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$[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$ – An Unprecedented Molecular Fluoridobromate(V) Anion in $\text{Cs}[\text{Br}_3\text{F}_{16}]$

Martin Möbs,^[a] Tim Graubner,^[a] Antti J. Karttunen,^[b] and Florian Kraus*^[a]

The reaction of $\text{Cs}[\text{BrF}_6]$ with BrF_5 gave the compound $\text{Cs}[\text{Br}_3\text{F}_{16}]$ with the unprecedented propeller-shaped, C_3 -symmetric $[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$ anion. All other currently known fluoridobromates(V) contain only octahedral $[\text{BrF}_6]^-$ anions, which, unlike the related $[\text{IF}_6]^-$ anions, never exhibited stereochemical activity of the lone pair on the Br atoms. Despite the same coordination number of six for the Br atom in the $[\text{BrF}_6]^-$ and $[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$ anions, the longer $\mu_3\text{-F-Br}$ bonds provide

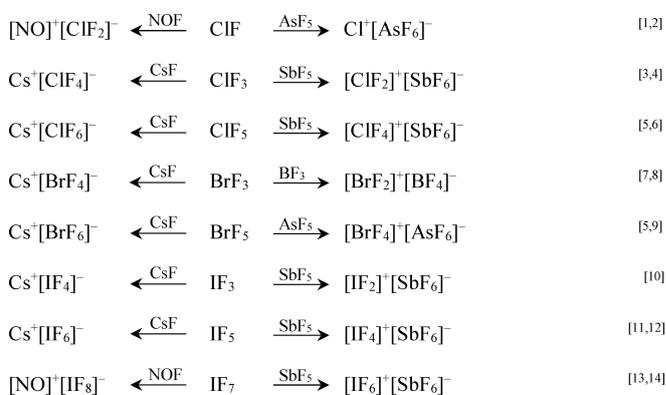
additional space, allowing the lone pairs on the Br atoms to become stereochemically active. $\text{Cs}[\text{Br}_3\text{F}_{16}]$ was characterized by single-crystal X-ray diffraction, Raman spectroscopy, and quantum-chemical calculations for both the solid-state compound and the isolated anion at 0 K. Intrinsic bond orbital calculations show that the $\mu_3\text{-F-Br}$ bond is essentially ionic in nature and also underpin the stereochemical activity of the lone pairs of the Br(V) atoms.

Introduction

Halogen fluorides can both act as F^- acceptors when reacted with fluorobasic compounds, for example alkali metal fluorides, or as F^- donors in presence of strong Lewis acids. This results in the respective formation of corresponding fluoridohalogenate anions or fluoridohalonium cations as exemplified in Scheme 1.

Recently, several review articles on polyhalides and polyinterhalides have been published,^[15–19] as the field gained new interest. The currently known cations and anions are summarized in Tables S1 and S2 in the Supporting Information. Analyzing these tables leads to the conclusion that halogen fluoride ions containing μ - and μ_3 -bridging F atoms are particularly rare, and most of the known representatives have been obtained only within the last decade. These include the anions $[(\mu_3\text{-F})(\text{ClF}_3)_3]^-$,^[20] $[(\mu_3\text{-F})(\text{ClF}_3)_3]^-$,^[21] $[(\mu\text{-F})(\text{BrF}_3)_2]^-$,^[22–24] $[(\mu_3\text{-F})(\text{BrF}_3)_3]^-$,^[24] and the different isomers of the $[\text{Br}_4\text{F}_{13}]^-$ ^[25] and $[\text{I}_3\text{F}_{16}]^-$ anions.^[9,26] To the best of our knowledge, only $[\text{Br}_2\text{F}_5]^+$ and $[\text{Br}_3\text{F}_8]^+$ are known on the cationic side, as of yet.^[27]

These halogen fluoride anions all consist of two or three halogen fluoride moieties ClF , XF_3 ($X=\text{Cl}$, Br), XF_5 ($X=\text{Br}$, I)



Scheme 1. Examples of reactions of halogen fluorides with F^- donors and F^- acceptors.

