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Published in:
Chemical Communications

DOI:
[10.1039/c6cc06761a](https://doi.org/10.1039/c6cc06761a)

Published: 01/01/2016

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Ivlev, S. I., Ostvald, R. V., Kraus, F., & Karttunen, A. (2016). Br_2F_7^- and $\text{Br}_3\text{F}_{10}^-$: Peculiar anions showing μ_2 - and μ_3 -bridging F-atoms. *Chemical Communications*, 52(81), 12040-12043. <https://doi.org/10.1039/c6cc06761a>



Cite this: *Chem. Commun.*, 2016, 52, 12040

Received 17th August 2016,
Accepted 12th September 2016

DOI: 10.1039/c6cc06761a

www.rsc.org/chemcomm

Br₂F₇[−] and Br₃F₁₀[−]: peculiar anions showing μ₂- and μ₃-bridging F-atoms†

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RbCl and CsCl react with BrF₃ yielding the corresponding decafluoridotribromates(III), MBr₃F₁₀ (M = Rb, Cs), which were structurally characterized for the first time. The Br₃F₁₀[−] anion is surprisingly not linear but contains a μ₃-bridging fluorine atom and seems to be the first example of μ³-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 BrF₃ 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 μ₂-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 the literature.^{2–13} Bridges among three atoms (μ₃-F) are even more rare;^{14–21} however, μ₄-F^{22,23} and even cage-like μ₆-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 μ₂-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 μ₃-F type among nonmetals was fully established only for Xe³⁶ and I.^{20,21}

Here, we report the results of our investigations on the non-common fluorine bridging in rubidium and cesium decafluoridotribromates(III): RbBr₃F₁₀ (compound 1) and CsBr₃F₁₀ (compound 2), respectively, as well as in rubidium heptafluoridodibromate(III), RbBr₂F₇ (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} MBr₃F₁₀ and MBr₂F₇ (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 Br₃F₁₀[−] but did not succeed.⁴¹ The Br₃F₁₀[−] (and Br₂F₇[−]) anion was reported to be chainlike with Br–μ-F–Br connections. We continued our previous works on BrF₄[−] compounds⁴ and started to investigate compounds of higher BrF₃ 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 Br₃F₁₀[−] anions are not chain-like but contain μ₃-bridging F atoms.

Compounds 1, 2 and 3 were synthesized using stoichiometric amounts of MCl (M = Rb, Cs) and BrF₃, according to eqn (1), which was previously applied in the synthesis of RbBrF₄.³⁸



RbBr₃F₁₀ and CsBr₃F₁₀ were obtained as yellowish-colored crystalline solids. Since both compounds are structurally isotopic, 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*2₁ (no. 4) with *a* = 7.6219(3) Å, *b* = 8.2593(4) Å, *c* = 8.4645(4) Å,

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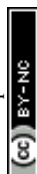
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† Electronic supplementary information (ESI) available: Experimental and computational details and results from quantum chemical calculations. CCDC 1499499–1499501. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc06761a



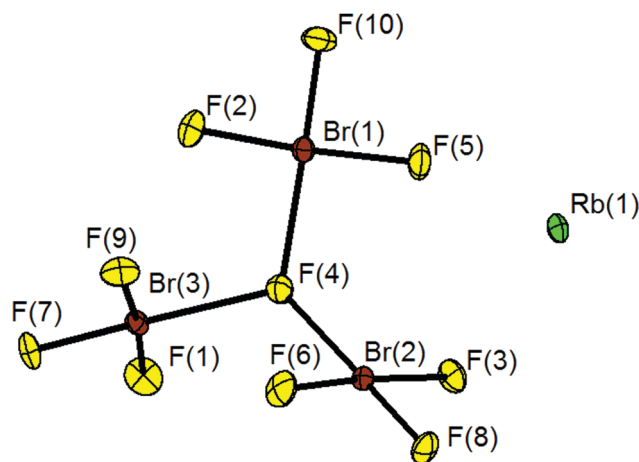


Fig. 1 The asymmetric unit of $\text{RbBr}_3\text{F}_{10}$. Displacement ellipsoids are shown at 70% probability level at 110 K.

