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■ **Fluoridobromates** | *Very Important Paper* |

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Soluble Fluoridobromates as Well-Behaved Strong Fluorination Reagents

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Abstract: We present a facile synthesis of the soluble fluorido-bromates [NEt₃Me][BrF₄] and [NEt₃Me][Br₂F₇] via fluorination of the corresponding bromide salts in acetonitrile, propionitrile or bromine. We structurally characterized the [BrF₂]⁻ anion, an inter-mediate during the synthesis, for the first time. Additionally, the dissolution of noble metals to form the corresponding halometal-lates as well as the application of [NEt₃Me][BrF₄] as a fluorination agent for disulfides to form pentafluorosulfanyls was studied.

Bromine, like almost any other element, forms binary compounds with fluorine. The neutral compounds and strong oxidizers bromine monofluoride (BrF) and bromine trifluoride (BrF₃) can form anions ([BrF₂]⁻ and [BrF₄]⁻) upon formal addition of a fluoride ion. The difluoridobromate(I) ([BrF₂]⁻) anion is known as its Cs⁺[1] and [NMe₄]⁺[2] salt. Cs[BrF₂] can be synthe-sized via the exposure of CsBr to XeF₂ or by careful condensa-tion of a mixture of Br₂ and BrF₃ onto CsF.[1,3] However, these procedures were not suitable to isolate pure samples.[3] The tetramethylammonium salt was obtained as a decomposition product of [NMe₄][Br(OCF₃)₂].[2] To date, it is only characterized by vibrational and NMR spectroscopy.[2,3] Significantly more ref-erences regarding the tetrafluoridobromate(III) ([BrF₄]⁻) can be found in the literature with several counterions, including Na⁺,[4] K⁺,[5–7] Rb⁺,[8] Cs⁺,[7,9,10] Ag⁺,[11] NO⁺,[10] NO₂⁺,[10] [NMe₄]⁺,[12] [NF₄]⁺[13] and Ba²⁺.[11,14] The synthesis is accom-plished by exposure of the corresponding fluorides or chlorides to BrF₃.[11] If chloride salts are used Cl₂ and Br₂ are generated during the reaction. The tetramethylammonium salt was ob-tained by a metathesis reaction from Cs[BrF₄] and [NMe₄]F.[12] If an excess of BrF₃ is used to dissolve RbCl, CsCl, CsF or PbF₂ larger anions of the type [F(BrF₃)ₙ]⁻ with n = 2 or 3 can be isolated. The [Br₂F₇]⁻ with a bridging μ₂-F atom is known as the Cs⁺,[15,16] Rb⁺[15,16] and [PbF]⁺[17] salt. The [Br₃F₁₀]⁻ complex with a bridging μ₃-F atom exists as the Rb⁺ and Cs⁺ salt.[15,16] They were studied via vibrational spectroscopy and X-ray diffraction.

Herein, we present the application of a direct fluorination to synthesize these anions, a method we published recently for the synthesis of di- and tetrafluoridochlorate(I/III).[18] We used this method for the fluorination of the organic halide salts, *i.e.* tetraethylammonium and triethylmethylammonium bromide, with dilute fluorine in the solvents acetonitrile, propionitrile, or bromine. In analogy to the lighter homologue [ClF₄]⁻, triethyl-methylammonium tetrafluoridobromate(III) is selectively formed from the exposure of the bromide salt to two equiva-lents of dilute fluorine (10 % in Ar) in acetonitrile or propio-nitrile at temperatures below –30 °C (Equation 1).

$$[NEt_3Me]Br \ + \ 2\,F_2 \xrightarrow[\substack{-30\,°C,\,R=Me \\ -50\,°C,\,R=Et}]{RCN} [NEt_3Me][BrF_4] \quad (1)$$
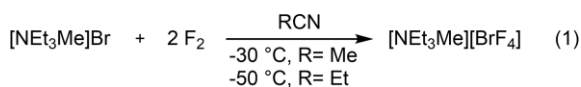
The ¹⁹F NMR chemical shift of [NEt₃Me][BrF₄] is –35.1 ppm.[12] We were able to grow single crystals suitable for X-ray diffrac-tion from a MeCN solution. The molecular structure in the solid-state is in line with already published structures of the [BrF₄]⁻

