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Experimental Part

General: All operations with RbBr₂F₇, RbBr₃F₁₀, and CsBr₃F₁₀ were carried out in an atmosphere of dry and purified argon (Westfalen AG, Germany), so that a possible contact of the substances with moisture or air was minimized ($O_2 < 1$ ppm, $H_2O < 1$ ppm). RbCl and CsCl (both of "chemically pure" grade, JSC Vekton, Russia) were used without further purification. BrF₃ was synthesized by slowly passing gaseous fluorine through liquid bromine in a nickel reactor with continuous cooling.^{1,2} After completion of the reaction, BrF₃ was distilled, and only the fraction with b.p. = 125 °C was used for the experiments. Then, RbCl, CsCl, and BrF₃ was used for the preparation of the title compounds.

*Synthesis of RbBr*₂*F*₇ (*3*): RbCl (2.30 g, 19.0 mmol, 1.00 equiv.) was placed in a PTFE tube and layered with Freon-113 (15 mL). Liquid BrF₃ (6.14 g, 44.8 mmol, 1.01 equiv.) was added dropwise under vigorous stirring. More portions of Freon-113 were added as needed. The total yield of the dry product after evacuation was 6.53 g (17.3 mmol giving a yield of 91.0 %).

*Synthesis of RbBr*₃ F_{10} (1): RbCl (2.11 g, 17.4 mmol, 1.00 equiv.) was placed in a PTFE tube and layered with Freon-113 (15 mL). Liquid BrF₃ (8.00 g, 58.4 mmol, 1.01 equiv.) was added dropwise under vigorous stirring. More Freon-113 was added portion wise as needed. The total yield of the dry product after evacuation was 8.81 g (17.1 mmol giving a yield of 98.3 %).

*Synthesis of CsBr*₃ F_{10} (2): CsCl (1.76 g, 10.4 mmol, 1.00 equiv.) was placed in a PTFE tube and layered with Freon-113 (15 mL). Liquid BrF₃ (4.82 g, 35.2 mmol, 1.01 equiv.) was added dropwise under vigorous stirring. More portions of Freon-113 were added as needed. The total yield of the dry product after evacuation was 5.66 g (10.1 mmol giving a yield of 97.1 %).

Comment on the syntheses: We expect that the syntheses of the title compounds in the absence of Freon-113 would lead to the same compounds as well as to the same structures of the aniona. The reason for this assumption is the fact that Freon-113 is not miscible with any phase present in the reaction mixture (therefore, it is not a solvent in our case). The purposes why we used this Freon are: 1) not to allow the reaction mixture to reach high temperatures resulting from the reaction exothermicity (b.p. of Freon-113 is 47.5 °C); 2) to form a layer on the surface of the reaction mixture. This means that the interaction in the system was carried out by the direct contact of MCI (M = Rb, Cs) with BrF₃, as if it would take place without addition of Freon-113.

Single-crystal X-ray Analyses: X-ray structure analysis of single crystals of RbBr₂F₇ and RbBr₃F₁₀ was carried out with a Bruker D8 Quest diffractometer with monochromated molybdenum radiation (Mo-K α , $\lambda = 0.71073$ Å) and a PHOTON 100 CMOS detector. Evaluation and integration of the diffraction data was carried out by using the Bruker APEX2 software ³, and an empirical absorption correction was applied (multi-scan).

X-ray structure analysis of $CsBr_3F_{10}$ was carried out using Stoe IPDS2 diffractometer with monochromated molybdenum radiation (Mo-K α , $\lambda = 0.71073$ Å) and an image plate detector. Evaluation and integration of the diffraction data was carried out by using the Stoe X-Area software suite ⁴, and an empirical absorption correction was applied (integration).

All three structures were solved using direct methods (SHELXT) and refined against F^2 (SHELXL).^{5,6} All atoms were located by Difference Fourier synthesis and refined anisotropically. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-431739 (RbBr₂F₇), CSD-431741 (RbBr₃F₁₀), and CSD-431740 (CsBr₃F₁₀).