$\beta = 114.414(1)^\circ$, $V = 485.21(4) \text{ \AA}^3$, 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[†]), 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 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, $\text{RbBr}_3\text{F}_{10}$ and $\text{CsBr}_3\text{F}_{10}$ are the first documented compounds which incorporate fluorine as a μ_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): KBrF_4 ,^{12,39} RbBrF_4 ,³⁸ CsBrF_4 ,⁴ CsBr_2F_7 ,⁴ and $\text{Ba}(\text{BrF}_4)_2$.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 $0.0095(4) \text{ \AA}$). The μ_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– μ_3 -F–Br angles are observed in the interval from $113.2(1)$ to $120.1(1)^\circ$. 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 $69.10(7)^\circ$. 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 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 \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[†] 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 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 $a = 7.5109(3) \text{ \AA}$, $b = 7.8759(3) \text{ \AA}$, $c = 13.6898(5) \text{ \AA}$, $\beta = 123.118(2)^\circ$, $V = 678.26(5) \text{ \AA}^3$, and $Z = 4$ at 110 K. It is structurally isotypic to 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 $2.145(2) \text{ \AA}$, and are

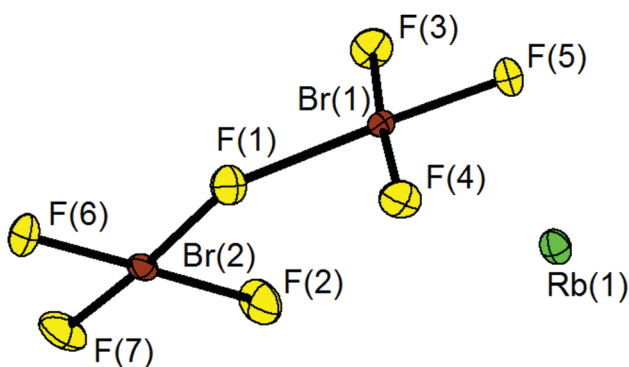
Table 1 Selected bond lengths and angles for the $\text{Br}_3\text{F}_{10}^-$ anion. The atom labels correspond to those in Fig. 1. The DFT-PBE0 data for the ideal D_3 -symmetric $\text{Br}_3\text{F}_{10}^-$ anion have been calculated for the gas-phase (see the ESI for computational details)

Parameter	Value (\AA°)		
	$\text{RbBr}_3\text{F}_{10}$	$\text{CsBr}_3\text{F}_{10}$	$\text{Br}_3\text{F}_{10}^-$ (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– <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)– 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 $\text{F}_3\text{M}-\mu\text{-F}-\text{MF}_3$ 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 ₃ F ₁₀ Rb	Br ₃ F ₁₀ Cs	Br ₂ F ₇ Rb
Color and appearance	Colorless plates, yellowish powders		
<i>M</i> /g mol ^{−1}	515.20	562.60	378.29
Crystal system	Monoclinic		
Space group	<i>P</i> 2 ₁ (no. 4)		<i>P</i> 2 ₁ / <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)
β /°	114.414(1)	115.31(3)	123.118(2)
<i>V</i> /Å ³	485.21(4)	519.4(2)	678.26(5)
<i>Z</i>	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 α)		
<i>T</i> /K	110	100	110
<i>R</i> _{int} , <i>R</i> _{σ}	0.0444, 0.0465	0.0472, 0.1449	0.0533, 0.0309
<i>R</i> (<i>F</i> ²) (all data), <i>wR</i> (<i>F</i> ²) (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 θ 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 ^{−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 RbBr₂F₇. 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 CsBr₂F₇⁴; 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 CsBr₂F₇ within the 3 σ 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 CsBr₂F₇). 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 RbBr₂F₇ and CsBr₂F₇ as well as for

Table 3 Selected bond lengths and angles in RbBr₂F₇, CsBr₂F₇, and CsAu₂F₇. The atom labels correspond to those in Fig. 2, and were changed in the cases of CsBr₂F₇ and CsAu₂F₇ to make the comparison possible

	Value (Å/°)		
Parameter	RbBr ₂ F ₇ (<i>P</i> 2 ₁ / <i>c</i>)	CsBr ₂ F ₇ (<i>P</i> 2 ₁ / <i>c</i>) ⁴	CsAu ₂ F ₇ (<i>C</i> 2/ <i>c</i>) ⁴⁰
<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)
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 ₃ M–μ–F–MF ₃ planes	65.31(6)	61.90(4)	48.1(3)

M = Br (RbBr₂F₇, CsBr₂F₇); Au (CsAu₂F₇).



CsAu₂F₇ (which is similar in terms of the anion geometry but is not structurally isotopic)⁴⁰ are shown in Table 3.

In comparison to the Br₃F₁₀[−] 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 Br₂F₇[−] anion are on average 0.025 Å longer than those in Br₃F₁₀[−]. 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 RbBr₂F₇, RbBr₃F₁₀ and CsBr₃F₁₀ 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 Br₄F₁₃[−] anion, with a μ₄-bridging F atom. Investigations in those directions are ongoing.

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