> Bridges among three atoms (μ<sub>3</sub>-F) are even more rare;<sup>14–21</sup> however, μ<sub>4</sub>-F<sup>22,23</sup> and even cage-like μ<sub>6</sub>-F<sup>22,24,25</sup> coordination types are known. In the vast majority of these compounds the fluorine atom bridges either metal atoms (thus, forming homo- or hetero (oligo-)nuclear complexes), or, more rarely, metal and nonmetal atoms. In comparison, compounds featuring μ<sub>2</sub>-F bridges between two nonmetal atoms are even more uncommon; examples are known for H,<sup>26</sup> Kr,<sup>27,28</sup> Xe,<sup>29</sup> Br,<sup>4,30</sup> and I,<sup>31</sup> as well

## Br<sub>2</sub>F<sub>7</sub><sup>−</sup> and Br<sub>3</sub>F<sub>10</sub><sup>−</sup>: peculiar anions showing μ<sub>2</sub>- and μ<sub>3</sub>-bridging F-atoms†

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as for several metalloid atoms: B,<sup>32</sup> As,<sup>33</sup> Sb,<sup>34</sup> and Si.<sup>35</sup> To the best of our knowledge, the μ<sub>3</sub>-F type among nonmetals was fully established only for Xe<sup>36</sup> and I.<sup>20,21</sup>

Here, we report the results of our investigations on the non-common fluorine bridging in rubidium and cesium decafluoridotribromates(III): RbBr<sub>3</sub>F<sub>10</sub> (compound 1) and CsBr<sub>3</sub>F<sub>10</sub> (compound 2), respectively, as well as in rubidium heptafluoridodibromate(III), RbBr<sub>2</sub>F<sub>7</sub> (compound 3). The compounds were synthesized during our research on the metal tetrafluoridobromate(III) series – powerful oxidizers which are promising for the dry-chemical recycling of noble metals.<sup>4,37,38</sup> MBr<sub>3</sub>F<sub>10</sub> and MBr<sub>2</sub>F<sub>7</sub> (M = Rb, Cs) were first reported by Stein,<sup>30</sup> however, their structures could only be deduced by Raman spectroscopy. Also, military personnel tried the synthesis of Br<sub>3</sub>F<sub>10</sub><sup>−</sup> but did not succeed.<sup>41</sup> The Br<sub>3</sub>F<sub>10</sub><sup>−</sup> (and Br<sub>2</sub>F<sub>7</sub><sup>−</sup>) anion was reported to be chainlike with Br–μ-F–Br connections. We continued our previous works on BrF<sub>4</sub><sup>−</sup> compounds<sup>4</sup> and started to investigate compounds of higher BrF<sub>3</sub> content to reveal how the chain elongation influences the structure of the anion and its reactivity. However, single crystal X-ray diffraction analyses, vibrational spectroscopy, as well as quantum chemical calculations showed that the Br<sub>3</sub>F<sub>10</sub><sup>−</sup> anions are not chain-like but contain μ<sub>3</sub>-bridging F atoms.

Compounds 1, 2 and 3 were synthesized using stoichiometric amounts of MCl (M = Rb, Cs) and BrF<sub>3</sub>, according to eqn (1), which was previously applied in the synthesis of RbBrF<sub>4</sub>.<sup>38</sup>



RbBr<sub>3</sub>F<sub>10</sub> and CsBr<sub>3</sub>F<sub>10</sub> were obtained as yellowish-colored crystalline solids. Since both compounds are structurally isotypic, we present a detailed structural description only for compound 1 (Rb). Further details of the compounds presented here, such as powder X-ray patterns, Rietveld refinements, thermal analyses, experimentally observed as well as calculated Raman and IR spectra and band assignments, are available from the ESI.†

Compound 1 crystallizes in the monoclinic space group type *P*2<sub>1</sub> (no. 4) with *a* = 7.6219(3) Å, *b* = 8.2593(4) Å, *c* = 8.4645(4) Å,