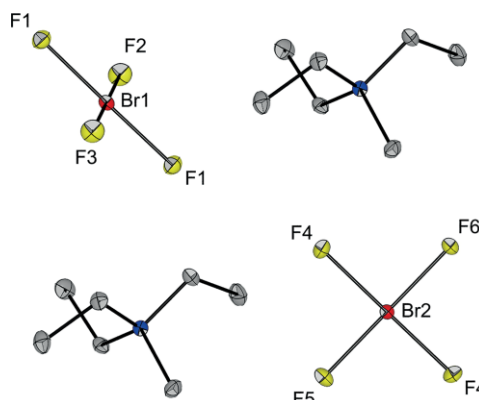Figure 1. Solid-state structure of [NEt₃Me][BrF₄]. Thermal ellipsoids are shown at 50 % probability at 100 K. Color code: yellow = fluorine, red = bromine, grey = carbon, blue = nitrogen. Selected bond lengths [pm] and bond angles [°]: F1–Br1 189.64(1), F2–Br1 190.47(1), F3–Br1 187.87(1), F4–Br2 189.38(1), F5–Br2 188.93(1), F6–Br2 189.33(1); F1–Br1–F2 90.277(2), F1–Br1–F3 89.729(2), F4–Br2–F5 90.189(2), F4–Br2–F6 89.810(2).

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anion with idealized D_{4h} symmetry (Figure 1).[5] It crystallizes in the monoclinic space group $P2_1/m$ with two crystallographically inequivalent anions. The single crystal Raman spectrum (Figure 2) shows three bands attributed to the anion at 519, 442 and 247 cm^{-1} corresponding to the a_{1g}, b_{1g}, and b_{2g} vibration.[7]
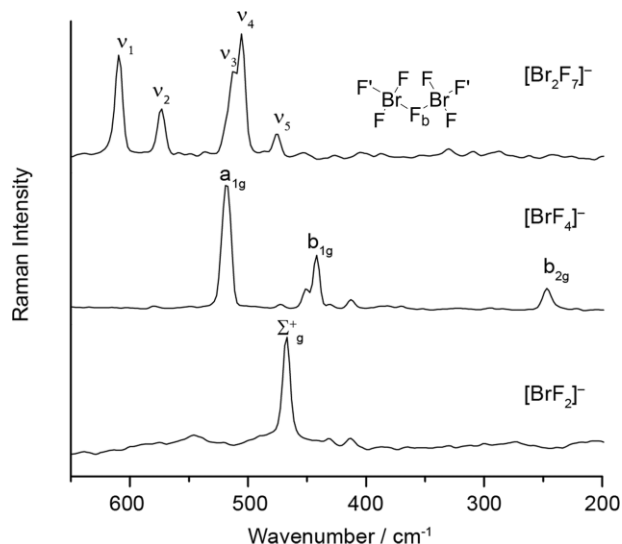

Figure 2. Single crystal Raman spectra of [NEt$_3$Me][Br$_2$F$_7$] (top), [NEt$_3$Me][BrF$_4$] (middle) and [NEt$_3$Me][BrF$_2$] (bottom) in the Br–F region. Selected bands [cm^{-1}]: ν_1 = 610 (in phase Br–F' stretching), ν_2 = 573 (out of phase Br–F' stretching), ν_3 = 513 (in phase asymmetric F–Br–F stretching), ν_4 = 505 (out of phase asymmetric F–Br–F stretching), ν_5 = 477 (in phase symmetric F–Br–F stretching), a_{1g} = 519, b_{1g} = 442, b_{2g} = 277, Σ^+_g = 467.

