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*Published in:*  
Angewandte Chemie - International Edition

*DOI:*  
[10.1002/anie.201803708](https://doi.org/10.1002/anie.201803708)

Published: 26/10/2018

*Document Version*  
Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

*Please cite the original version:*  
Ivlev, S. I., Karttunen, A. J., Buchner, M. R., Conrad, M., & Kraus, F. (2018). The Interhalogen Cations  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$ . *Angewandte Chemie - International Edition*, 57, 14640–14644.  
<https://doi.org/10.1002/anie.201803708>

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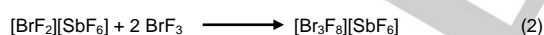
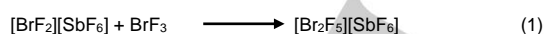
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The Interhalogen Cations  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$ Sergei I. Ivlev,<sup>[a]</sup> Antti J. Karttunen,<sup>[b]</sup> Magnus R. Buchner,<sup>[a]</sup> Matthias Conrad,<sup>[a]</sup> and Florian Kraus\*<sup>[a]</sup>Dedicated to the Technische Universität München on the Occurrence of its 150<sup>th</sup> Birthday

**Abstract:** We report on synthesis and characterization of so far unique polyhalogen cations containing  $\mu$ -bridging fluorine atoms. The  $[\text{Br}_2\text{F}_5]^+$  cation features a symmetric  $[\text{F}_2\text{Br}-\mu\text{-F}-\text{BrF}_2]$  bridge, whereas the  $[\text{Br}_3\text{F}_8]^+$  contains asymmetric  $\mu$ -F bridges. These fluoronium ions, obtained as  $[\text{SbF}_6]^-$  salts, were investigated using Raman and  $^{19}\text{F}$  NMR spectroscopy, as well as single crystal X-ray diffraction. Quantum chemical calculations were carried out for the gas-phase cations as well as for the solid state compounds. Population analyses show the  $\mu$ -F atoms to possess the most negative partial charge within the cations.

The chemistry of polyhalide anions experiences a renaissance and excellent reviews describe the rapid progress in the field.<sup>[1–8]</sup> A closer look on the currently known polyhalide anions (Table S1) unveils that interhalogen anions containing  $\mu$ -bridging F atoms are still rare. Only recently, anions containing  $\mu_2$ - and  $\mu_3$ -bridging F atoms were unambiguously reported.<sup>[9,10]</sup> In comparison to the polyhalide anions, much fewer polyhalogen cations are known (Table S2) and no multiply charged heteropolyhalogen cations seem to exist. Also, not a single cationic species containing  $\mu$ -bridging F atoms has been reported as of yet. That is, fluoronium ions are unknown for these systems.

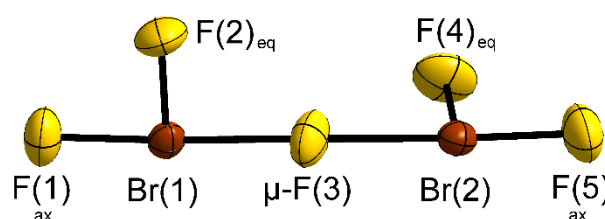
With  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$  we report on the first F-bridged heteropolyhalogen cations. The phase diagram of the two-component system  $\text{BrF}_3/\text{SbF}_5$  (Figure S1) has been investigated to some detail previously. However, the existing phases have not been characterized, with the exception of the congruent melting  $[\text{BrF}_2][\text{SbF}_6]$ .<sup>[11]</sup> The compounds  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$  and  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$  are obtained according to equations 1 and 2. Details of the syntheses are available in the Supporting Information.



Both syntheses resulted in slightly yellow crystals, which were investigated using X-ray diffraction and Raman spectroscopy. Due to the peritectic points in the phase diagram we were so far

unsuccessful in preparing both compounds in phase pure form from the two-component "melt".