forming “oligonuclear” complex ions considering the heavier halogen atoms X as the centers which are μ - or μ_3 -bridged by a F^- anion. The only exceptions known so far are the $[\text{Br}_4\text{F}_{13}]^-$ anions, of which two isomers exist: a branched one that is formally formed by two additional BrF_3 molecules attached each to a different F atom of the $[(\mu\text{-F})(\text{BrF}_3)_2]^-$ subunit and the second one consists of a $[(\mu_3\text{-F})(\text{BrF}_3)_3]^-$ building block with formally one additional BrF_3 molecule attached to one of the outer F atoms.^[25] Another exception is the anion in the compound $\text{Cs}[\text{I}_3\text{F}_{16}]$ in which the coordination number of the I atoms of seven leads to a three-dimensional infinite anion-network with μ - and μ_3 -bridging F atoms.^[9]

Of all known oligonuclear/polynuclear halogen fluoride ions, $[\text{I}_3\text{F}_{16}]^-$ was the first to be discovered in form of the compounds $\text{AF} \cdot 3\text{IF}_5$ ($A=\text{K}$, Rb , Cs).^[26] Crystal structures were later reported for the K and Cs compound, obviously without recognizing that structurally differing $[\text{I}_3\text{F}_{16}]^-$ anions were present.^[9] $\text{K}[\text{I}_3\text{F}_{16}]$ contains molecular $[(\mu_3\text{-F})(\text{IF}_5)_3]^-$ anions,^[9] which represent the heavier congener of $[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$ presented here, while in $\text{Cs}[\text{I}_3\text{F}_{16}]$ a three-dimensional infinite anionic network is present. $\text{Cs}[\text{I}_3\text{F}_{16}]$ is directly accessible by the reaction of CsF and IF_5 at 60°C and shows a negligible

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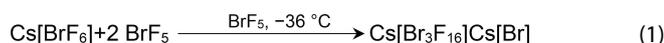
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dissociation pressure at room temperature, likely because of the anionic network.^[26] When heated in vacuo to 90 °C, the compound loses two equivalents of IF₅ and Cs[IF₆] is formed.^[26] The compounds Cs[(μ-F)(BrF₃)₂] and Cs[(μ₃-F)(BrF₃)₃] were obtained by the reaction of CsCl with stoichiometric amounts of BrF₃.^[24] Both compounds are stable at room temperature, and no sign of decomposition was observed even under reduced pressure.^[24] In contrast, the BrF₃-richer compound Ba₂[Br₃F₁₀]₂[Br₄F₁₃]₂ containing molecular [Br₄F₁₃]⁻ anions was reported to be sensitive towards BrF₃-loss at ambient temperature and pressure and decomposed under formation of Ba[BrF₄]₂. In addition, the compound undergoes a phase transition at about 10 °C. A BrF₃-moiety is cleaved off from the anion above that temperature resulting in spatially separated BrF₃ molecules of crystallization in the isomeric compound Ba[(μ₃-F)(BrF₃)₃]₂-BrF₃.^[25] The compounds containing trinuclear anions of ClF₃ and ClF, namely Cs[(μ₃-F)(ClF₃)₃] and [NMe₄][(μ₃-F)(ClF)₃], show even lower thermal stability and thus have to be prepared and handled at temperatures of 0 °C or even lower.^[20,21] At elevated temperature, the loss of the respective halogen fluoride and the formation of room temperature stable [ClF₄]⁻ or [ClF₂]⁻ salts, respectively, has to be expected.^[20,21,28,29]

Here we present the synthesis and characterization of the compound Cs[(μ₃-F)(BrF₃)₃] containing an unprecedented fluoride-bridged Br(V) anion. In addition, the compound represents the first example of a fluoridobromate(V) anion with stereochemically active lone pairs on the Br atoms.

Results and Discussion

At room temperature, CsF reacts with an excess of BrF₅ under formation of the compound Cs[BrF₆].^[30,31,9] Cooling of a solution of CsF or Cs[BrF₆], respectively, in an excess of BrF₅ to -36 °C, led to formation of colorless crystals of which the composition was determined by single-crystal X-ray diffraction to be Cs[Br₃F₁₆]. The formation of the compound may be described by Equation (1); the experimental and crystallographic details are given in the Supporting Information, Tables S3–S5.



