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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.1 The most common type of F-bridging is the μ$_2$-connection (either straight mono(μ-F) or bent di(μ-F)).2–13 The highly strained tri(μ-F)-bridges between various elements1 are scarce with only some examples in literature.2–13 Bridges among three atoms (μ$_3$-F) are even more rare;14–21 however, μ$_3$-F22,23 and even cage-like μ$_4$-F24,25 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$31 as well as for several metalloid atoms: B$_3$32 As$_3$33 Sb$_3$34 and Si$_3$35. To the best of our knowledge, the μ$_3$-F type among nonmetals was fully established only for Xe$_3$16 and I$_3$.20,21

Here, we report the results of our investigations on the non-common fluorine bridging in rubidium and cesium decafluorodibromates(III): RbBr$_3$F$_{10}$ (compound 1) and CsBr$_3$F$_{10}$ (compound 2), respectively, as well as in rubidium heptafluorodibromate(III), RbBr$_2$F$_7$ (compound 3). The compounds were synthesized during our research on the metal tetrafluorodibromates series – powerful oxidizers which are promising for the dry-chemical recycling of noble metals.4,37,38 RbBr$_3$F$_{10}$ and MBr$_2$F$_7$ (M = Rb, Cs) were first reported by Stein;30 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.41 The Br$_3$F$_{10}^-$ (and Br$_2$F$_7^-$) anion was reported to be chain-like with Br-μ-F-Br connections. We continued our previous works on BrF$_4^-$ compounds4 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$_4$.38

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

RbBrF$_{10}$ and CsBr$_3$F$_{10}$ 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 $a = 7.6219(3)\ \text{Å}$, $b = 8.2593(4)\ \text{Å}$, $c = 8.4645(4)\ \text{Å}$,
The Br–F distances are 2.115(2) and 2.145(2) Å, and are shortest for compound 2) above the virtual plane built by the three Br atoms. The Br–μ-F–Br angles are observed in the interval from 113.2(1) to 120.1(1). All three planar 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). The point group of the Br$_3$F$_{10}^-$ anion is C$_i$; however, its symmetry is very close to D$_{3h}$. In DFT calculations on the isolated anion point group D$_3$ is obtained. We also carried out two gas-phase DFT calculations on the Br$_3$F$_{10}^-$ anion to compare the relative energetics of the μ$_{3}$-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 D$_3$-symmetric, μ$_{3}$-bridging structure is energetically 15 kJ mol$^{-1}$ more favorable than the C$_{2v}$-symmetric, chainlike structure (structural data are available in the ESI†). As expected, the Br-F bonds in the trans-position with respect to the μ$_{3}$-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 Br$_3$F$_{10}^-$ anion is also interesting and is discussed in the ESI† for reasons of brevity. Selected atomic distances and angles of the Br$_3$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 Br$_3$F$_{10}^-$ anion. All corresponding Br–F bond lengths (including those to μ$_{3}$-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 μ$_{3}$-F distance from the virtual Br(1)-Br(2)-Br(3) plane.

Compositions 3, rubidium heptafluoridodibromate(III), appears as a yellowish crystalline solid. However, the product of reaction (1) contains a mixture of RbBrF$_4$, RbBr$_2$F$_7$, and BrF$_3$, rather than pure compound 3 (see the ESI†), which confirms the results obtained by Stein.⁶ RbBr$_2$F$_7$ crystallizes in the monoclinic space group type P2$_1$/c (no. 14) with $a = 7.5109(3)$ Å, $b = 7.8759(3)$ Å, $c = 13.6898(5)$ Å, $\beta = 123.118(2)$°, $V = 678.26(5)$ Å$^3$, and $Z = 4$ at 110 K. It is structurally isotypic to CsBr$_2$F$_7$.⁴ The crystallographic details of RbBr$_2$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†) respectively.

RbBr$_2$F$_7$ contains a Br$_2$F$_7$ anion with the fluorine atom F(1) acting as a μ$_{3}$-bridging ligand between the two bromine atoms. The Br–μ-F distances are 2.115(2) and 2.145(2) Å, and are

![Fig. 1](Image) The asymmetric unit of RbBr$_3$F$_{10}$. Displacement ellipsoids are shown at 70% probability level at 110 K.

Table 1 Selected bond lengths and angles for the Br$_3$F$_{10}^-$ anion. The atom labels correspond to those in Fig. 1. The DFT-PBE0 data for the ideal D$_3$-symmetric Br$_3$F$_{10}^-$ anion have been calculated for the gas-phase (see the ESI for computational details)
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 \(\text{trans}^-\) 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 2

| Compound 1 | Compound 2 | Compound 3 |
|------------|------------|------------|
| Br\(_3\)F\(_{10}\)Rb | Br\(_3\)F\(_{10}\)Cs | Br\(_2\)F\(_7\)Rb |
| Colorless plates, yellowish powders | | |
| M/g mol\(^{-1}\) 515.20 | 562.60 | 378.29 |
| Crystal system | Monoclinic | |
| Space group | \(P_2_1\) (no. 4) | \(P_2_1/c\) (no. 14) |
| \(a/\AA\) 7.6219(3) | 7.4399(16) | 7.5109(3) |
| \(b/\AA\) 8.2593(4) | 8.4037(17) | 7.8759(3) |
| \(c/\AA\) 8.4645(4) | 8.8365(18) | 13.6898(5) |
| \(\beta/°\) | 114.414(1) | 115.31(3) | 123.118(2) |
| \(V/\AA^3\) | 485.21(4) | 519.4(2) | 678.26(5) |
| \(Z\) 2 | 4 | |
| \(\rho_{calc}/\text{g cm}^{-3}\) 3.526 | 3.597 | 3.705 |
| \(\rho_{exp}/\text{g cm}^{-3}\) 3.687 | 3.460 | 3.786 |
| \(S\) (all data) 1.024 | 0.790 | 1.055 |
| Flack parameter \(x\) 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 |
| \(\Delta\rho_{max}, \Delta\rho_{min}/\text{e Å}^{-3}\) 1.22, −1.45 | 1.43, −1.21 | 0.94, −0.94 |
| \(\Delta\rho_{max}\) (all data), w\(\rho(F^2)\) (all data) 0.001 | 0.000 | 0.001 |
| ICSD number 431741 | 431740 | 431739 |

Table 3

| Parameter | Value (Å/°) | RbBr\(_2\)F\(_7\) (\(P_2_1/c\)) | CsBr\(_2\)F\(_7\) (\(P_2_1/c\))^4 | CsAu\(_2\)F\(_7\) (C2/c)^40 |
|-----------|-------------|-------------------------------|---------------------------------|---------------------------------|
| \(a/\AA\) | 7.5109(3) | 7.7078(1) | 11.365(6) |
| \(b/\AA\) | 7.8759(3) | 8.0218(2) | 10.820(15) |
| \(c/\AA\) | 13.6898(5) | 14.1384(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) | 1.980(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\(_3\)M–m F–MF\(_3\) planes | 65.31(6) | 61.90(4) | 48.1(3) |

\(M = \text{Br (RbBr}_2\text{F}_7, \text{CsBr}_2\text{F}_7); \text{Au (CsAu}_2\text{F}_7).\)
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In comparison to the BrF$_{10}^-$ 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 BrF$_7^-$ anion are on average 0.025 Å longer than those in BrF$_{10}^-$. 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$_3$ due to its high mass content (72.4, 79.7, 73.0%) 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 BrF$_{13}^-$ anion, with a µ$_4$-bridging F atom. Investigations in those directions are ongoing.

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