The compound  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$ ,  $\mu$ -fluorido bis(difluoridobromine(III)) hexafluoridostibiate(V), melts at approximately 30 °C. It crystallizes in the monoclinic crystal system, space group  $P2_1/c$ , with  $a = 10.111(2)$ ,  $b = 9.0433(18)$ ,  $c = 9.986(2)$  Å,  $\beta = 94.16(3)^\circ$ ,  $V = 910.8(3)$  Å<sup>3</sup>,  $Z = 4$  at  $T = 100$  K. Further crystallographic details are available in the Supporting Information. The compound contains the  $[\text{Br}_2\text{F}_5]^+$  cation (Figure 1), which may be theoretically disassembled into two symmetrically  $\mu$ -F bridged  $[\text{BrF}_2]^+$  cations of the type  $[\text{F}_2\text{Br}-\mu\text{-F}-\text{BrF}_2]^+$ . Both Br atoms are coordinated in a trigonal planar manner which may be expected according to the VSEPR theory ( $\psi$ -trigonal bipyramidal due to the two lone pairs on each Br atom). The shape of the lone pairs is of course s- and p-orbital-like (no hybridization) as shown by quantum chemical calculations (see below). Also, the VSEPR approach fails for the prediction of the  $\text{Br}-\mu\text{-F}-\text{Br}$  angle, which should be more pointed.



**Figure 1.** The  $[\text{Br}_2\text{F}_5]^+$  cation of the crystal structure of  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$ . Anisotropic displacement parameters shown with 70% probability at 100 K. Selected atom distances [Å] and angles [°]:  $\text{Br}(1)-\text{F}(1)_{\text{ax}}$  1.738(3),  $\text{Br}(2)-\text{F}(5)_{\text{ax}}$  1.738(3),  $\text{Br}(1)-\text{F}(2)_{\text{eq}}$  1.708(3),  $\text{Br}(2)-\text{F}(4)_{\text{eq}}$  1.708(3),  $\text{Br}(1)-\mu\text{-F}(3)$  2.041(3),  $\text{Br}(2)-\mu\text{-F}(3)$  2.042(3);  $\text{Br}-\mu\text{-F}-\text{Br}$  164.36(15)°,  $\text{F}_{\text{ax}}-\text{Br}-\mu\text{-F}$  175.63(12) and 177.14(14)°.

The distances of the Br to the terminally bound F atoms F(2) and F(4), which will be called  $\text{F}_{\text{eq}}$  atoms in the following to make use of the simple picture of the  $\psi$ -trigonal bipyramid, are 1.708(3) Å. The distance of the Br atoms to the F atoms F(1) and F(5), called  $\text{F}_{\text{ax}}$  atoms from now on, are 1.738(3) Å. Thus, the  $\text{F}_{\text{ax}}$  atoms show a larger Br–F distance in comparison to the  $\text{F}_{\text{eq}}$  atoms. This finding is in accordance with the expectation for distances of a central atom to homoleptic ligands in a trigonal bipyramidal coordination mode. The observed Br–F distances compare nicely with those obtained from compounds containing "isolated"  $[\text{BrF}_2]^+$  cations. So far, only  $[\text{BrF}_2][\text{AuF}_4]$ ,<sup>[12]</sup>  $[\text{BrF}_2][\text{SbF}_6]$ ,<sup>[13]</sup> and  $[\text{BrF}_2][\text{GeF}_6]$ <sup>[14]</sup> have been characterized by single-crystal X-ray diffraction. The Br–F distances are approximately 1.69(2) Å for these cases. As may be expected from the higher coordination number of the  $\mu$ -F atom, the  $\mu\text{-F}-\text{Br}$  distances are longer with 2.041(3) and 2.042(3) Å in comparison to the axial and terminal Br–F bonds. The  $\mu\text{-F}-\text{Br}$  distances are identical within the standard deviation. This clearly shows that the  $[\text{Br}_2\text{F}_5]^+$  cation cannot be regarded as a  $[\text{BrF}_2]^+$