Cs[Br₃F₁₆] crystallizes in the cubic crystal system, space group *P* $\bar{4}3n$ (No. 218, *abel*⁶, *cP*160) with the lattice parameter *a* = 13.4868(6) Å, *V* = 2453.2(3) Å³, *Z* = 8, at *T* = 100 K. The compound contains a molecular, C₃-symmetric [(μ₃-F)(BrF₃)₃]⁻ anion that consists of a central, μ₃-bridging F⁻ anion with three BrF₅ molecules attached so that a pyramidal shape results around the μ₃-F atom. The coordination number of the Br atoms is six.

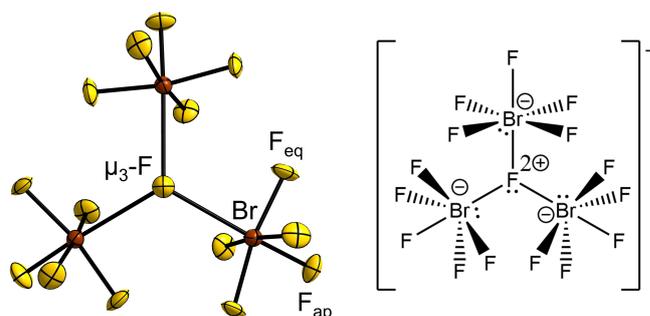


Figure 1. Left: A section of the crystal structure of Cs[Br₃F₁₆] showing the [(μ₃-F)(BrF₃)₃]⁻ anion viewed along its C₃ axis. Displacement ellipsoids are shown at 70% probability level at 100 K. Selected bond lengths (Å) and angles (°): Br–F_{ap} 1.709(6), Br–F_{eq} 1.785(4) to 1.799(5), μ₃-F–Br 2.462(2), μ₃-F–Br–F_{ap} 165.0(3), F_{ap}–Br–F_{eq} 83.4(3) to 84.6(3), Br–μ₃-F–Br 115.9(2). Right: Structural formula of the title anion.

Figure 1 shows the anion within the crystal structure and its Lewis formula.

The bond length of the Br to the apical F atom, Br–F_{ap}, is the shortest with 1.709(6) Å, while the bonds to the equatorial F atoms, Br–F_{eq}, are in the range from 1.785(4) to 1.799(5) Å. Thus, the bond lengths are slightly elongated compared with the Br–F_{eq} bond lengths in solid BrF₅ that range from 1.741(2) to 1.777(2) Å and also for the Br–F_{ap} bond which is 1.678(2) Å long.^[32] The elongation can be attributed to the weakening of the Br–F bonds due to the interaction of the LUMO of the BrF₅-moiety with one of the lone pairs of the μ₃-F⁻ anion, the increasing coordination number and the negative charge of the anion. This is a frequently observed phenomenon for polyhalogen and polyinterhalogen anions.^[19] In the case of Cs[(μ₃-F)(BrF₃)₃] however, the elongation of the Br–F_{ap} and Br–F_{eq} bonds is comparably small, so that the anion can be best described as a central μ₃-F anion bridging three BrF₅ molecules. This is also consistent with the quantum-chemical description of the bonding situation discussed below. As expected, the μ₃-F–Br bond is with 2.462(2) Å by far the longest bond within the anion. Compared to the μ₃-F–X bond lengths in other trinuclear halogen fluoride anions (X = Cl, Br, I), the one in the [Br₃F₁₆]⁻ anion is in the upper range similar to the respective bond lengths in the [I₃F₁₆]⁻ anion between 2.477 and 2.514 Å.^[9] Within the known anions, the μ₃-F–X bond lengths increase in the order X = Cl, Br, I and with increasing coordination number/oxidation state of the X atoms, see Table 1, and can therefore mainly be attributed to increasing overall steric bulkiness of the halogen fluoride moieties.

The μ₃-F atom resides 0.503(5) Å above a virtual plane spanned by the Br atoms and the pyramidalization of the anion

Table 1. μ₃-F–X bond lengths (X = Cl, Br, I) within the known trinuclear halogen fluoro anions.