To avoid side products of the fluorination the reactions were done at –30 °C or below. At these temperatures the solubility of the starting material [NEt$_3$Me]Br can be quite low. However, the solubility can be increased by the addition of one equivalent of bromine to form the well-known tribromide anion. In case of the [NEt$_3$Me]$^+$ cation, however, the [Br$_3$]$^-$ salt is structurally unknown. Hence, we characterized it via Raman spectroscopy and single-crystal X-ray diffraction. Surprisingly, we realized that in the solid state the [Br$_6$]$^{2-}$ dianion had formed. This is not only evident from the molecular structure in the solid state (Figure S2) but also from the Raman spectrum (Figure S1). A polybromide anion with the composition of [Br$_6$]$^{2-}$ was previously reported by our group.[19] However, this structure significantly differs from the previously reported structure. This might be due to the altered cations which show different intermolecular interactions, possibly orchestrating their metrics. In the reported structure the cation possesses a bromine atom which interacts with the anion via halogen bonding (for a detailed discussion see Supporting Information). Raman spectra in acetonitrile solution (Figure S1) suggest the dissociation of the [Br$_6$]$^{2-}$ in two [Br$_3$]$^-$ fragments when in solution. We used a propionitrile solution of [NEt$_3$Me][Br$_3$] and exposed it to one equivalent of dilute fluorine (10 % in Ar) to obtain the difluoridobromate(I) anion (Equation 2).

$$\text{[NEt}_3\text{Me][Br}_3\text{]} + F_2 \xrightarrow[\text{-40 °C}]{\text{EtCN}} \text{[NEt}_3\text{Me][BrF}_2\text{]} + Br_2 \quad (2)$$
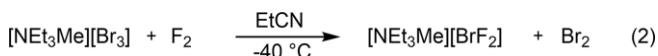
This anion has only been characterized spectroscopically (Raman, IR, ^{19}F NMR) and X-ray diffraction data are to the best of

our knowledge unknown. Slow cooling of the reaction mixture resulted in the growth of single crystals of [NEt$_3$Me][BrF$_2$]. The single crystal Raman spectrum (Figure 2) shows one prominent band at 467 cm^{-1} that corresponds to the symmetric stretching.[1,2] The molecular structure in the solid-state (Figure 3) indeed shows the idealized $D_{\infty h}$ symmetry of the anion. The two Br–F bond lengths differ only slightly with d(F1–Br) = 197.3(1) pm and d(F2–Br) = 193.2(1) pm. The F1–Br–F2 bond angle is 179.34(4)°. We calculated the Hirshfeld surface (Figure S13) which revealed multiple short cation anion contacts. The ^{19}F NMR spectrum (Figure S3) of the reaction solution shows three signals, at –35.8 ppm ([BrF$_4$]$^-$), –83.3 ppm (fluorinated solvent) and –216.8 ppm. We attribute the latter to [BrF$_2$]$^-$ in good agreement with literature values.[3] To avoid contamination from a fluorination of the solvent we changed the solvent to elemental bromine. Any occurring fluorination of bromine at 0 °C and ambient pressure leads to the formation of BrF$_3$ which can function as an oxidizing agent for Br$^-$. The Raman spectrum (Figure S5) reveals the successful formation of [BrF$_4$]$^-$ in bromine. Therefore, the addition of more than two equivalents of fluorine leads to a mixture of [BrF$_4$]$^-$ and BrF$_3$. These can form a Lewis acid-base adduct, i.e. a higher fluoridobromate(III) as first described by Stein.[15] We obtained single crystals of [NEt$_3$Me][Br$_2$F$_7$] from a reaction of [NEt$_3$Me]Br with four equivalents of F$_2$ in bromine and subsequent recrystallization from SO$_2$ClF (Figure 4). The Raman spectrum (Figure 2) of a single crystal of [NEt$_3$Me][Br$_2$F$_7$] shows bands at 610 cm^{-1} (in phase Br–F' stretching), 573 cm^{-1} (out of phase Br–F' stretching), 513 cm^{-1} (in phase asymmetric F–Br–F stretching), 505 cm^{-1} (out of phase asymmetric F–Br–F stretching) and at 477 cm^{-1} (in phase symmetric F–Br–F stretching) which is in agreement with the data reported by Kraus and Stein.[15,16] Small differences are attributed to different structural parameters. Most significantly, the Br–F–Br bond angle is wider (166.86(5)° this work, 140.27(6) Cs[Br$_2$F$_7$]), as well as the torsion angle between the two planar [BrF$_4$]$^-$ fragments (70.11(3)° this work, 61.90(4)° Cs[Br$_2$F$_7$]). Interestingly, the smaller angles in the Kraus structure are closer to the gas-phase optimized structure (see Table S1). To gain a deeper understanding we performed NBO analyses of the optimized structure [B3LYP-D3(BJ)/def2-TZVPP] as well as of the solid-state structures from this work and from the Kraus group. In the NBO analysis, the bonding between the bridging fluoride atom F$_b$ and the bromine centers is mainly an interaction between the bridging fluoride F$_b$ lone pair and the
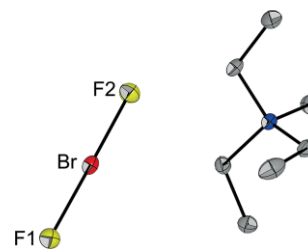