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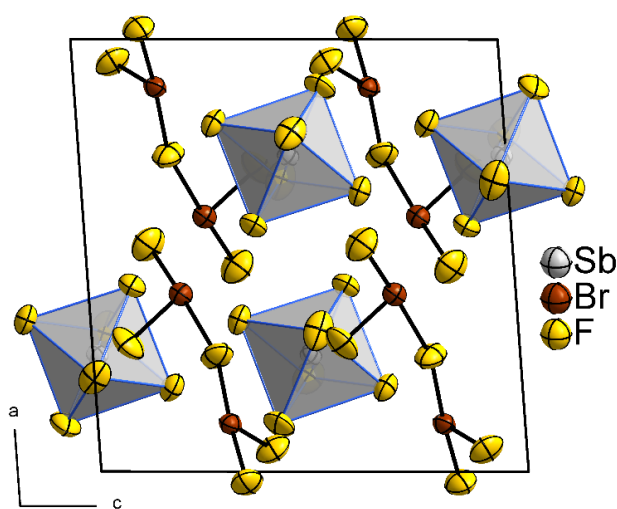
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cation with a loosely bound  $\text{BrF}_3$  molecule like  $[\text{F}_2\text{Br}^+\cdots\text{F}-\text{BrF}_2]$ , but must be seen as a symmetrically bridged cation.

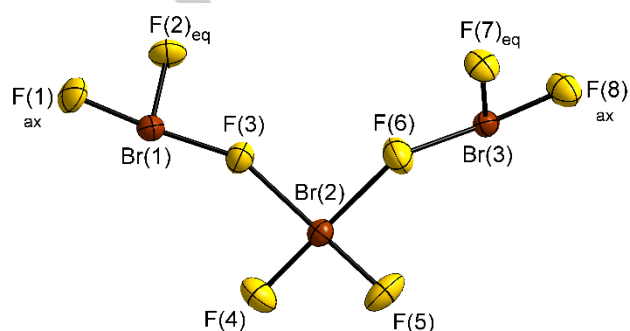
The crystallographic site symmetry of the  $[\text{Br}_2\text{F}_5]^+$  cation is only  $C_1$ . The bond angles between the axial  $\text{F}_{\text{ax}}$  atoms and the bridging F atom,  $\text{F}_{\text{ax}}-\mu\text{-F}$ , are almost linear with  $175.63(12)$  and  $177.14(14)^\circ$ , and also the  $\text{Br}-\mu\text{-F}-\text{Br}$  angle deviates with  $164.36(15)^\circ$  only a little from  $180^\circ$ . The  $\mu\text{-F}-\text{Br}-\text{F}_{\text{eq}}$  angles are with  $84.69(12)$  and  $86.00(14)^\circ$  strikingly close to  $90^\circ$ . Again, this may be expected from the VSEPR model but is also quantum chemically calculated for the gas-phase cation. Table S3 contains a compilation of observed and calculated atom distances and angles for the  $[\text{Br}_2\text{F}_5]^+$  cation. The agreement of the calculated atom distances with those obtained from the crystal structure is very good, for further details see the Supporting Information. The crystal structure is shown in Figure 2.

A quantum chemical structure optimization on the three-dimensional periodic solid using DFT-PBE0 method within the CRYSTAL14 software<sup>[15,16]</sup> shows only small deviations between the observed and calculated lattice parameters and atom coordinates (Table S3, S7). Harmonic frequency calculation confirms the structure as a true local minimum. The calculated Raman spectrum is in a good agreement with the measured one (Table S5). If the Raman spectrum of solid  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$  (Figure S3) is compared to the one of  $[\text{BrF}_2][\text{SbF}_6]$ , very similar band positions are observed for the  $[\text{SbF}_6]^-$  anions, as expected. The virtual  $\text{BrF}_2$  units of  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$  show stretch and deformation modes ( $600 - 700 \text{ cm}^{-1}$ ,  $260 - 340 \text{ cm}^{-1}$ , respectively) which nicely compare to those of  $[\text{BrF}_2][\text{SbF}_6]$ . However, an overlap of bands with those of the anion is present as well as a coupling of some of the modes. In addition to these bands, the  $\text{Br}-\mu\text{-F}-\text{Br}$  vibration is observed at circa  $440 \text{ cm}^{-1}$ . From the quantum chemical calculations for the solid, two Raman-active bands are obtained for this vibration as two symmetry-independent Br atoms are present in the crystal structure. With calculated values of  $429$  and  $431 \text{ cm}^{-1}$  these bands are so nearby that the closeness of the  $[\text{Br}_2\text{F}_5]^+$  cation to  $C_2$  symmetry is very nicely shown.



**Figure 2.** A section of the crystal structure of  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$ .  $[\text{SbF}_6]^-$  anions are shown as transparent polyhedra. Anisotropic displacement parameters shown with 70% probability at 100 K. CSD-434288.