[(μ ₃ -F)(XF _m) _n] ⁻	[(μ ₃ -F)(ClF ₃) ₃] ^{-[20]}	<	[(μ ₃ -F)(ClF ₃) ₃] ^{-[21]}	<	[(μ ₃ -F)(BrF ₃) ₃] ^{-[24]}	<	[(μ ₃ -F)(BrF ₃) ₃] ⁻	<	[(μ ₃ -F)(IF ₃) ₃] ^{-[9]*}
<i>d</i> (μ ₃ -F–X)/Å	2.139(2) to 2.194(2)		2.243(2) to 2.265(2)		2.238(10) to 2.329(10)		2.462(2)		2.477 to 2.514

* The bond lengths refer to the molecular anion in the compound K[I₃F₁₆].

agrees with the one of the Cl(III)-containing $[(\mu_3\text{-F})(\text{ClF}_3)_3]^-$ anion of 0.522(2) Å,^[21] while the pyramidalization of the Cl(I)-containing $[(\mu_3\text{-F})(\text{ClF}_3)]^-$ anion^[20] is much more pronounced with 0.812(2) Å. This may be attributed to the steric bulkiness of the “ligands” BrF_5 , ClF_3 , and ClF around the $\mu_3\text{-F}$ atoms as well as to the Coulomb and hydrogen bond interactions of the $\mu_3\text{-F}$ atom with the $[\text{NMe}_4]^+$ cations in the latter case. In the title compound, no direct interaction of the $\mu_3\text{-F}$ atom with the Cs^+ cations is present.

While the lone pair on the Br atom in the octahedral $[\text{BrF}_6]^-$ anion shows no stereochemical activity,^[9,26,32–34] a weak stereochemical effect is observed within the $[\text{Br}_3\text{F}_{16}]^-$ anion, which is evident in the $\mu_3\text{-F}-\text{Br}-\text{F}_{\text{ap}}$ bond angle of 165.0(3)°, deviating from 180°. The difference is attributed to the small size of the bromine central atom, which cannot accommodate the stereochemically active lone pair in its coordination sphere when it is already surrounded by six similarly bound fluorido ligands in $[\text{BrF}_6]^-$. However, in the case of the $[\text{Br}_3\text{F}_{16}]^-$ anion, the elongated $\mu_3\text{-F}-\text{Br}$ bond provides a sufficient amount of space in the coordination sphere of the Br atom, so that the lone pair becomes stereochemically active. $\text{Cs}[\text{Br}_3\text{F}_{16}]$ is therefore the first example of a fluoridobromate(V) anion with stereochemically active lone pairs on the Br atoms.

$\text{Cs}[\text{Br}_3\text{F}_{16}]$ is structurally related to the monoclinic compound $\text{K}[\text{I}_3\text{F}_{16}]$ containing molecular $[\text{I}_3\text{F}_{16}]^-$ anions. In these $[\text{I}_3\text{F}_{16}]^-$ anions, the stereochemical effect of the lone pair is more pronounced, as the $\mu_3\text{-F}-\text{I}-\text{F}_{\text{ap}}$ angles in this anion reach from 141.4 to 149.0°.^[9] Both $\text{Cs}[\text{Br}_3\text{F}_{16}]$ and $\text{Cs}[\text{I}_3\text{F}_{16}]$ crystallize in space group $P\bar{4}3n$ and are isopoint to another. However, the two compounds do not crystallize isotypic, that is, the crystal structures are different, as the Br atoms show coordination numbers of six but the iodine atoms of seven.^[9] This difference leads to the presence of molecular $[\mu_3\text{-F}(\text{BrF}_5)_3]^-$ anions in contrast to $[\mu_3\text{-F}(\text{IF}_5)_3]^-$ anions.

The crystal structure of $\text{Cs}[\text{Br}_3\text{F}_{16}]$ is of AB type and best described with a $2a \times 2a \times 2a$ superstructure of the CsCl structure type with the Cs^+ cations residing in the center, on the corners, and on the edge and face centers of the unit cell. The virtual centers of gravity of the $[\text{Br}_3\text{F}_{16}]^-$ anions, close to the $\mu_3\text{-F}$ atoms, reside in the cubic voids opened by the Cs^+ cations. However, these imagined centers of gravity are differently displaced from the cubic voids along the space diagonals of the unit cell, therefore requiring the superstructure for the global structure description.

A Raman spectrum was recorded on various single crystals of the compound suspended in perfluoropolyether at -60°C and is shown in Figure 2. The Raman spectrum of the solid-state structure was calculated on the DFT-PBE0/TZVP(F,Br)/SVP(Cs) level of theory and is shown below for comparison. The lattice parameters of the DFT-optimized structure deviate from the SCXRD lattice parameters by less than 1.5%, and harmonic frequency calculations confirmed the optimized structure to be a true local minimum. Further details on the DFT calculations are given in the Supporting Information, Tables S6 and S7.