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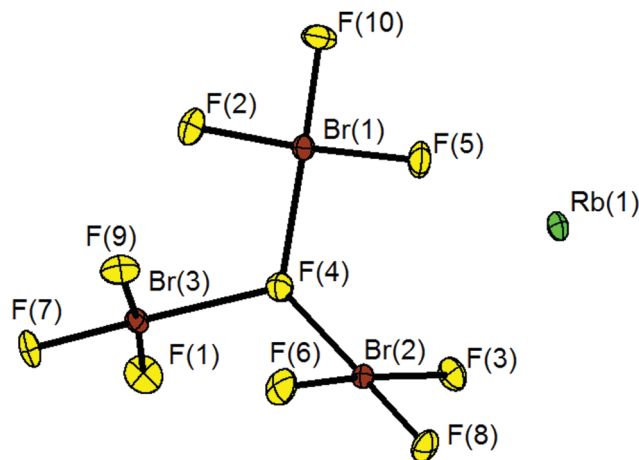


Fig. 1 The asymmetric unit of  $\text{RbBr}_3\text{F}_{10}$ . Displacement ellipsoids are shown at 70% probability level at 110 K.

$\beta = 114.414(1)^\circ$ ,  $V = 485.21(4) \text{ \AA}^3$ , and  $Z = 4$  at 110 K. Further crystallographic details are given in Table 2. The asymmetric unit and the crystal packing of compound **1** are shown in Fig. 1 and Fig. S10 (ESI<sup>†</sup>), respectively.

An unexpected and unusual feature of compounds **1** and **2** is the shape of the  $\text{Br}_3\text{F}_{10}^-$  anion. It contains a  $\mu_3$ -bridging fluorine atom and not two  $\mu_2$ -bridging fluorine atoms as was previously deduced from Raman spectroscopic investigations on the compound.<sup>30</sup> To the best of our knowledge,  $\text{RbBr}_3\text{F}_{10}$  and  $\text{CsBr}_3\text{F}_{10}$  are the first documented compounds which incorporate fluorine as a  $\mu_3$ -bridging ligand between Br atoms.

The bromine atoms in  $\text{RbBr}_3\text{F}_{10}$  are coordinated by four fluorine atoms, each in an almost square-planar shape. The F–Br–F angles are observed in the range of  $86.8(1)$  to  $95.8(1)^\circ$ , which is typical for known tetrafluoridobromates(III):  $\text{KBrF}_4$ ,<sup>12,39</sup>  $\text{RbBrF}_4$ ,<sup>38</sup>  $\text{CsBrF}_4$ ,<sup>4</sup>  $\text{CsBr}_2\text{F}_7$ ,<sup>4</sup> and  $\text{Ba}(\text{BrF}_4)_2$ .<sup>37</sup> The Br atoms are located almost exactly in the virtual planes formed by the corresponding fluorine atoms (the distances from the least-squares planes are only  $0.0026(4)$ ,  $0.0033(5)$ , and  $0.0095(4) \text{ \AA}$ ). The  $\mu_3$ -F atom is slightly ( $0.458(2) \text{ \AA}$  for compound **1**,  $0.370(8) \text{ \AA}$  for compound **2**) above the virtual plane built by the three Br atoms. The Br– $\mu_3$ -F–Br angles are observed in the interval from  $113.2(1)$  to  $120.1(1)^\circ$ . All three planar  $\text{BrF}_3$ -units are tilted

towards each other, and the angles between the virtual planes are equal to  $65.46(6)$ ,  $66.22(7)$ , and  $69.10(7)^\circ$ . The point group of the  $\text{Br}_3\text{F}_{10}^-$  anion is  $C_1$ ; however, its symmetry is very close to  $D_3$ . In DFT calculations on the isolated anion point group  $D_3$  is obtained. We also carried out two gas-phase DFT calculations on the  $\text{Br}_3\text{F}_{10}^-$  anion to compare the relative energetics of the  $\mu_3$ -bridging, experimentally observed structure and the previously postulated chain-like structure with Br– $\mu$ -F–Br connections. At the DFT-PBE0/def2-TZVP level of theory, the  $D_3$ -symmetric,  $\mu_3$ -bridging structure is energetically  $15 \text{ kJ mol}^{-1}$  more favorable than the  $C_{2h}$ -symmetric, chainlike structure (structural data are available in the ESI<sup>†</sup>). As expected, the Br–F bonds in the *trans*-position with respect to the  $\mu_3$ -F atom are shortened by *circa*  $0.1 \text{ \AA}$  (for both compounds) in comparison to the other terminal F atoms. The coordination sphere of the  $\text{Br}_3\text{F}_{10}^-$  anion is also interesting and is discussed in the ESI<sup>†</sup> for reasons of brevity. Selected atomic distances and angles of the  $\text{Br}_3\text{F}_{10}^-$  anions, experimentally observed as well as theoretically predicted, are given in Table 1.