The compound  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$ , bis (trifluoridobromine(III)) difluoridobromine(III) hexafluoridostibate(V), melts between  $-30$  and  $-20^\circ\text{C}$ . It crystallizes in the monoclinic crystal system, space group  $P2_1$ , with  $a = 9.3783(1)$ ,  $b = 9.3550(19)$ ,  $c = 13.133(3) \text{ \AA}$ ,  $\beta = 91.95(3)^\circ$ ,  $V = 1151.5(4) \text{ \AA}^3$ ,  $Z = 4$  at  $T = 100 \text{ K}$ . The crystal structure was refined as a non-merohedral twin along  $[001]$ , further details are available in the Supporting Information. The compound contains two symmetry-independent  $[\text{Br}_3\text{F}_8]^+$  cations. Due to crystallographic site symmetry, their point group symmetry is only  $C_1$ . However, both are structurally so similar (Table S4), that only one will be discussed in the following (Figure 3).



**Figure 3.** One of the two symmetry-independent  $[\text{Br}_3\text{F}_8]^+$  cations of the compound  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$ . Anisotropic displacement parameters shown with 70% probability at 100 K. Selected atom distances [ $\text{\AA}$ ] and angles [ $^\circ$ ]:  $\text{Br}(1)-\text{F}(1)_{\text{ax}}$   $1.741(7)$ ,  $\text{Br}(1)-\text{F}(2)_{\text{eq}}$   $1.711(7)$ ,  $\text{Br}(1)-\mu\text{-F}(3)$   $1.986(7)$ ,  $\text{Br}(2)-\mu\text{-F}(3)$   $2.177(9)$ ,  $\text{Br}(2)-\text{F}(4)$   $1.721(7)$ ;  $\text{Br}(1)-\mu\text{-F}(3)-\text{Br}(2)$   $143.4(4)^\circ$ ,  $\text{Br}(2)-\mu\text{-F}(6)-\text{Br}(3)$   $146.5(4)^\circ$ .

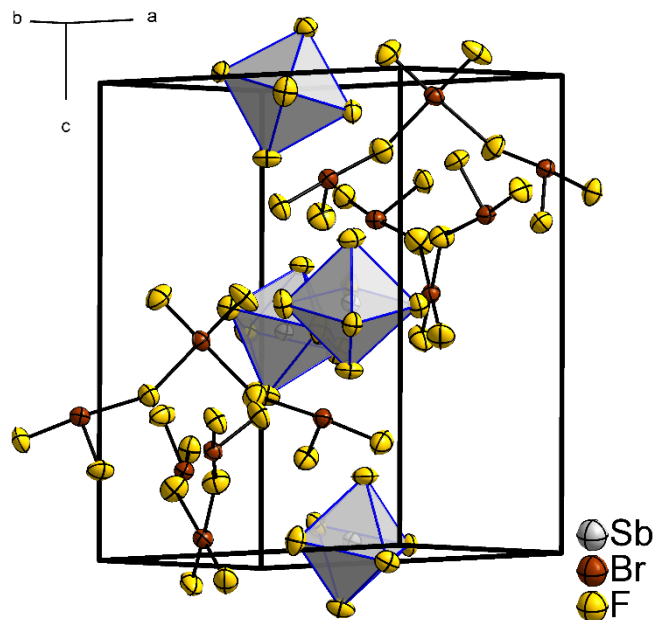
The coordination sphere of the outer Br atoms can be described best as  $\psi$ -trigonal bipyramidal. Again, terminally bound F-atoms are present, denominated as  $\text{F}_{\text{ax}}$  and  $\text{F}_{\text{eq}}$ . The  $\mu\text{-F}$  atoms are again in axial position, similar to the case of the  $[\text{Br}_2\text{F}_5]^+$  cation. The central Br atom is coordinated by four F atoms in a trapezoid and almost planar manner. The two bridging  $\mu\text{-F}$  atoms are considerably further away from the central Br atom ( $2.177(9)$  and  $2.154(8) \text{ \AA}$ ) compared to the terminally bound F atoms  $\text{F}(4)$  and  $\text{F}(5)$  ( $1.721(7)$  and  $1.727(7) \text{ \AA}$ ). The atom distances of the  $[\text{Br}_3\text{F}_8]^+$  cation are very well in line with those of the  $[\text{Br}_2\text{F}_5]^+$  cation, as the  $\text{Br}-\text{F}_{\text{ax}}$  as well as the  $\text{Br}-\text{F}_{\text{eq}}$  distances agree within the standard deviation. However, the  $\mu\text{-F}-\text{Br}$  distances of the two species diverge from this observation. Therefore, the  $[\text{Br}_3\text{F}_8]^+$  cation is described best by an approximate  $C_{2v}$ -symmetric, central  $[\text{BrF}_2]^+$  unit, to which two  $\text{BrF}_3$  molecules are bound. The  $\text{Br}-\text{F}$  distances of both  $\text{BrF}_3$  molecules, agree nicely with those of pure, solid bromine trifluoride.<sup>[17,18]</sup> Also, both  $\text{BrF}_3$  molecules seem to avoid each other sterically as the two Br atoms reside about  $0.85 \text{ \AA}$  above and below the virtual, almost planar, central  $[\text{BrF}_4]$ -trapezoid and the  $\text{F}_{\text{eq}}$  atoms point in different directions. Torsion angles are available in Table S4. The arrangement of the two symmetry-independent  $[\text{Br}_3\text{F}_8]^+$  cations of  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$  is as if they would embrace each other (Figure 4). Together with the