The quantum-chemically calculated and observed Raman spectra agree reasonably. The assignment of the bands is given in the Supporting Information, Table S8.

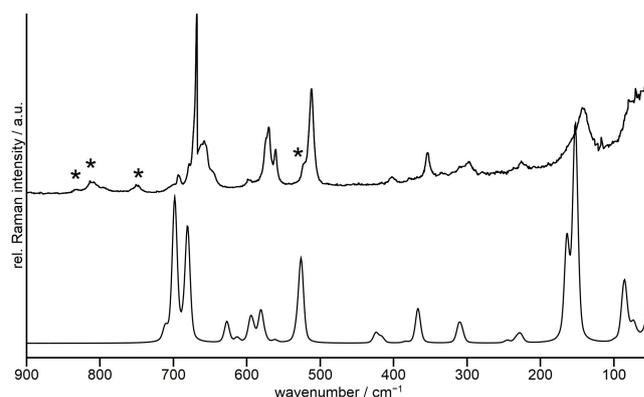


Figure 2. Recorded (top) and calculated (bottom) Raman spectrum of $\text{Cs}[\text{Br}_3\text{F}_{16}]$. The measured spectrum was obtained at -60°C on single crystals suspended in perfluorinated oil. Raman bands caused by the oil are marked with an asterisk. DFT calculation at the DFT-PBE0/TZVP(F,Br)/SVP(Cs) level of theory.

In order to estimate the thermal stability of the compound, the sample suspended in perfluorinated oil was allowed slowly to warm up to room temperature inside the Raman spectrometer, while the temperature increase was monitored and the decomposition of the sample was followed visually by means of a light microscope. Decomposition was observed at a temperature of -40°C , when the crystals of $\text{Cs}[\text{Br}_3\text{F}_{16}]$ started to decompose under formation of a liquid. A Raman spectrum identified the formed liquid as BrF_5 , presumably with some $\text{Cs}[\text{BrF}_6]$ dissolved in it. However, we obtained $\text{Cs}[\text{Br}_3\text{F}_{16}]$ at -36°C and therefore attribute this to the compound being suspended in an excess of BrF_5 during the synthesis. This shifts the equilibrium of Equation (1) to the right and so the decomposition is hindered at -36°C .

From this and the previously obtained results,^[9,20–26] the thermal stability of oligonuclear halogen fluoride anions seems to depend on several factors: the fluoride ion affinity, FIA, of the corresponding halogen fluoride, the vapor and partial pressure of the halogen fluoride and its concentration respectively, the size of the counter ion, and the number and the steric bulkiness of halogen fluoride moieties within the anion.

A quantum-chemical calculation of the isolated $[\text{Br}_3\text{F}_{16}]^-$ anion was carried out at the DFT-PBE0/def2-TZVP level of theory with a consecutive analysis of the bonding situation using the intrinsic bonding orbital (IBO) formalism.^[35,36] The structure optimization ended up in a true local minimum in point group C_3 , which also corresponds to the crystallographic site symmetry of the anion. The calculated bond lengths agree with those determined by single-crystal X-ray diffraction within the tripled standard uncertainties of the latter, except for the $\mu_3\text{-F}-\text{Br}$ bond length. The calculated $\mu_3\text{-F}-\text{Br}$ bond length is with 2.432 Å shorter than the one observed with 2.462(2) Å. However, the calculation resulted in 164.5° for the $\mu_3\text{-F}-\text{Br}-\text{F}_{\text{ap}}$ bond angle which agrees with the observed one of 165.0(3)°. The pyramidalization of the anion, described by the height of the $\mu_3\text{-F}$ atom above a virtual plane through the Br atoms, is slightly smaller with 0.396 Å compared to 0.503(5) Å.

One of the IBOs representing the μ_3 -F–Br bond of the $[\text{Br}_3\text{F}_{16}]^-$ anion is shown in Figure 3. The percentages next to the atoms indicate the contribution of each atom to the IBO. The higher the percentage, the more polarized the bond. For comparison: For a gas-phase NaF molecule, in which the bond should be highly ionic, the contribution of the F atom is 96%. In the H_2 molecule, which has a purely covalent bond, the contribution of each atom is 50%.

