Reactions of the “Naked” Fluoride Ion: Syntheses and Structures of SeF_6^{2-} and BrF_6^-

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Abstract: 1,1,3,3,5,5-Hexamethylpiperidinium fluoride (pip^+F^-) and 1,2-dimethylpropyltrimethylammonium fluoride have been prepared. They dissolve in fluorohydrocarbons (CH_2F_2, CF_3-CHF-CF_3, CHF_3) even at very low temperatures. The nature of these solutions is indicated by the crystal structure of the adduct $pip^+F^-\cdot 4CH_2F_2$, which shows (C)H $\cdots$ F bridging. The high fluoride activity is exemplified by the previously unknown reaction between SeF_5^- and F^- to yield SeF_6^{2-}. The salt $pip^+BrF_6^-$ is obtained by a metathesis reaction of $Cs^+BrF_6^-$ with pip^+F^-. The distortion of the SeF_6^{2-} structure from octahedral symmetry is intermediate between IF_6^- (strongly distorted) and BrF_6^- (octahedral). The electron-pair repulsion model is checked against these results.

Keywords
crystal structure · fluorides · hexafluorobromate(v) · hexafluoroselenate(IV) · naked fluoride

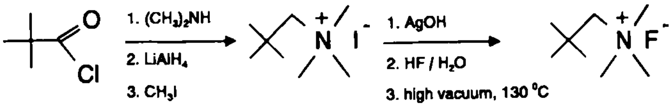
Introduction

In order to achieve high fluoride ion activity, the size of the cation must be large. Solvate free $(CH_3)_4N^+F^-$ is already much more reactive than CsF,[1] and it was thus used in the first syntheses of anions such as XeF_5^-,[2] IOF_6^-,[3] TeF_7^-,[4] $CH_3OTeF_6^-$,[4] $(CH_3O)_2TeF_5^-$,[4] and PF_4^-.[5] Phosphazenium fluorides of the type $[\{(CH_3)_2N\}_3P{=}N{=}P\{N(CH_3)_2\}_3]^+F^-$ are probably even more reactive than $(CH_3)_4N^+F^-$;[6, 7] however, their stability towards strongly oxidizing and fluorinating inorganic materials has not been tested so far.

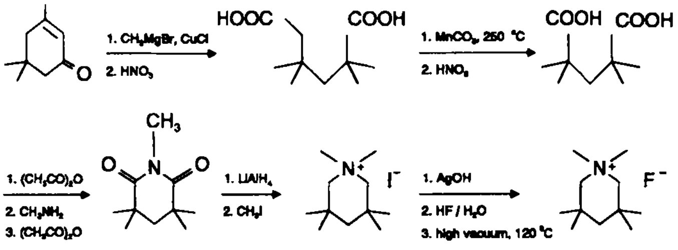
When the size of the quartenary ammonium cation in the fluorides is increased, β-hydrogen atoms in the substituents at nitrogen must be strictly avoided; otherwise Hofmann elimination, catalyzed by the highly basic F^-, will occur. We have chosen $[(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_3]^+$ and (1,1,3,3,5,5)-hexamethylpiperidinium as suitable ions. Recently the synthesis of adamantyltrimethylammonium fluoride has been reported.[8]

Results and Discussion

$[(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_3]^+F^-$ and 1,1,3,3,5,5-hexamethylpiperidinium fluoride (pip^+F^-) were prepared by application or modification of known procedures (see Schemes 1 and 2, and Experimental Procedure).[9, 10] Removing all traces of water from both fluorides by prolonged pumping under high vacuum was found to be essential. We observed that pip^+F^- and its reaction products in general crystallize better than the neopentyl derivative and its reaction products, so in the following only the former are described in detail. Qualitatively, however, the behavior of both derivatives was very similar.



Scheme 1. Synthesis of $[(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_3]^+F^-$.



Scheme 2. Synthesis of pip^+F^-.