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$[\text{SbF}_6]^-$  anions, strands are formed. As the strands are perpendicular and otherwise essentially similar to each other, this appears to result in the similarity of the lattice parameters  $a$  and  $b$ , the small deviation of  $\beta$  from  $90^\circ$ , as well as the twin operation  $\bar{4}$  along  $[001]$ . We therefore speculate that a tetragonal high-temperature modification of  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$  exists which should be stable slightly below the melting point of the compound. Further details of the crystal structure as well as further comments to the high-temperature modifications are available in the Supporting Information.

The quantum chemical structure optimization for the three-dimensional periodic solid leads also to only small deviations between observed and calculated lattice parameters and atom coordinates (Table S4, S6). The optimized structure is again a true local minimum and the calculated Raman spectrum is in a surprisingly good agreement with the one obtained on molten  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$  (Figure S4). Thus we assume that the species observed for the crystalline solid and the liquid phase should be very similar. We conclude that the  $[\text{Br}_3\text{F}_8]^+$  cation is also stable in the melt at room temperature.

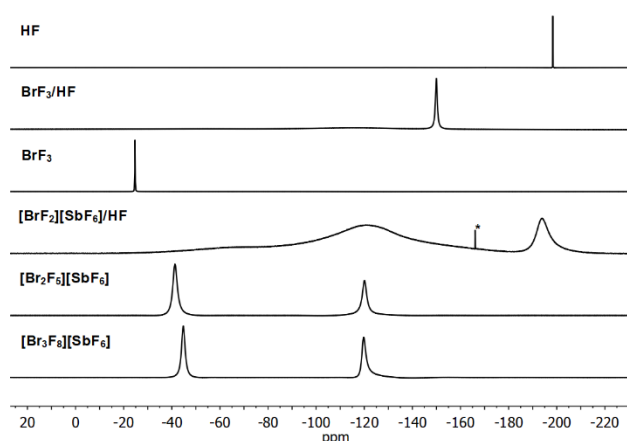
According to equations 1 and 2, Gibbs free energies were calculated for the formation of  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$  and  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$ . For the first it amounts to  $\Delta G^{298} = -10$  kJ/mol and  $\Delta G^{398} = -13$  kJ/mol, for the latter to  $\Delta G^{298} = -14$  kJ/mol and  $\Delta G^{398} = -20$  kJ/mol. The reactions can therefore be seen as exothermic under the conditions of the syntheses. Further details are available in the Supporting Information.



**Figure 4.** A section of the crystal structure of  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$ . The  $[\text{SbF}_6]^-$  anions are shown as transparent polyhedra. Anisotropic displacement parameters shown with 70% probability at 100 K. CSD-434289.