Figure 3. Solid-state structure of [NEt$_3$Me][BrF$_2$]. Thermal ellipsoids are shown at 50 % probability at 100 K. Color code: yellow = fluorine, red = bromine, grey = carbon, blue = nitrogen. Selected bond lengths [pm] and bond angles [°]: F1–Br 197.3(1), F2–Br 193.2(1), F1–Br–F2 179.34(4).

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σ* orbital of the opposite Br–F′ bond (Figure 5). The bonding of the perpendicular fluorine ligands is best described as a 3-center-4-electron bond (detailed discussion of the NBO analysis in the Supporting Information).
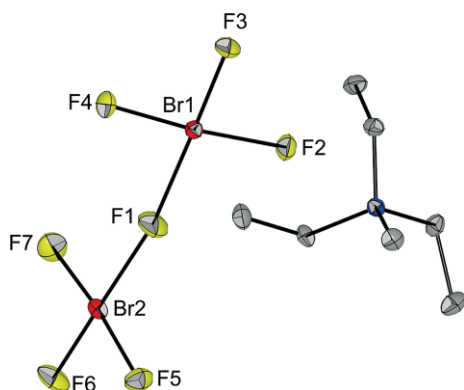

Figure 4. Solid-state structure of [NEt$_3$Me][Br$_2$F$_7$]. Thermal ellipsoids are shown at 50 % probability at 100 K. Color code: yellow = fluorine, red = bromine, grey = carbon, blue = nitrogen. Selected bond lengths [pm] and bond angles [°]: F1–Br1 206.68(7), F1–Br2 218.61(7), F3–Br1 179.18, F6–Br2 176.38(7), F2–Br1 188.10, F7–Br2 184.76(8); Br1–F1–Br2 166.86(5).
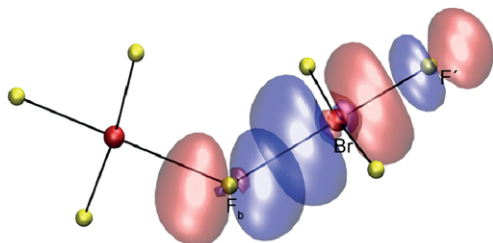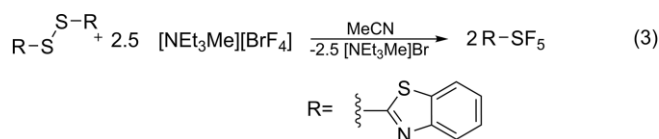

Figure 5. Natural MOs of optimized [Br$_2$F$_7$]$^-$ [B3LYP-D3(BJ)/def2-TZVPP] showing the strongest interaction between lone pair of the bridging fluorine atom F$_b$ and the σ*(Br–F′).