With a contribution of 94% for the μ_3 -F and 2% for the Br atom, there is almost no covalent contribution of the Br atom to the bond, which is therefore essentially of ionic nature. The missing other 4% are due to minor contributions of less than

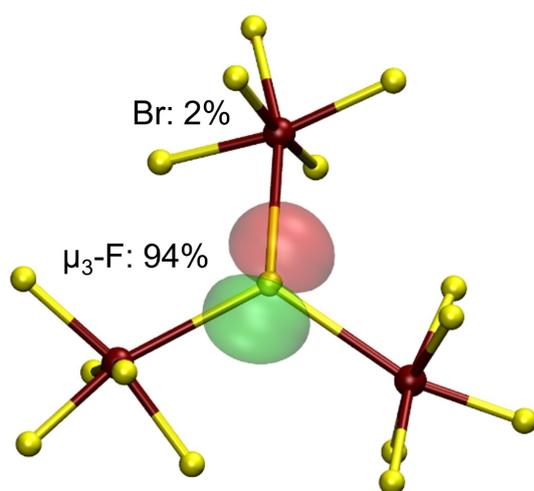


Figure 3. Intrinsic bond orbital (IBO) showing the μ_3 -F–Br bond in the $[\text{Br}_3\text{F}_{16}]^-$ anion.^[35] The percentages next to the atoms indicate the contribution of each atom to the IBO. The higher the percentage, the more ionic the bond. For comparison: For a gas-phase NaF molecule, in which the bond should be highly ionic, the contribution of the F atom is 96%. In the H_2 molecule, which has a purely covalent bond, the contribution of each atom is 50%. If the sum does not add up to a total contribution of 100%, then other atoms contribute – less than 2% – to the IBO. The contributions of the other Br atoms are less than 2%, therefore they are not explicitly discussed. The IBO isosurfaces are shown at 80% of the total density. Br atoms in brown, F atoms in yellow.

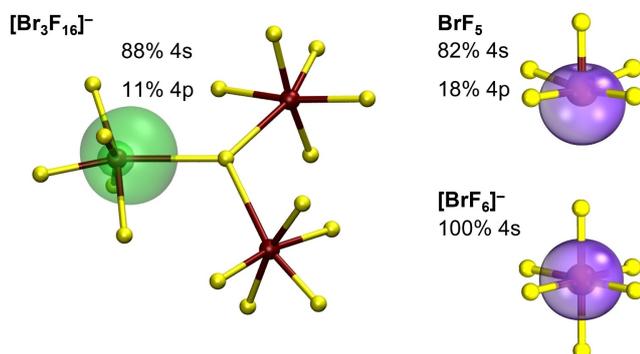


Figure 4. IBOs of the lone pair located at the Br atoms of the $[\text{Br}_3\text{F}_{16}]^-$ anion (left), of the BrF_5 molecule (top right), and of the $[\text{BrF}_6]^-$ anion (bottom right). The percentages next to the IBO indicate the contribution of the involved atomic orbitals. If the sum does not add up to a total contribution of 100%, then other atomic orbitals contribute – less than 2% – to the IBO. The IBO isosurface contains 80% of the total density. Br atoms in dark red, F atoms in yellow. Additional IBOs of the title anion are shown in Figure S3.

2% of the two other Br atoms. The 94%-contribution of the μ_3 -F atom shown in Figure 3 consists of exclusively 2p orbitals. In comparison, the 2%-contribution of the Br atom is dominated by its 4p orbital with 89% followed by 11% of its 4s orbital.

A lone pair of one of the Br atoms of the $[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$ anion is visualized by the IBO in Figure 4. With a 4s-contribution of 88% and a 4p-contribution of 11%, the IBO is mostly 4s-like. It is slightly more 4s-like than the lone pair of the Br atom in the BrF_5 molecule, but shows less 4s-character than the Br atom of the $[\text{BrF}_6]^-$ anion for which no stereochemical effect was observed.^[9,26,32–34] The lone pair of the Br atom in the $[\text{Br}_3\text{F}_{16}]^-$ anion points sideways with respect to the μ_3 -F–Br bond axis, consistent with the observed μ_3 -F–Br– F_{ap} bond angle of $165.0(3)^\circ$.