The melts of both compounds were investigated using  $^{19}\text{F}$  NMR spectroscopy. In the spectra shown in Figure 5, we only observe

two signals for each melt, with chemical shifts of  $-41.32$  and  $-120.10$  ppm for  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$ , and  $-44.78$  and  $-119.77$  ppm for  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$  (Table S8). The signal with the chemical shift of circa  $-120$  ppm is due to the  $[\text{SbF}_6]^-$  anion and agrees very well with the literature.<sup>[19]</sup> The other signals are therefore assigned to the  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$  cations. The signal of the  $[\text{Br}_2\text{F}_5]^+$  cation appears a little more low-field shifted in comparison to that of the  $[\text{Br}_3\text{F}_8]^+$  cation. This observation may be expected as the positive charge of the latter cation is delocalized over more atoms which should result in a higher electron density on the  $^{19}\text{F}$  nuclei. The signals of both cations are shifted to much higher fields when compared to pure, liquid  $\text{BrF}_3$ . We observe its chemical shift at  $-24.68$  ppm, which is close to literature reports.<sup>[20]</sup> The shift to higher fields is likely due to the exchange of the  $^{19}\text{F}$  atoms of the  $[\text{SbF}_6]^-$  anions with the F atoms of the  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$  cations. Due to this exchange process, both signals are shifted towards each other.<sup>[21]</sup> The existence of such exchange processes is further substantiated by the relatively large line width.<sup>[22]</sup> This dynamic exchange also results in the observation of only one averaged signal for all the F atoms of the cations. In contrast to  $[\text{Br}_2\text{F}_5][\text{SbF}_6]$  and  $[\text{Br}_3\text{F}_8][\text{SbF}_6]$ , the compound  $[\text{BrF}_2][\text{SbF}_6]$  is a solid at room temperature (melting point circa  $130^\circ\text{C}$ <sup>[11]</sup>). So, no  $^{19}\text{F}$  NMR spectrum could be obtained from the pure substance. From a solution of  $[\text{BrF}_2][\text{SbF}_6]$  in anhydrous hydrogen fluoride (aHF) (1:30 Mol-%), three very broad signals are observed in the  $^{19}\text{F}$  NMR spectrum with chemical shifts of  $-65.81$ ,  $-120.49$ , and  $-193.88$  ppm. These are assigned to the molecules  $[\text{BrF}_2]^+$ ,  $[\text{SbF}_6]^-$ , and HF, respectively. The chemical shift of the  $[\text{SbF}_6]^-$  anion is again in good agreement with the literature,<sup>[19]</sup> whereas the signal of HF appears slightly shifted to lower field in comparison to pure aHF.<sup>[23]</sup> The signal of the  $[\text{BrF}_2]^+$  cation is shifted by circa 8 ppm in comparison to the literature, where the measurements were conducted at  $-40^\circ\text{C}$ , however.<sup>[24]</sup> The very broad line widths in the system  $[\text{BrF}_2][\text{SbF}_6]/\text{aHF}$  have been reported previously. Very likely, these are due to the exchange of F atoms in between the molecules. For further details, see the Supporting Information.<sup>[24]</sup>

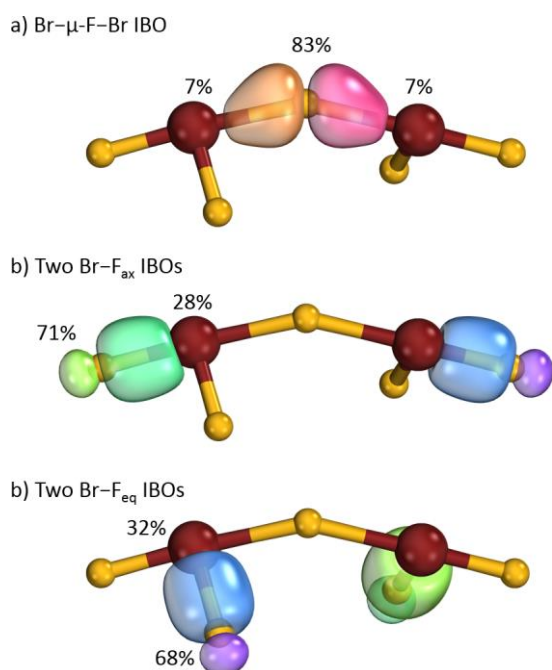


**Figure 5.**  $^{19}\text{F}$  NMR spectra of aHF, of a 1:8-Mol-% solution of  $\text{BrF}_3$  in aHF, of pure  $\text{BrF}_3$ , of a 1:30-Mol-% solution of  $[\text{BrF}_2][\text{SbF}_6]$  in aHF, and of the melts of the formal composition „ $[\text{Br}_2\text{F}_5][\text{SbF}_6]$ “ and „ $[\text{Br}_3\text{F}_8][\text{SbF}_6]$ “. The signal marked with an asterisk is due to an unknown impurity.