X-ray Powder Diffractometry: Powder X-ray diffraction patterns were obtained with a Stadi-MP diffractometer (Stoe, Germany) using Cu- $K_{\alpha 1}$ radiation, a germanium monochromator, and a Mythen1K detector. The data were handled using the WinXPOW software.⁷ The compounds were filled into flame-dried quartz capillaries (\emptyset 0.3 mm), which, in due, were inserted into wider glass capillaries (\emptyset 0.5 mm) and then flame-sealed. Le Bail profile fitting and Rietveld refinement were done in the Jana2006 software.⁸

Density Measurements: The densities of the compounds were measured using the automated gas displacement pycnometry system AccuPyc II 1340 (Micromeritics) with a calibrated 0.1 cm³ sample holder and helium as the gas being displaced. The number of preliminary purges was set to 30, while the subsequent density measurements were done 50 times with further averaging.

IR and Raman Spectroscopy: The IR spectra were recorded on a Bruker Alpha FTIR spectrometer under an Ar atmosphere and handled in the OPUS software.⁹ The Raman spectra were collected using a Labram HR 800 (JobinYvon) instrument equipped with a He/Ne laser tube (λ =

632.817 nm). The samples were filled in the fluorine-passivated FEP tubes under Ar, and the collected data were handled in the LabSpec software.¹⁰

Computational Details:

The structural and spectroscopic properties of RbBr₃F₁₀, CsBr₃F₁₀, RbBr₂F₇, and CsBr₂F₇ were investigated using the CRYSTAL14 program package.^{11,12} Both the atomic positions and lattice constants were fully optimized using the PBE0 hybrid density functional method.^{13,14} Split-valence + polarization (SVP) level basis sets were applied for all atoms (see below for additional basis set details). The reciprocal space of RbBr₃F₁₀ and CsBr₃F₁₀, was sampled using a 4x4x4 Monkhorst-Pack-type k-point grid.¹⁵ For RbBr₂ F_7 and CsBr₂ F_7 , an anisotropic 4x4x2 k-point grid was applied. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Default optimization convergence thresholds and DFT integration grids were applied in all calculations. The harmonic vibrational frequencies,^{16,17} IR intensities,¹⁸ and Raman intensities^{19,20} were obtained by using the computational schemes implemented in CRYSTAL. The predicted spectra are based on the harmonic approximation and the wavenumbers have been scaled by a factor of 0.975 to account for the overestimation typical for ab initio harmonic frequencies.²¹ The applied scaling factor results in good agreement of the highest-energy theoretical and experimental Raman shifts. The Raman and IR spectra for RbBrF4 were taken from our previous study, applying the same scaling factor.²² The Raman intensities have been calculated for a polycrystalline powder sample (total isotropic intensity in arbitrary units). The Raman final spectrum was obtained by using pseudo-Voigt peak profile (50:50 Lorenzian: Gaussian) and FWHM of 8 cm⁻¹. When simulating the Raman spectrum, the temperature and laser wavelength were set to values corresponding to the experimental setup (T = 298.15 K, λ = 632.8 nm) For the IR spectrum, Gaussian lineshape and FWHM of 8 cm⁻¹ was used. The peak assignment was carried out by visual inspection of the normal modes (Jmol program package²³). In addition to the solid-state calculations, we also carried out a molecular gas-phase calculation on the Br_3F_{10} anion with ideal D_3 -symmetry using the TURBOMOLE program package and DFT-PBE0/def2-TZVP level of theory.^{24,25} Harmonic frequency calculation showed the gas-phase structure to be a true local minimum (XYZ coordinates given below in the Computational results section).

Additional basis set details

The following split-valence + polarization (SVP) basis sets were applied for Rb, Cs, Br, and F: **Rb**: The SVP level basis set was taken from our previous study on RbBrF₄.²²

