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Br2F7 - and Br3F10 -

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Br$_2$F$_7$ and Br$_3$F$_{10}^-$: peculiar anions showing µ$_2$- and µ$_3$-bridging F-atoms†

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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. The most common type of F-bridging is the µ$_3$-connection (either straight mono(µ-F), or bent di(µ-F)). The highly strained tri(µ-F)bridges between various elements are scarce with only some examples in the literature. Bridges among three atoms (µ$_3$-F) are even more rare; however, µ$_4$-F bridges and even cage-like µ$_6$-F 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$_2$-F bridges between two nonmetal atoms are even more uncommon; examples are known for H$_2$-26 Kr$_2$-27,28 Xe$_2$-29 Br$_2$-30 and I$_2$-31 as well as for several metalloid atoms: B-32, As-33, Sb-34 and Si-35. To the best of our knowledge, the µ$_3$-F type among nonmetals was fully established only for Xe-36 and I-20,31.

Here, we report the results of our investigations on the non-common fluorine bridging in rubidium and cesium decafluoroditribromates(III), MBr$_2$F$_7$ (M = Rb, Cs), which were structurally characterized for the first time. The Br$_3$F$_{10}^-$ anion is surprisingly not linear but contains a µ$_3$-bridging fluorine atom and seems to be the first example of µ$_3$-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$_3$ content.

RbCl and CsCl react with BrF$_3$ yielding the corresponding decafluoroditribromates(III), MBr$_2$F$_7$ (M = Rb, Cs), which were structurally characterized for the first time. The Br$_3$F$_{10}^-$ anion is surprisingly not linear but contains a µ$_3$-bridging fluorine atom and seems to be the first example of µ$_3$-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$_3$ 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. The most common type of F-bridging is the µ$_3$-connection (either straight mono(µ-F), or bent di(µ-F)). The highly strained tri(µ-F)bridges between various elements are scarce with only some examples in the literature. Bridges among three atoms (µ$_3$-F) are even more rare; however, µ$_4$-F bridges and even cage-like µ$_6$-F 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$_2$-F bridges between two nonmetal atoms are even more uncommon; examples are known for H$_2$-26 Kr$_2$-27,28 Xe$_2$-29 Br$_2$-30 and I$_2$-31 as well as for several metalloid atoms: B-32, As-33, Sb-34 and Si-35. To the best of our knowledge, the µ$_3$-F type among nonmetals was fully established only for Xe-36 and I-20,31.

Here, we report the results of our investigations on the non-common fluorine bridging in rubidium and cesium decafluoroditribromates(III): RbBr$_2$F$_7$ (compound 1) and CsBr$_2$F$_7$ (compound 2), respectively, as well as in rubidium heptafluorodidobromate(III), RbBr$_2$F$_7$ (compound 3). The compounds were synthesized during our research on the metal tetrafluoridobromates(III) series – powerful oxidizers which are promising for the dry-chemical recycling of noble metals. RbBr$_2$F$_7$ and MBr$_2$F$_7$ (M = Rb, Cs) were first reported by Stein; however, their structures could only be deduced by Raman spectroscopy. Also, military personnel tried the synthesis of Br$_3$F$_{10}^-$ but did not succeed. The Br$_3$F$_{10}^-$ (and Br$_2$F$_7$−) anion was reported to be chainlike with Br-µ-F-Br connections. We continued our previous works on Br$_2$F$_7$− compounds and started to investigate compounds of higher BrF$_3$ 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$_3$F$_{10}^-$ anions are not chain-like but contain µ$_3$-bridging F atoms.

Compounds 1, 2 and 3 were synthesized using stoichiometric amounts of MCl (M = Rb, Cs) and BrF$_3$, according to eqn (1), which was previously applied in the synthesis of RbBrF$_4$:

$$6\text{MCl} + (6\text{n} + 2)\text{BrF}_3 \rightarrow 6\text{MBr}_2\text{F}_{(3\text{n} + 1)} + \text{Br}_2 + 3\text{Cl}_2 \quad (1)$$

RbBr$_2$F$_7$ and CsBr$_2$F$_7$ 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 $P2_1$ (no. 4) with $a = 7.6219(3)$ Å, $b = 8.2593(4)$ Å, $c = 8.4645(4)$ Å,
The asymmetry of the RbBrF₁₀ anion. Displacement ellipsoids are shown at 70% probability level at 110 K.

β = 114.414(1)°, V = 485.21(4) Å³, 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†), respectively.

An unexpected and unusual feature of compounds 1 and 2 is the shape of the Br₃F₁₀ anion. It contains a μ₂-bridging fluoride atom and not two μ₂-bridging fluoride atoms as was previously deduced from Raman spectroscopic investigations on the compound.³⁰ To the best of our knowledge, RbBrF₁₀ and CsBrF₁₀ are the first documented compounds which incorporate fluoride as a μ₂-bridging ligand between Br atoms.