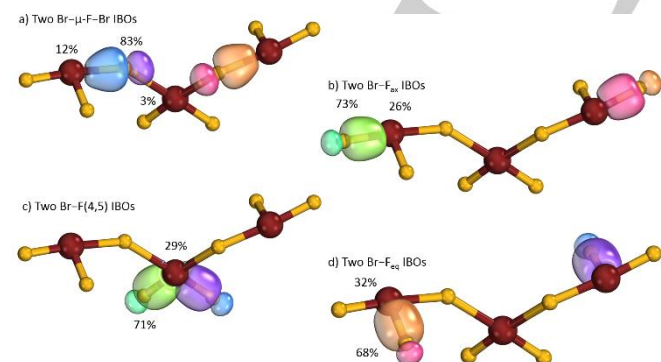


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The molecular structures of both cations were optimized at the DFT-PBE0/def2-TZVP level of theory.<sup>[25–31]</sup> In the case of  $[\text{Br}_2\text{F}_5]^+$ , the optimization led to a  $C_2$ -symmetric ground state (Figure 6). Atom distances and angles obtained this way are in excellent agreement with those obtained from the single crystal structure. The only exception is the Br- $\mu$ -F-Br angle, which is for the gas-phase species a little smaller (152.9°) in comparison to the solid state structure (164.36(15)°).



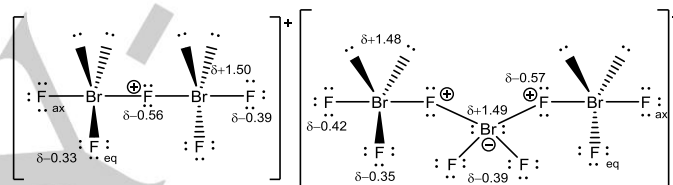
**Figure 6.** Intrinsic bond orbitals (IBOs) showing the Br-F bonds of  $[\text{Br}_2\text{F}_5]^+$ . Percentages indicate the contribution of each atom to the IBO. The larger a percentage, the more polarized is the covalent bond. If the summation does not add up to 100%, then other atoms contribute – less than 1% – to the IBO. For further details, see the Supporting Information. F atoms in golden, Br atoms in reddish-brown color.



**Figure 7.** Intrinsic bond orbitals (IBOs) of the Br-F bonds of the cis- $[\text{Br}_3\text{F}_8]^+$  cation. For further details, see the caption of Figure 6.

For  $[\text{Br}_3\text{F}_8]^+$ , a  $C_2$ -symmetric ground state (Figure 7) is obtained from the structure optimization. It agrees well with the molecular structure obtained from single-crystal diffraction and so the calculated atomic distances are very close to the experimentally determined ones. However, the  $[\text{SbF}_6]^-$  anions seem to strongly influence the molecular structure of the cation in the solid, as the torsion angles within the gas-phase cation clearly diverge to those of the cation in the solid. Further details are available in the Supporting Information.

Using the simple VSEPR concept, the structure prediction of the cations is limited (Scheme 1), as a more pointed Br- $\mu$ -F-Br angle is expected. As the molecules are cations and contain  $\mu_2$ -bridging F atoms, the analogy to the fluoronium ions  $[\text{H}_2\text{F}]^+$  and  $[\text{H}_3\text{F}_2]^+$ , becomes obvious. We may therefore speak of the Fluoronium ions  $[(\text{F}_2\text{Br})_2\text{F}]^+$  and  $[(\text{F}_2\text{Br})_3\text{F}_2]^+$ . One should not mix up the terms “formal charge”, “partial charge”, and “charge”. Also, the “onium-nomenclature” does not refer to the atom carrying the formal charge, but on the whole, positively charged molecule. It seems there was some confusion in the past,<sup>[32,33]</sup> only sparked by the imprecise language usage of “scientific” magazine writers.