Br: The SVP level basis set was taken from our previous study on Ba(BrF₄)₂.²⁶

F: The SVP level basis set was taken from our previous study on $Ba(BrF_4)_2$.²⁶

Cs: The all-electron def2-SVP basis set was used as a starting point (46 core electrons described by a pseudopotential).²⁵ The most diffuse s- and p-type functions were removed (exponents 0.012 (s) and 0.0176 (p), respectively). The exponents of the remaining valence s-type functions (0.027, 0.16, and 0.37) were increased to 0.10, 0.20, and 0.40 (keeping an exponent ratio of 2.0). The exponent of the outermost p-type function was increased from 0.091 to 0.10 and the outermost s and p functions with the exponent of 0.10 were combined into a single sp-type function to increase the efficiency of the CRYSTAL code The diffuse d-type polarization functions with an exponent of 0.2026.

```
Full basis set listing for Cs in CRYSTAL14 input format
255 6
INPUT
9.022210
4.07975066 84.54773062 0
2.41740635 16.65417395 0
5.51408016 157.04905939 0
2.16031682 26.42330704 0
1.80741000 13.17275381 0
0.85818223 3.34283398 0
3.12326906 -28.88430917 0
0 0 3 2.0 1.0
                   .12859994983
  5.8778113443
 4.3631538286
                   -.34632569725
                   .69930637051
  1.8048475155
0 0 1 1.0 1.0
                    1.000000000
  0.40
0 0 1 0.0 1.0
                    1.000000000
 0.20
0 1 1 0.0 1.0
                    1.0 1.0
  0.10
0 2 4 6.0 1.0
                   .45723074174E-01
  4.2751856154
  1.9656663360
                  -.25019961976
  0.47689195212
                    .55660850066
  0.21529749588
                     .58218553406
0 3 1 0.0 1.0
  0.2026
                       1.0000000
```

Investigation on the purity of the compounds

Due to relatively low yields (especially in the case of $RbBr_2F_7$) all three compounds were checked for the phase purity.

a) Compound 1 ($RbBr_3F_{10}$)

4 | J. Name., 2012, 00, 1-3

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The powder diffraction pattern of compound **1** is shown on Figure S1. According to the diffraction data the major constituent of compound **I** is RbBr₃F₁₀. A number of reflections of low intensity can be assigned to RbBr₂F₇ and, therefore, were included it in the Rietveld refinement. The phase percentage extracted from the results of the refinement gives the following values: ω (RbBr₃F₁₀) = 97.5 %; ω (RbBr₂F₇) = 2.5 %.



Figure S1. Powder X-ray diffraction pattern of compound 1 measured at 293 K: experimental data (black crosses), calculated Rietveld profile (red), and difference profile (bottom, black). The calculated reflection positions are shown as black ticks (Phase #1: RbBr₃F₁₀; Phase #2: RbBr₂F₇). $R_p = 0.0571$; $wR_p = 0.0800$

Additionally, a sample of compound 1 with a mass of 0.3688 g was thermally decomposed in a corundum ampule at 500 °C for 3 hours which resulted in the loss of BrF₃. The residue of RbF had a mass of 0.0717 g, which is in correspondence with a calculated residual mass for a RbBr₂F₇/RbBr₃F₁₀ mixture with a mass ratio obtained from the Rietveld refinement (0.0755 g). The difference between the observed and calculated residual masses can be attributed to the presence of some amount of bromine trifluoride (or more probably, a saturated solution of RbBr_nF_(3n+1) in BrF₃).

b) Compound 2 ($CsBr_3F_{10}$)

Due to the extreme reactivity of this compound (presumably due to the presence of the saturated solution of $\text{CsBr}_n\text{F}_{(3n+1)}$ in BrF_3) it was not possible to measure a reliable powder X-ray diffraction

pattern even in the conditions described above. Thus, only the results of the thermal decomposition are available so far.

For this purpose, a sample of compound **2** with a mass of 0.4411 g was used for the decomposition. The observed residual mass of CsF equaled to 0.1290 g. The calculated residual mass for a pure sample of CsBr₃F₁₀ is 0.1191 g. The non-negligible difference can be attributed to the presence of CsBr₂F₇, similarly to the case of compound **1**. Thus, the mass ratio of CsBr₂F₇/CsBr₃F₁₀ can be calculated giving the following values: ω (CsBr₃F₁₀) = 74.1 %; ω (CsBr₂F₇) = 25.9 %.

c) Compound 3 ($RbBr_2F_7$)

The powder diffraction pattern of Compound **3** is shown in Figure S2.



Figure S2. Powder X-ray diffraction pattern of compound **3** measured at 293 K: experimental data (black crosses), calculated Rietveld profile (red), and difference profile (bottom, black). The calculated reflection positions are shown as black ticks (Phase #1: RbBrF₄; Phase #2: RbBr₂F₇). $R_p = 0.0983$; $wR_p = 0.1597$

According to the diffraction data, compound **3** contains (besides RbBr₂F₇) a significant amount of rubidium tetrafluoridobromate(III), RbBrF₄. The phase percentage obtained from the Rietveld refinement gives the following values: ω (RbBr₂F₇) = 75.0 %; ω (RbBrF₄) = 25.0 %. The fact that RbBr₂F₇ is not obtained as a pure phase confirms the previous statements in the literature.²⁷