The lighter homologue of the $[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$ anion, $[(\mu_3\text{-F})(\text{ClF}_5)_3]^-$, has not been observed, as of yet. Therefore, we studied the latter quantum-chemically for comparison. It shows the same respective orbital contributions to the μ_3 -F–Cl bond. The influence of the lone pair on the surrounding of the Cl atoms is, as may be expected, smaller. Figure S1 in the Supporting Information shows the IBOs of the lone pairs. In case of the heavier homologous $[(\mu_3\text{-F})(\text{IF}_5)_3]^-$ anion, its I and F contributions to the μ_3 -F–I bond are also similar compared to the other two related anions with Cl and Br atoms. The stereochemical demand of the lone pairs of the I atoms within the IF_5 subunits increases significantly, as the μ_3 -F–I– F_{ap} angle decreases to 147.3° . The energy difference between the lowest-energy C_3 structure and an idealized, higher-symmetry D_{3h} structure is 9, 8, and 45 kJ/mol for $[(\mu_3\text{-F})(\text{ClF}_5)_3]^-$, $[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$, and $[(\mu_3\text{-F})(\text{IF}_5)_3]^-$, respectively. This can be interpreted as stereochemical demand of the active lone pairs in the IF_5 subunits. The relevant IBOs are illustrated in Figure S5. More details are shown in the Supporting Information in Figures S2, S4, and S6. An overview of μ_3 -F–X bond lengths, of the μ_3 -F–X– F_{ap} angles to indicate the stereochemical activity of the lone pair as well as the degree of pyramidalization, is given in Table 2. More details on the IBOs of the $[(\mu_3\text{-F})(\text{XF}_5)_3]^-$ anions are given in the Supporting Information.

Conclusions

$\text{Cs}[\text{Br}_3\text{F}_{16}]$ has been obtained at -36°C in form of colorless crystals from the reaction of $\text{Cs}[\text{BrF}_6]$ in BrF_5 . The compound

Table 2. Comparison of the μ_3 -F–X bond lengths ($X = \text{Cl–I}$), the μ_3 -F–X– F_{ap} angles, and the degrees of pyramidalization of the $[\text{X}_3\text{F}_{16}]^-$ anions in point group C_3 , calculated at the DFT-PBE0/def2-TZVP level of theory. Pyramidalization is defined by the height of the respective μ_3 -F atom residing above a virtual plane spanned by the X atoms.

$[(\mu_3\text{-F})(\text{XF}_5)_3]^-$ anion	$\mu_3\text{-F–X/}$ Å	$\mu_3\text{-F–X–F}_{\text{ap/}}$ deg	pyramidalization/ Å
$[(\mu_3\text{-F})(\text{ClF}_5)_3]^-$	2.388	176.7	0.160
$[(\mu_3\text{-F})(\text{BrF}_5)_3]^-$	2.432	164.5	0.396
$[(\mu_3\text{-F})(\text{IF}_5)_3]^-$	2.528	147.3	0.347

contains molecular C_3 -symmetric anions in which a central F^- anion bridges μ_3 -like to the Br atoms of three BrF_5 molecules, $[(\mu_3-F)(BrF_5)_3]^-$. Being a F^- -bridged oligonuclear interhalogen Br(V) species makes it unprecedented. In addition, it presents the first example of a fluoridobromate(V) anion with stereochemically active lone pairs on the Br atoms. So far, we have no evidence for the formation of the lighter alkali metal salts of the $[Br_3F_{16}]^-$ anion. Attempts to prepare these compounds for K^+ and Rb^+ under the same conditions as applied for the synthesis of $Cs[(\mu_3-F)(BrF_5)_3]$ were unsuccessful. We were also so far unsuccessful in the synthesis of BrF_5 -poorer or -richer anions, such as $[(\mu-F)(BrF_5)_2]^-$ or $[(\mu_4-F)(BrF_5)_4]^-$, respectively. Our investigations are ongoing.

Experimental Section

Full synthetic details, along with crystallographic, Raman and computational data are available in the Supporting Information.

Deposition Number 2261797 (for $Cs[Br_3F_{16}]$) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: bromine pentafluoride · crystal structure · fluorine · interhalogen compounds · quantum-chemical calculation

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