It is interesting to note that the cation type seems to have a rather low impact on the molecular structure of the  $\text{Br}_3\text{F}_{10}^-$  anion. All corresponding Br–F bond lengths (including those to  $\mu_3$ -F as well as to *trans*-F atoms) do not change significantly ( $3\sigma$ ) if the Rb atoms are exchanged by Cs atoms. However, the bond angles seem to be more susceptible to the cation size and undergo a noticeable change resulting also in the change in the  $\mu_3$ -F distance from the virtual Br(1)–Br(2)–Br(3) plane.

Compound **3**, rubidium heptafluoridodibromate(III), appears as a yellowish crystalline solid. However, the product of reaction (1) contains a mixture of  $\text{RbBrF}_4$ ,  $\text{RbBr}_2\text{F}_7$ , and  $\text{BrF}_3$  rather than pure compound **3** (see the ESI<sup>†</sup>), which confirms the results obtained by Stein.<sup>30</sup>  $\text{RbBr}_2\text{F}_7$  crystallizes in the monoclinic space group type  $P2_1/c$  (no. 14) with  $a = 7.5109(3) \text{ \AA}$ ,  $b = 7.8759(3) \text{ \AA}$ ,  $c = 13.6898(5) \text{ \AA}$ ,  $\beta = 123.118(2)^\circ$ ,  $V = 678.26(5) \text{ \AA}^3$ , and  $Z = 4$  at 110 K. It is structurally isotypic to  $\text{CsBr}_2\text{F}_7$ .<sup>4</sup> The crystallographic details of  $\text{RbBr}_2\text{F}_7$  are given in Table 2. The asymmetric unit and the crystal packing of compound **3** are shown in Fig. 2 and Fig. S11 (ESI<sup>†</sup>) respectively.

$\text{RbBr}_2\text{F}_7$  contains a  $\text{Br}_2\text{F}_7^-$  anion with the fluorine atom F(1) acting as a  $\mu_2$ -bridging ligand between the two bromine atoms. The Br– $\mu$ -F distances are  $2.115(2)$  and  $2.145(2) \text{ \AA}$ , and are

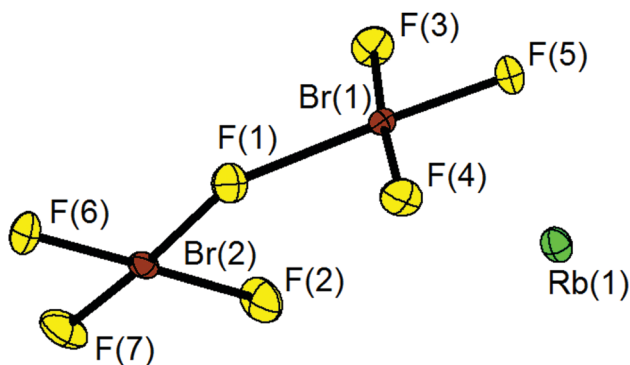
Table 1 Selected bond lengths and angles for the  $\text{Br}_3\text{F}_{10}^-$  anion. The atom labels correspond to those in Fig. 1. The DFT-PBE0 data for the ideal  $D_3$ -symmetric  $\text{Br}_3\text{F}_{10}^-$  anion have been calculated for the gas-phase (see the ESI for computational details)