A sample of compound **3** with a mass of 0.3326 g was thermally decomposed in a corundum ampule at 500 °C for 3 hours resulted in the loss of BrF₃. The residue of RbF had a mass of 0.1028 g, which is in correspondence with a calculated residual mass for a RbBr₂F₇/RbBrF₄ mixture with a mass ratio obtained from the Rietveld refinement (0.1049 g). The difference between the observed and calculated residual masses can be attributed to the presence of some amount of bromine trifluoride (or more probably, a saturated solution of RbBr_nF_(3n+1) in BrF₃).

Computational results

a) Structural optimizations

The unit cell parameters of the studied structures, optimized at the DFT-PBE0 level of theory, are listed in Table S1 together with comparisons to the corresponding experimental values. The cell parameters of the optimized structures are in line with the experimental values, the *a*-parameter of $CsBr_3F_{10}$ and the *b*-parameter of $RbBr_2F_7$ showing the only differences larger than 2%

Table S1. Unit cell parameters of the studied structures at PBE0-DFT level of theory. The percentages in parentheses show the difference to the experimental X-Ray structures.

	RbBr ₃ F ₁₀	CsBr ₃ F ₁₀	$RbBr_2F_7$	CsBr ₂ F ₇
Space group	<i>P</i> 2 ₁ (#4)	<i>P</i> 2 ₁ (#4)	$P2_1/c$ (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)
a (Å)	7.55 (-1.0%)	7.68 (3.2 %)	7.43 (-1.1 %)	7.70 (-0.1 %)
b (Å)	8.11 (-1.8 %)	8.27 (-1.6 %)	7.68 (-2.4 %)	7.89 (-1.6 %)
c (Å)	8.45 (-0.2 %)	8.75 (-0.9 %)	13.71 (0.1 %)	14.27 (0.8 %)
β (°)	115.6 (1.0 %)	116.0 (0.6 %)	123.5 (0.3 %)	124.3 (1.3 %)

b) Interpretation of the theoretical Raman spectra

The theoretical Raman spectra are compared with the experimental spectra in Figures S3-S5. The calculated spectra correspond well to the experimental spectra and enable the full interpretation of the spectral data (Table S2). All three experimental spectra show one peak at ~470 cm⁻¹ that does not arise from the compounds discussed here (this peak was observed also by Stein et al. in a previous study).²⁷



Figure S3. Experimental and theoretical Raman spectrum of $RbBr_3F_{10}$, together with a theoretical Raman spectrum of $RbBr_2F_7$ (intensities of $RbBr_2F_7$ scaled by a factor of 0.5)

Comparison of the experimental Raman spectrum of $RbBr_3F_{10}$ with the theoretical spectrum of $RbBr_3F_{10}$ and $RbBr_2F_7$ (Figure S3) reveals that the $RbBr_3F_{10}$ sample contains $RbBr_2F_7$ as impurity: The peak at 585 cm⁻¹ is the clearest evidence since no peaks from $RbBr_3F_{10}$ are expected in that region. The peak at ~615 cm⁻¹ arises from $RbBr_2F_7$ and the peak at ~624 cm⁻¹ from $RbBr_3F_{10}$. The $RbBr_2F_7$ peak at ~500 cm⁻¹ is mixed with $RbBr_3F_{10}$ peaks. The presence of $RbBr_2F_7$ impurities is in agreement with the experimental phase purity analysis carried out above.

Comparison of the experimental Raman spectrum of $RbBr_2F_7$ with the theoretical spectrum of $RbBr_2F_7$ and $RbBrF_4$ (Figure S4) reveals that the $RbBr_2F_7$ sample contains $RbBrF_4$ as impurity: The peak at ~450 cm⁻¹ is the clearest evidence since no peaks from $RbBr_2F_7$ are expected in that region. The $RbBrF_4$ peak at ~530 cm⁻¹ is also present in the spectrum of $RbBr_2F_7$. The presence of $RbBrF_4$ impurities is in agreement with the experimental phase purity analysis carried out above.