The bromine atoms in RbBrF₁₀ are coordinated by four fluoride 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)°, which is typical for known tetrafluorobromates(III): KBrF₄,³¹ RbBrF₄,³² CsBrF₄,³³ and Ba[BrF₄]₂.³⁴ The Br atoms are located almost exactly in the virtual planes formed by the corresponding fluoride atoms (the distances from the least-squares planes are only 0.0026(4), 0.0033(5), and 0.0095(4) Å). The μ₁-F atom is slightly (0.458(2) Å for compound 1, 0.370(8) Å for compound 2) above the virtual plane built by the three Br atoms. The Br–μ₁-F–Br angles are observed in the interval from 113.2(1) to 120.1(1). All three planar BrF₃-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)°. The point group of the Br₃F₁₀ anion is C₁; however, its symmetry is very close to D₁. In DFT calculations on the isolated anion point group D₁ is obtained. We also carried out two gas-phase DFT calculations on the Br₃F₁₀ anion to compare the relative energetics of the μ₂-bridging, experimentally observed structure and the previously postulated chain-like structure with Br-μ-F–Br connections. At the DFT-PBE0/def2-TZVP level of theory, the D₁-symmetric, μ₂-bridging structure is energetically 15 kJ mol⁻¹ more favorable than the C₁₉₆-symmetric, chainlike structure (structural data are available in the ESI†). As expected, the Br-F bonds in the trans-position with respect to the μ₂-F atom are shortened by circa 0.1 Å (for both compounds) in comparison to the other terminal F atoms. The coordination sphere of the Br₃F₁₀ anion is also interesting and is discussed in the ESI† for reasons of brevity. Selected atomic distances and angles of the Br₃F₁₀ 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 Br₃F₁₀ anion. All corresponding Br–F bond lengths (including those to μ₂-F as well as to trans-F atoms) do not change significantly (3σ) 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 μ₂-F distance from the virtual Br(1)–Br(2)–Br(3) plane.

Table 1 Selected bond lengths and angles for the Br₃F₁₀ anion. The atom labels correspond to those in Fig. 1. The DFT-PBE0 data for the ideal D₁-symmetric Br₃F₁₀ anion have been calculated for the gas-phase (see the ESI for computational details)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbBrF₁₀</td>
<td>CsBrF₁₀</td>
</tr>
<tr>
<td>Br(1)–μ₁-F</td>
<td>2.243(3)</td>
</tr>
<tr>
<td>Br(2)–μ₁-F</td>
<td>2.248(2)</td>
</tr>
<tr>
<td>Br(3)–μ₁-F</td>
<td>2.320(3)</td>
</tr>
<tr>
<td>Br–μ₁-F–Br(2)</td>
<td>1.745(2)–1.752(2)</td>
</tr>
<tr>
<td>Br–μ₁-F–Br(3)</td>
<td>1.837(2)–1.874(2)</td>
</tr>
<tr>
<td>Distance from μ₁-F to Br(1)–Br(2)–Br(3) plane</td>
<td>0.458(2)</td>
</tr>
<tr>
<td>Tilting angles between F₃M–μ₁-F–MF₃ least-squares planes</td>
<td>66.22(7)</td>
</tr>
<tr>
<td>69.10(7)</td>
<td>72.0(2)</td>
</tr>
</tbody>
</table>
essentially equal to 2.113(1) and 2.143(1) Å as observed in CsBr$_2$F$_7$; however, the Br–m–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$_2$F$_7$ within the 3σ 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$_2$F$_7$). 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$_2$F$_7$ and CsBr$_2$F$_7$ as well as for

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (Å/°)</th>
</tr>
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<tbody>
<tr>
<td>a/Å</td>
<td>7.5109(3)</td>
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<tr>
<td>b/Å</td>
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<tr>
<td>c/Å</td>
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<tr>
<td>β/°</td>
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<td>1.871(2)</td>
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<td>M(1)–F(4)</td>
<td>1.855(2)</td>
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<td>M(1)–F(5)</td>
<td>1.767(2)</td>
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<td>M(2)–F(1)</td>
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<tr>
<td>M(2)–F(2)</td>
<td>1.890(2)</td>
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<tr>
<td>M(2)–F(3)</td>
<td>1.843(2)</td>
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<tr>
<td>M(2)–F(7)</td>
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<td>M(1)–F(1)–M(2)</td>
<td>134.75(9)</td>
</tr>
<tr>
<td>F(5)–M(1)–F(1)</td>
<td>175.17(8)</td>
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<tr>
<td>F(7)–M(2)–F(1)</td>
<td>176.04(8)</td>
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<td>Tilting angle between F$_3$M–μ–F–MF$_3$ planes</td>
<td>65.31(6)</td>
</tr>
</tbody>
</table>

M = Br (RbBr$_2$F$_7$, CsBr$_2$F$_7$); Au (CsAu$_2$F$_7$).


0.025 Å longer than those in Br3F10

investigations in those directions are ongoing.

the "problematic" BrF3 can be replaced by these comparatively

carriers for BrF3 due to its high mass content (72.4, 79.7, 73.0%

only a slight elongation of approximately 0.01 Å.

inner environment and the corresponding Br–F bonds show

fluorine atoms are not so susceptible to the change of the

due to smaller Coulomb repulsion between the two Br atoms.

highly symmetrical Br4F13

indication for the existence of such interhalide anions in

easy to handle solid compounds. To date there has been no

compounds with cations other than Rb or Cs, which is possibly

not structurally isotypic)40 are shown in Table 3.

CsAu2F7 (which is similar in terms of the anion geometry but is

not structurally isotypic)40 are shown in Table 3.

In comparison to the BrF10 – 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 BrF7 – anion are on average

0.025 Å longer than those in BrF10 –. 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 BrF3 due to its high mass content (72.4, 79.7, 73.0%

by mass in RbBrF3, RbBrF3,10 and CsBrF3,10 respectively). So, the

"problematic" BrF3 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 BrF13 – anion, with a μ4-bridging F atom.

Investigations in those directions are ongoing.

Notes and references

1 T. Birk, ChemistryOpen, 2013, 2, 13–16.