Parameter	Value ( $\text{\AA}/^\circ$ )		
	$\text{RbBr}_3\text{F}_{10}$	$\text{CsBr}_3\text{F}_{10}$	$\text{Br}_3\text{F}_{10}^-$ (DFT-PBE0)
Br(1)– $\mu_3$ -F	2.243(3)	2.238(10)	2.30
Br(2)– $\mu_3$ -F	2.248(2)	2.246(9)	2.30
Br(3)– $\mu_3$ -F	2.320(3)	2.329(10)	2.30
Br– <i>trans</i> -F (F7, F8, F10)	1.745(2) ··· 1.752(2)	1.746(6) ··· 1.767(7)	1.76
Br–F (other)	1.837(2) ··· 1.874(2)	1.824(10) ··· 1.878(7)	1.84
Br(1)– $\mu_3$ -F–Br(2)	120.1(1)	122.0(3)	120
Br(2)– $\mu_3$ -F–Br(3)	114.7(1)	115.0(4)	120
Br(3)– $\mu_3$ -F–Br(1)	113.2(1)	115.1(4)	120
Distance from $\mu_3$ -F to Br(1)–Br(2)–Br(3) plane	0.458(2)	0.370(8)	0
Tilting angles between $\text{F}_3\text{M}-\mu\text{-F}-\text{MF}_3$ least-squares planes	65.46(6)	62.1(3)	81.8
	66.22(7)	66.2(2)	
	69.10(7)	72.0(2)	



Table 2 Crystallographic details of the title compounds

	Compound 1	Compound 2	Compound 3
Empirical formula	Br <sub>3</sub> F <sub>10</sub> Rb	Br <sub>3</sub> F <sub>10</sub> Cs	Br <sub>2</sub> F <sub>7</sub> Rb
Color and appearance	Colorless plates, yellowish powders		
<i>M</i> /g mol <sup>-1</sup>	515.20	562.60	378.29
Crystal system	Monoclinic		
Space group	<i>P</i> 2 <sub>1</sub> (no. 4)		<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
<i>a</i> /Å	7.6219(3)	7.4399(16)	7.5109(3)
<i>b</i> /Å	8.2593(4)	8.4037(17)	7.8759(3)
<i>c</i> /Å	8.4645(4)	8.8365(18)	13.6898(5)
$\beta$ /°	114.414(1)	115.31(3)	123.118(2)
<i>V</i> /Å <sup>3</sup>	485.21(4)	519.4(2)	678.26(5)
<i>Z</i>	2		4
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	3.526	3.597	3.705
$\rho_{\text{exp}}$ /g cm <sup>-3</sup>	3.687 ± 0.006	3.460 ± 0.026	3.786 ± 0.007
$\lambda$ /Å	0.71073 (Mo-K $\alpha_2$ )		
<i>T</i> /K	110	100	110
<i>R</i> <sub>int</sub> , <i>R</i> <sub><math>\sigma</math></sub>	0.0444, 0.0465	0.0472, 0.1449	0.0533, 0.0309
<i>R</i> ( <i>F</i> <sup>2</sup> ) (all data), <i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.0294, 0.0509	0.0730, 0.0732	0.0336, 0.0507
<i>S</i> (all data)	1.024	0.790	1.055
Flack parameter <i>x</i>	0.050(6)	0.00(2)	—
No. of reflections, parameters, constraints, restraints	4132, 128, 0, 1	3195, 128, 0, 1	2035, 92, 0, 0
2 $\theta$ range refined (min, max)	2.643, 35.843	2.912, 31.900	3.138, 30.362
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ /e Å <sup>-3</sup>	1.22, -1.45	1.43, -1.21	0.94, -0.94
( $\Delta\sigma$ ) <sub>max</sub>	0.001	0.000	0.001
ICSD number	431741	431740	431739

Fig. 2 The asymmetric unit of RbBr<sub>2</sub>F<sub>7</sub>. Displacement ellipsoids are shown at 70% probability level at 110 K.

essentially equal to 2.113(1) and 2.143(1) Å as observed in CsBr<sub>2</sub>F<sub>7</sub>;<sup>4</sup> however, the Br–μ–F–Br angle is 134.75(9)° being *circa* 6° smaller than the analogous angle of 140.27(6)° reported for the Cs compound. The *trans*-F–Br distances are equal to 1.767(2) and 1.780(2) Å, while the other terminal Br–F bond lengths lie in the range of 1.845(2) to 1.890(2) Å, therefore, being equal to the corresponding bonds in CsBr<sub>2</sub>F<sub>7</sub> within the 3 $\sigma$  criterion. The F–Br–F angles are observed within the interval from 87.46(7) to 95.65(7)° (87.74(6) to 95.12(5)° in CsBr<sub>2</sub>F<sub>7</sub>). These facts imply again that these counter-ions do not significantly influence the molecular structure of the fluoridobromate anions. The cell parameters together with the selected bond lengths and angles for RbBr<sub>2</sub>F<sub>7</sub> and CsBr<sub>2</sub>F<sub>7</sub> as well as for