Figure S4. Experimental and theoretical Raman spectrum of $RbBr_2F_7$, together with a theoretical Raman spectrum of $RbBrF_4$ (intensities of $RbBrF_4$ scaled by a factor of 0.25)



Figure S5. Experimental and theoretical Raman spectrum of $CsBr_3F_{10}$, together with a theoretical Raman spectrum of $CsBr_2F_7$ (intensities of $CsBr_2F_7$ scaled by a factor of 0.25)

Comparison of the experimental Raman spectrum of $CsBr_3F_{10}$ with the theoretical spectrum of $CsBr_3F_{10}$ and $CsBr_2F_7$ (Figure S5) suggests that the $CsBr_3F_{10}$ sample contains $CsBr_2F_7$ as impurity: The peak at ~620 cm⁻¹ possesses a $CsBr_2F_7$ shoulder at ~615 cm⁻¹ and there is a weak feature at

about ~585 cm⁻¹ corresponding to $CsBr_2F_7$. The presence of $CsBr_2F_7$ impurities is in agreement with the experimental phase purity analysis carried out above.

Table S2. Peak assignment for the high-energy region of the theoretical Raman spectra. Only the Rb species are listed here, since the spectra for the Cs species can be interpreted in analogous way.

Raman	Assignment
peak (cm ⁻¹)	
$RbBr_3F_{10}$	
647	Symmetric Br–(terminal trans-F) stretch
631	Antisymmetric Br–(terminal trans-F) stretch
617	Antisymmetric Br-(terminal trans-F) stretch
566	Antisymmetric Br-(terminal cis-F) stretch
555	Antisymmetric Br-(terminal cis-F) stretch
540	Symmetric Br-(terminal cis-F) stretch
529	Symmetric Br-(terminal cis-F) stretch
~320– <mark>300</mark>	Br-(bridging F) stretch, coupled with Br-F out-of-plane bending
~ <mark>300</mark> –240	Br-(bridging F) stretch, coupled with F scissoring
$RbBr_2F_7$	
616	Symmetric Br–(terminal trans-F) stretch
589	Antisymmetric Br–(terminal trans-F) stretch
549	Antisymmetric Br-(terminal cis-F) stretch
522	Symmetric Br–(terminal cis-F) stretch
500	Symmetric Br–(terminal cis-F) stretch
350-300	Br-(bridging F) stretch, coupled with Br-F out-of-plane bending
280–260	Br–(bridging F) stretch, coupled with F scissoring

c) Interpretation of the theoretical IR spectra

The theoretical IR spectra are compared with the experimental spectra in Figures S6-S8. In comparison to the Raman spectra, the calculated IR spectra are not very helpful for interpreting the experimental spectra. A possible reason for the poor correspondence of the experimental and theoretical spectra is that the intensities of the solid-state IR spectra are strongly affected by absorption at the surface of the particles. Correction schemes for various particle shapes are available in CRYSTAL, but in this case, they result only in minor improvements. Hence, we show only the raw absorption spectrum for all calculated spectra. All experimental spectra appear to show a strong feature at ~ 480 cm⁻¹ that does not originate from any of the compounds characterized here.



Figure S6. Experimental and theoretical IR spectrum of $RbBr_3F_{10}$, together with a theoretical IR spectrum of $RbBr_2F_7$ (intensities of $RbBr_2F_7$ scaled by a factor of 0.50)



Figure S7. Experimental and theoretical IR spectrum of $RbBr_2F_7$, together with a theoretical IR spectrum of $RbBrF_4$ (intensities of $RbBrF_4$ scaled by a factor of 0.25)



Figure S8. Experimental and theoretical IR spectrum of $CsBr_3F_{10}$, together with a theoretical IR spectrum of $CsBr_2F_7$ (intensities of $CsBr_2F_7$ scaled by a factor of 0.25)

Unit cell coordinates of the studied structures

Lattice parameters (Å) and fractional atomic coordinates for the studied structures are listed below (PBE0/SVP level of theory). The coordinates are given in the CRYSTAL input format:

```
Space group number
Minimal set of lattice parameters a,b,c,\alpha,\beta,\gamma
Number of non-equivalent atoms in the asymmetric unit
<atomic number> <fractional x> < fractional y> < fractional z>
```