The isolation of [Br$_3$F$_{10}$]$^-$ and [Br$_4$F$_{13}$]$^-$ by direct fluorination of a bromide salt with dilute fluorine in liquid bromine was not successful so far, despite their proposed stability.[20] The obtained Raman spectra from the reactions of [NEt$_3$Me]Br with 5 to 8 equivalents of dilute fluorine in the solvent bromine looks promising, however, due to broad bands an unambiguous assignment is not possible. We were able to obtain single crystals from reactions with 4 and 7 eq of F$_2$, however, they consisted of [NEt$_3$Me][Br$_2$F$_7$]. Figure S8 shows the Raman spectra of [NEt$_3$Me]Br after a reaction with 5 to 8 equivalents of dilute F$_2$ in liquid Br$_2$. To achieve sufficient sensitivity for Br–F containing species in the Raman spectrum the excess Br$_2$ had to be removed at low temperatures.

We studied the chemical properties of an acetonitrile solution of [NEt$_3$Me][BrF$_4$], especially with regard to its oxidation and fluorination properties. It has been previously shown that K[BrF$_4$] can be used for the recovery of precious metals in dry chemical reactions at 400 °C, a process referred to as urban mining.[21] We were able to dissolve elemental silver and gold in an acetonitrile solution of [NEt$_3$Me][BrF$_4$] at room temperature by formation of [NEt$_3$Me][Ag$_2$Br$_3$] and [NEt$_3$Me][AuF$_4$]. However, the dissolution of Au was rather inefficient and only traces of tetrafluoridoaurate(III) were found in the ^{19}F NMR

spectrum. In the case of Ag we were able to grow single crystals of the mentioned silver complex (see Supporting Information). During these experiments we observed slow decomposition reactions with the solvent.[22] In analogy to the reaction of diphenyl disulfide with [NEt$_3$Me][ClF$_4$] we were able to convert a disulfide into the corresponding pentafluorosulfanyl compound (Equation 3).[18] Here, we used 2,2′-dibenzothiazolyl disulfide because the corresponding SF$_5$ product could be a valuable intermediate for an SF$_5$-transfer reagent.[23] Previously, the compound was synthesized in a two-step reaction involving IF$_5$.[24] A direct fluorination with dilute fluorine of the disulfide to form the SF$_5$ product at low temperatures in acetonitrile was not successful.

$$R-S\overset{S-R}{} + 2.5\ [NEt_3Me][BrF_4] \xrightarrow[-2.5\ [NEt_3Me]Br]{MeCN} 2\,R-SF_5 \qquad (3)$$

$$R= \overset{S}{\underset{N}{\diagdown}}$$

In conclusion, we used the direct fluorination of triethylmethylammonium bromide in solution to obtain organo-soluble tetraalkylammonium fluoridobromate salts. Depending on the solvent (acetonitrile, propionitrile or bromine) and the amount of fluorine added we obtained different anions. This includes the difluoridobromate(I) [BrF$_2$]$^-$ anion which was structurally characterized for the first time. Additionally, the synthesis of the highly soluble tetrafluoridobromate(III) [BrF$_4$]$^-$ and heptafluoridodibromate(III) [Br$_2$F$_7$]$^-$ was achieved and we showed the application of [BrF$_4$]$^-$ as a fluorination and oxidation agent for disulfides and noble metals such as gold and silver.

Caution! Fluorine, even under dilute conditions, is extraordinarily reactive and can react violently with organic materials under the formation of HF. Similarly, fluoridobromates are strongly oxidizing compounds, which can decompose violently under certain conditions when exposed to organic materials. Exposure to acidic compounds (e.g. water or boron trifluoride) greatly enhances the reactivity due to the in-situ formation of BrF$_3$.

Deposition Numbers 2015010, 2015014, 2015013, 2015012, and 2015008 contain 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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