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$Br_2F_7^-$ and $Br_3F_{10}^-$: peculiar anions showing μ_2- and μ_3-bridging F-atoms†

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RbCl and CsCl react with BrF_3 yielding the corresponding decafluoridotribromates(III), MBr_3F_{10} (M = Rb, Cs), which were structurally characterized for the first time. The $Br_3F_{10}^-$ 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.[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 elements[1] are scarce with only some examples in the literature.[2–13] Bridges among three atoms (μ_3-F) are even more rare;[14–21] however, μ_4-F[22,23] and even cage-like μ_6-F[22,24,25] 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,[26] Kr,[27,28] Xe,[29] Br,[4,30] and I,[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.[20,21]

Here, we report the results of our investigations on the non-common fluorine bridging in rubidium and cesium decafluoridotribromates(III): $RbBr_3F_{10}$ (compound **1**) and $CsBr_3F_{10}$ (compound **2**), respectively, as well as in rubidium heptafluoridodibromate(III), $RbBr_2F_7$ (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.[4,37,38] MBr_3F_{10} and MBr_2F_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 $Br_3F_{10}^-$ but did not succeed.[41] The $Br_3F_{10}^-$ (and $Br_2F_7^-$) anion was reported to be chainlike with Br–μ-F–Br connections. We continued our previous works on BrF_4^- compounds[4] 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 $Br_3F_{10}^-$ 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]

$$6MCl + (6n + 2)BrF_3 \rightarrow 6MBr_nF_{(3n+1)} + Br_2 + 3Cl_2 \quad (1)$$

$RbBr_3F_{10}$ and $CsBr_3F_{10}$ 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) Å, b = 8.2593(4) Å, c = 8.4645(4) Å,

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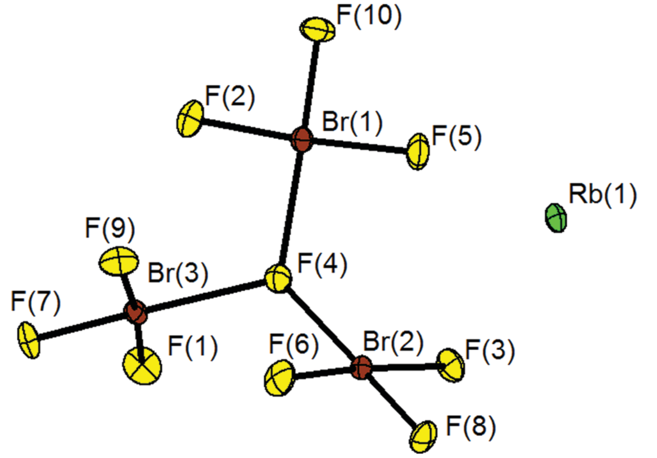

Fig. 1 The asymmetric unit of $RbBr_3F_{10}$. Displacement ellipsoids are shown at 70% probability level at 110 K.

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

An unexpected and unusual feature of compounds **1** and **2** is the shape of the $Br_3F_{10}^-$ anion. It contains a μ_3-bridging fluorine atom and not two μ_2-bridging fluorine atoms as was previously deduced from Raman spectroscopic investigations on the compound.[30] To the best of our knowledge, $RbBr_3F_{10}$ and $CsBr_3F_{10}$ are the first documented compounds which incorporate fluorine as a μ_3-bridging ligand between Br atoms.

The bromine atoms in $RbBr_3F_{10}$ 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)°, which is typical for known tetrafluoridobromates(III): $KBrF_4$,[12,39] $RbBrF_4$,[38] $CsBrF_4$,[4] $CsBr_2F_7$,[4] and $Ba(BrF_4)_2$.[37] 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) Å). The μ_3-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–μ_3-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 $Br_3F_{10}^-$ 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 $Br_3F_{10}^-$ 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_{2h}-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 $Br_3F_{10}^-$ anion is also interesting and is discussed in the ESI† for reasons of brevity. Selected atomic distances and angles of the $Br_3F_{10}^-$ 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 $Br_3F_{10}^-$ 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.

Compound **3**, rubidium heptafluoridodibromate(III), appears as a yellowish crystalline solid. However, the product of reaction (1) contains a mixture of $RbBrF_4$, $RbBr_2F_7$, and BrF_3 rather than pure compound **3** (see the ESI†), which confirms the results obtained by Stein.[30] $RbBr_2F_7$ 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, β = 123.118(2)°, V = 678.26(5) Å^3, and Z = 4 at 110 K. It is structurally isotypic to $CsBr_2F_7$.[4] The crystallographic details of $RbBr_2F_7$ 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.