RbBr₃F₁₀

```
4
7.54900770 8.11188163 8.44937768 115.586450
14
    -9.389296637182E-02
                          4.412137770836E-01
                                               3.707683054984E-01
237
235
    -3.482088319431E-01
                         -3.034845437376E-01
                                              -3.175652179552E-01
235
    -1.761565961177E-01
                          2.506595000271E-01
                                              -1.701309329987E-01
                          4.350667677788E-01
                                              -1.160965177252E-01
     3.859044396793E-01
235
     1.990605292407E-01
                          3.107233743666E-01
                                              -2.985891023881E-01
9
9
     4.579146645302E-01 -2.278306316757E-01 -2.565506001642E-01
     -1.919146240425E-01
                          2.173385712696E-01
                                              -3.960878134641E-01
9
     -4.086946999688E-01
                          4.440525173460E-01
                                              -2.512444925230E-01
9
                         -3.663754556905E-01
                                              -3.785784738395E-01
9
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g
     -1.488879604454E-01
                          2.682202924422E-01
                                               5.829959440777E-02
9
     2.283192367778E-01
                          4.233159894319E-01 -9.351741506766E-03
9
     1.574069580801E-02
                          1.002935516577E-01
                                              -9.210487495897E-02
     -4.434179755336E-01 -4.397112956065E-01
                                               7.166048639348E-02
9
9
     -3.120179941607E-01 -9.553241469326E-02 -3.683319357061E-01
```

RbBr₂F₇

14 7.43194151 7.68431465 13.70975131 123.463219 10 237 -2.639616262120E-01 8.620062830448E-02 3.110298111289E-01 235 -4.357245738150E-01 -2.209644528492E-01 -4.810381386270E-01 235 -1.119979457548E-02 -4.251286738139E-01 3.755429188752E-01

9	2.994948351691E-01	-3.867057713509E-01	4.106632697891E-01
9	-6.417013367473E-03	-2.222102700367E-01	4.557570035942E-01
9	-4.122338749174E-01	-2.767773381560E-01	-3.403549007650E-01
9	-4.584848423944E-01	-1.529976831503E-01	3.814756641042E-01
9	-2.119578916772E-01	-7.211047340756E-02	-4.028966793904E-01
9	-2.292779988519E-02	3.732623653078E-01	2.964370068062E-01
9	-2.715284912208E-01	-4.821367973088E-01	3.486268764603E-01

RbBrF₄

140 6.20060576 11.74260362 3 235 -3.688149651427E-17 -5.0000000000E-01 -4.089336285253E-17 237 0.0000000000E+00 -1.837632034747E-19 2.50000000000E-01 9 -1.540166754613E-01 3.459833245387E-01 -1.145437755647E-01

CsBr₃F₁₀

4

-			
7.67	594067 8.27008958 8.7	5302528 116.024932	
14			
255	8.708072297933E-02	4.460204141289E-01	-3.753043398704E-01
235	1.871955263730E-01	2.519648124082E-01	1.655156650233E-01
235	3.585088172352E-01	-3.079685799616E-01	3.103793796024E-01
235	-3.830130319921E-01	4.335527005117E-01	1.087941772044E-01
9	4.110386385937E-01	4.454294233938E-01	2.361973965701E-01
9	-2.251609719310E-01	4.166232043456E-01	9.679608805837E-03
9	1.635796551367E-01	-3.627294859854E-01	3.763114553071E-01
9	2.067593178805E-01	2.234737642692E-01	3.860314609497E-01
9	1.563499669237E-01	2.651382317432E-01	-5.645484041004E-02
9	4.577818128309E-01	-4.389868927795E-01	-7.293775282961E-02
9	-4.532518953302E-01	-2.393056722125E-01	2.461758501566E-01
9	-2.039048750149E-01	3.073124652820E-01	2.860677182696E-01
9	3.365214463524E-01	-1.030602137951E-01	3.656036890130E-01
9	4.276568501777E-04	1.018958286514E-01	9.335430779805E-02

CsBr₂F₇

14 7.70009374 7.89469275 14.27365198 124.285385 10 2552.635167707906E-014.153218176827E-011.921064873198E-012352.267180953231E-034.274630072952E-013.797711529840E-01235-4.364992991026E-012.169301741229E-01-4.752876287768E-01 -1.073989929297E-04 -3.793793107633E-01 3.034452307457E-01 -4.730777048871E-03 2.32888722930EE-01 4.552589009395E-01 9 9 -4.730777048871E-03 2.328887229305E-01 4.552589009395E-01 9 -2.539549322147E-01 4.882558570817E-01 3.464931880212E-01 3.815981909105E-01 4.206742634168E-01 2.702238383230E-01 -3.408009823602E-01 9 3.062444557676E-01 -4.164909872148E-01 9 9 -2.194129406530E-01 7.208691415533E-02 -3.960468705635E-01 9 -4.506530073459E-01 1.520347255929E-01 3.943687112242E-01