Table 3 Selected bond lengths and angles in RbBr<sub>2</sub>F<sub>7</sub>, CsBr<sub>2</sub>F<sub>7</sub>, and CsAu<sub>2</sub>F<sub>7</sub>. The atom labels correspond to those in Fig. 2, and were changed in the cases of CsBr<sub>2</sub>F<sub>7</sub> and CsAu<sub>2</sub>F<sub>7</sub> to make the comparison possible

Parameter	Value (Å/°)		
	RbBr <sub>2</sub> F <sub>7</sub> ( <i>P</i> 2 <sub>1</sub> / <i>c</i> )	CsBr <sub>2</sub> F <sub>7</sub> ( <i>P</i> 2 <sub>1</sub> / <i>c</i> ) <sup>4</sup>	CsAu <sub>2</sub> F <sub>7</sub> ( <i>C</i> 2/ <i>c</i> ) <sup>40</sup>
<i>a</i> /Å	7.5109(3)	7.7078(1)	11.365(6)
<i>b</i> /Å	7.8759(3)	8.0218(2)	10.820(15)
<i>c</i> /Å	13.6898(5)	14.1584(3)	7.374(3)
$\beta$ /°	123.118(2)	122.742(2)	123.40(3)
M(1)–F(1)	2.145(2)	2.143(1)	1.988(8)
M(1)–F(3)	1.871(2)	1.868(2)	1.89(2)
M(1)–F(4)	1.855(2)	1.858(2)	1.92(2)
M(1)–F(5)	1.767(2)	1.769(1)	1.86(2)
M(2)–F(1)	2.115(2)	2.112(2)	1.988(8)
M(2)–F(2)	1.890(2)	1.884(2)	1.89(2)
M(2)–F(6)	1.845(2)	1.849(1)	1.92(2)
M(2)–F(7)	1.780(2)	1.779(2)	1.86(2)
M(1)–F(1)–M(2)	134.75(9)	140.27(6)	130.08(4)
F(5)–M(1)–F(1)	175.17(8)	176.18(6)	176.0(6)
F(7)–M(2)–F(1)	176.04(8)	176.44(7)	176.0(6)
Tilting angle between F <sub>3</sub> M–μ–F–MF <sub>3</sub> planes	65.31(6)	61.90(4)	48.1(3)

M = Br (RbBr<sub>2</sub>F<sub>7</sub>, CsBr<sub>2</sub>F<sub>7</sub>); Au (CsAu<sub>2</sub>F<sub>7</sub>).



CsAu<sub>2</sub>F<sub>7</sub> (which is similar in terms of the anion geometry but is not structurally isotypic)<sup>40</sup> are shown in Table 3.

In comparison to the Br<sub>3</sub>F<sub>10</sub><sup>−</sup> anions, a shortening of the Br–μ–F–Br bridges of *circa* 0.1 to 0.2 Å is observed which may be due to smaller Coulomb repulsion between the two Br atoms. The Br–*trans*-F distances in the Br<sub>2</sub>F<sub>7</sub><sup>−</sup> anion are on average 0.025 Å longer than those in Br<sub>3</sub>F<sub>10</sub><sup>−</sup>. The other terminal fluorine atoms are not so susceptible to the change of the inner environment and the corresponding Br–F bonds show only a slight elongation of approximately 0.01 Å.

All compounds reported in this work may be convenient carriers for BrF<sub>3</sub> due to its high mass content (72.4, 79.7, 73.0% by mass in RbBr<sub>2</sub>F<sub>7</sub>, RbBr<sub>3</sub>F<sub>10</sub> and CsBr<sub>3</sub>F<sub>10</sub> respectively). So, the “problematic” BrF<sub>3</sub> can be replaced by these comparatively easy to handle solid compounds. To date there has been no indication for the existence of such interhalide anions in compounds with cations other than Rb or Cs, which is possibly due to the cation size. Also, it is unknown if suitable reaction conditions can be found that would lead to the formation of the highly symmetrical Br<sub>4</sub>F<sub>13</sub><sup>−</sup> anion, with a μ<sub>4</sub>-bridging F atom. Investigations in those directions are ongoing.

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