$RbBr_2F_7$ contains a $Br_2F_7^-$ anion with the fluorine atom F(1) acting as a μ_2-bridging ligand between the two bromine atoms. The Br–μ-F distances are 2.115(2) and 2.145(2) Å, and are

Table 1 Selected bond lengths and angles for the $Br_3F_{10}^-$ anion. The atom labels correspond to those in Fig. 1. The DFT-PBE0 data for the ideal D_3-symmetric $Br_3F_{10}^-$ anion have been calculated for the gas-phase (see the ESI for computational details)

	Value (Å/°)		
Parameter	$RbBr_3F_{10}$	$CsBr_3F_{10}$	$Br_3F_{10}^-$ (DFT-PBE0)
Br(1)–μ_3-F	2.243(3)	2.238(10)	2.30
Br(2)–μ_3-F	2.248(2)	2.246(9)	2.30
Br(3)–μ_3-F	2.320(3)	2.329(10)	2.30
Br–*trans*-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)–μ_3-F–Br(2)	120.1(1)	122.0(3)	120
Br(2)–μ_3-F–Br(3)	114.7(1)	115.0(4)	120
Br(3)–μ_3-F–Br(1)	113.2(1)	115.1(4)	120
Distance from μ_3-F to Br(1)–Br(2)–Br(3) plane	0.458(2)	0.370(8)	0
Tilting angles between F_3M–μ-F–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	$Br_3F_{10}Rb$	$Br_3F_{10}Cs$	Br_2F_7Rb
Color and appearance	Colorless plates, yellowish powders		
M/g mol^{-1}	515.20	562.60	378.29
Crystal system	Monoclinic		
Space group	$P2_1$ (no. 4)		$P2_1/c$ (no. 14)
a/Å	7.6219(3)	7.4399(16)	7.5109(3)
b/Å	8.2593(4)	8.4037(17)	7.8759(3)
c/Å	8.4645(4)	8.8365(18)	13.6898(5)
β/°	114.414(1)	115.31(3)	123.118(2)
V/Å^3	485.21(4)	519.4(2)	678.26(5)
Z	2		4
ρ_{calc}/g cm^{-3}	3.526	3.597	3.705
ρ_{exp}/g cm^{-3}	3.687 ± 0.006	3.460 ± 0.026	3.786 ± 0.007
λ/Å	0.71073 (Mo-K$_\alpha$)		
T/K	110	100	110
R_{int}, R_σ	0.0444, 0.0465	0.0472, 0.1449	0.0533, 0.0309
$R(F^2)$ (all data), w$R(F^2)$ (all data)	0.0294, 0.0509	0.0730, 0.0732	0.0336, 0.0507
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
2θ range refined (min, max)	2.643, 35.843	2.912, 31.900	3.138, 30.362
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	1.22, −1.45	1.43, −1.21	0.94, −0.94
$(\Delta\sigma)_{max}$	0.001	0.000	0.001
ICSD number	431741	431740	431739

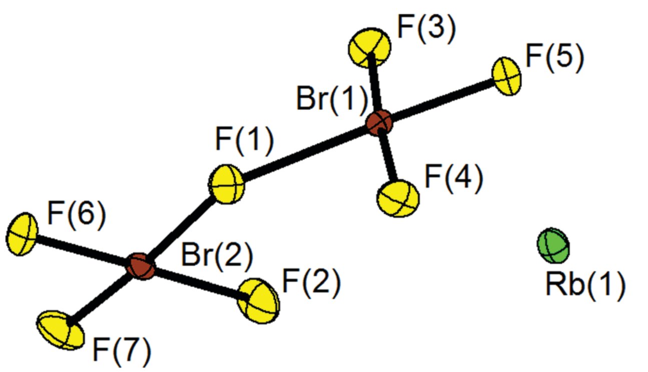

Fig. 2 The asymmetric unit of $RbBr_2F_7$. Displacement ellipsoids are shown at 70% probability level at 110 K.

essentially equal to 2.113(1) and 2.143(1) Å as observed in $CsBr_2F_7$;[4] 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 $CsBr_2F_7$ 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 $CsBr_2F_7$). 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 $RbBr_2F_7$ and $CsBr_2F_7$ as well as for

Table 3 Selected bond lengths and angles in $RbBr_2F_7$, $CsBr_2F_7$, and $CsAu_2F_7$. The atom labels correspond to those in Fig. 2, and were changed in the cases of $CsBr_2F_7$ and $CsAu_2F_7$ to make the comparison possible

	Value (Å/°)		
Parameter	$RbBr_2F_7$ ($P2_1/c$)	$CsBr_2F_7$ ($P2_1/c$)[4]	$CsAu_2F_7$ ($C2/c$)[40]
a/Å	7.5109(3)	7.7078(1)	11.365(6)
b/Å	7.8759(3)	8.0218(2)	10.820(15)
c/Å	13.6898(5)	14.1584(3)	7.374(3)
β/°	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_3M–μ-F–MF_3 planes	65.31(6)	61.90(4)	48.1(3)

M = Br ($RbBr_2F_7$, $CsBr_2F_7$); Au ($CsAu_2F_7$).

$CsAu_2F_7$ (which is similar in terms of the anion geometry but is not structurally isotypic)[40] are shown in Table 3.

In comparison to the $Br_3F_{10}^-$ 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 $Br_2F_7^-$ anion are on average 0.025 Å longer than those in $Br_3F_{10}^-$. 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% by mass in $RbBr_2F_7$, $RbBr_3F_{10}$ and $CsBr_3F_{10}$ respectively). So, the ''problematic'' BrF_3 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 $Br_4F_{13}^-$ anion, with a μ_4-bridging F atom. Investigations in those directions are ongoing.

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