**Scheme 1.** Lewis structures of the  $C_2$  symmetric  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$  cations. Partial charges of the atoms, obtained from IAO-analyses, are shown.

In order to describe the chemical bonds of the cations, population analyses were carried out using natural population analysis (NPA) and the Intrinsic Atomic Orbital method (IAO), see Table S9.<sup>[30,34]</sup> The different methods yield very nicely agreeing trends for both cations. As expected, the Br atoms of the cations carry partial positive charge (each +1.5). The  $\text{F}_{\text{eq}}$  atoms show the least negative partial charge, whereas the  $\mu$ -F atoms carry the most negative partial charges. Therefore, the  $\mu$ -F-Br bonds can be regarded as the most polarized covalent bonds of these molecular cations, whereas the Br- $\text{F}_{\text{eq}}$  bonds are less polarized. This is shown in Figure 7 and 8 where the chemical bonds are shown with the aid of Intrinsic Bond Orbitals (IBOs). Their shape shows the polarization of the bond.<sup>[30,34]</sup> The IBOs of a  $\text{BrF}_3$  molecule and of a  $[\text{BrF}_2]^+$  cation are shown for comparison in Figure S7.

In conclusion, we have shown that the cations  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$  can be formally derived from the fluoronium ions  $[\text{H}_{n+1}\text{F}_n]^+$  by replacing the protons by  $[\text{BrF}_2]^+$  units. The species  $[(\text{F}_2\text{Br})_{n+1}\text{F}_n]^+$  ( $n = 1, 2$ ) result. The  $[\text{Br}_2\text{F}_5]^+$  cation features a symmetric Br- $\mu$ -F-Br bridge whereas the  $[\text{Br}_3\text{F}_8]^+$  cation is described best as a central, almost  $C_{2v}$  symmetric  $[\text{BrF}_2]^+$  cation, to which two  $\text{BrF}_3$  molecules are bound. Population analyses show, as is expected by the differences in electronegativity of the atoms involved, that the Br atoms of the cations possess positive partial charge. The  $\mu$ -bridging F atoms are the ones with the highest negative partial charge.  $^{19}\text{F}$  NMR spectra show that the molecular cations seem to exist also in the melts of the

compounds, that the F atoms have a high mobility, and that vivid exchange processes are occurring in between them.

We expect that further cations of the general composition  $[\text{Br}_n\text{F}_{3n-1}]^+$  exist. Attempts to obtain the corresponding compounds of chlorine and iodine,  $[\text{X}_n\text{F}_{3n-1}]^+$  ( $\text{X} = \text{Cl}, \text{I}$ ), are in progress. Time will tell if cations of the compositions  $[\text{X}_n\text{F}_{5n-1}]^+$  and  $[\text{X}_n\text{F}_{7n-1}]^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) can be obtained.

## Acknowledgement

We would like to especially thank the Deutsche Forschungsgemeinschaft. A. J. Karttunen thanks the Academy of Finland (Grant 294799), as well as the Finnish IT-Center for science CSC. For the usage of the Raman microscope we thank Prof. Dr. Bernhard Roling.

**Keywords:** Fluoronium ions • Heteropolyhalogen cations • Bromine trifluoride • Antimony pentafluoride • crystal structure

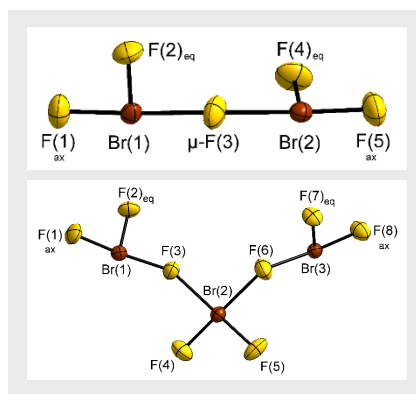
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## Entry for the Table of Contents

## COMMUNICATION

The fluoronium ions  $[\text{Br}_2\text{F}_5]^+$  and  $[\text{Br}_3\text{F}_8]^+$  are the first polyheteroalogen cations with bridging F-atoms. They have been isolated in form of their  $[\text{SbF}_6]^-$  salts.



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