Two gas phase structures for the Br₃F₁₀⁻ anion (XYZ format)

13					
D3	symmetry, DFT	-PBE0/def2-TZVP	Total Energy	-8719.192892505	a.u.
Br	1.1494690	-1.9909386	0.0000000		
Br	1.1494690	1.9909386	0.0000000		
Br	-2.2989379	0.000000	0.0000000		
F	0.000000	0.000000	0.0000000		
F	0.1667116	2.6971201	<mark>-1.3922804</mark>		
F	2.0304382	-3.5168221	0.0000000		
F	2.2524187	1.4929365	1.3922804		
F	2.2524187	-1.4929365	<mark>-1.3922804</mark>		
F	0.1667116	-2.6971201	1.3922804		
F	2.0304382	3.5168221	0.0000000		
F	-4.0608763	0.000000	0.0000000		
F	-2.4191303	1.2041836	1.3922804		
T.	-2 /101303	_1 20/1936	<u>1 3022001</u>		

<mark>13</mark>					
C2h	symmetry,	DFT-PBE0/def2-7	IZVP Total Energy	r = -8719.187250593	3 a.u.
Br	0.103877	7 -3.9588342	0.0000000		
Br	-0.000000	0.0000000	0.0000000		
Br	-0.103877	3.9588342	0.0000000		
F	0.906359	4 -1.7056787	0.0000000		
F	-0.906359	4 1.7056787	0.0000000		
F	0.072188	4.1031862	-1.8296499		
F	-0.366016	2 -5.6469163	0.0000000		
F	1.639579	0.8920441	0.0000000		
F	-1.639579	0 -0.8920441	0.0000000		
F	-0.072188	4.1031862	1.8296499		
F	0.366016	5.6469163	0.0000000		
F	-0.072188	4.1031862	-1.8296499		
E.	0 072100	1 1 1021062	1 9206400		

Crystallographic Details on the Outer Coordination Sphere of Br₃F₁₀⁻



Figure S9. The arrangement of Rb atoms around one $Br_3F_{10}^-$ anion. Displacement ellipsoids are shown at 70% probability level at 110 K. Symmetry operations for the generation of equivalent atoms: #1 1–x, –1/2+y, 1–z; #2 x, y, 1+z; #3 2–x, –1/2+y, 1–z; #4 2–x, 1/2+y, 1–z; #5 1–x, 1/2+y, 1–z; #6 –1+x, y, z.

In total, each $Br_3F_{10}^-$ anion is coordinated by seven rubidium atoms, among which Rb(1), Rb(1)#2, Rb(1)#3 and Rb(1)#4 are coordinated by two fluorine atoms each (F(3), F(5), F(6), F(8), F(9), F(10)), Rb(1)#5 binds only one fluorine atom F(2), and Rb(1)#1 and Rb(1)#6 share one common F(1) atom. Besides μ_3 -F(4), only one fluorine atom F(7) has no Rb atoms in the vicinity up to 4.743(2) Å, which is even farther than the distance between Rb and μ_3 -F being equal to 4.604(3) Å.

Such a coordination of $Br_3F_{10}^-$ yields each rubidium cation to be coordinated by eleven (or eight crystallographically different) fluorine atoms donated by seven different $Br_3F_{10}^$ anions. The Rb–F distances lie in the range of 2.994(2) to 3.073(3) Å (the next nearest fluorine atom is located 4.585(3) Å away). Among these seven $Br_3F_{10}^-$ anions, four anions share with the Rb cation two fluorine atoms each (in two cases F atoms are bonded to the

one Br atom; in the other two cases F atoms belong to different Br atoms of the same $Br_3F_{10}^{-}$ anion), while each of the other three anions gives only one fluorine atom.

Crystal structures of RbBr₃F₁₀ and RbBr₂F₇



Figure S10. The crystal structure of $RbBr_3F_{10}$. Displacement ellipsoids are shown at 70% probability level at 110 K.



Figure S11. The crystal structure of $RbBr_2F_7$. Displacement ellipsoids are shown at the 70% probability level at 110 K.

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