When pure, pip^+F^- is a colorless crystalline solid that is readily soluble in CHF_3, CF_3-CHF-CF_3, CH_2F_2, and similar solvents. A small amount of insoluble residue is largely consists of hydrofluoride. Solutions of pip^+F^- in CH_2Cl_2 are only stable for a few hours at −30 °C; chlorine–fluorine exchange is observed with formation of CH_2F_2. It is interesting to note that CH_2FCl exchanges chlorine much faster than CH_2Cl_2. Similar reactions are observed with all chlorofluorocarbons. In acetonitrile solution, nice crystals of HF_2^- are formed within a short period of time, but this solvent can still be used for rapid reactions. For reactions and recrystallizations at temperatures below the melting point of CH_3CN (−45 °C), propionitrile can be used as an alternative solvent.

Recrystallization of pip^+F^- from CH_2F_2 was achieved in two ways: Warming from −78 °C to room temperature afforded the unsolvated fluoride, whereas cooling to −110 °C afforded a solvate with four molecules of CH_2F_2. Between 0 and −78 °C

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the solubility of the salt was so high that a reliable limit cannot be given. At −90 °C possibly metastable pip$^+$F$^-\cdot$2CH$_2$F$_2$ and pip$^+$F$^-\cdot$1.5CH$_2$F$_2$ were occasionally observed and identified by single-crystal structure determinations.[11] The crystal structure of unsolvated pip$^+$F$^-$ shows seven weak hydrogen bonds with (C)H$\cdots$F distances of between 196 and 247 pm (Fig. 1). As expected, only α-hydrogen atoms make such short contacts, since they are more positively polarized by the neighboring nitrogen atom.

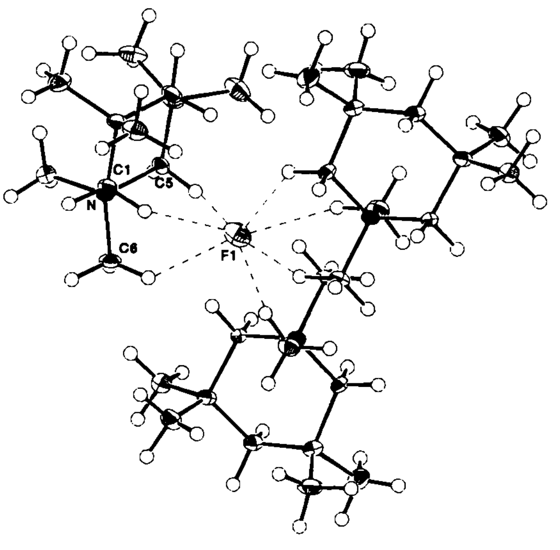

Fig. 1. The environment of F$^-$ in the crystal structure of pip$^+$F$^-$ (ellipsoids at the 50% probability level). Solid circles = nitrogen atoms; dashed lines = H$\cdots$F distances of less than 247 pm.

Insight into the nature of the solutions in fluorohydrocarbons can be derived from the crystal structure of the solvate pip$^+$F$^-\cdot$4CH$_2$F$_2$. The interaction between F$^-$ and CH$_2$F$_2$ is naturally weak, and the material looses CH$_2$F$_2$ slowly even at the measurement temperature of −163 °C; thus, the lifetime of the crystal was limited. Also the refraction power of the crystal was weak from the beginning, so the structural solution is based on a reflection/parameter ratio of only 6.2:1. It nevertheless can be concluded that F$^-$ is solvated by CH$_2$F$_2$ molecules through five (C)-H$\cdots$F bonds with lengths of 200–220 pm; two additional contacts are observed through the α-hydrogen atoms of the cation (Fig. 2). The entire molecular unit can be considered as an ion pair that is solvated by very weak interactions. Obviously the cation–anion interactions and those between solvate molecules and the anion are comparatively weak. In order to achieve a yet more "naked" fluoride ion, a change of both the cation and the solvent would be necessary.

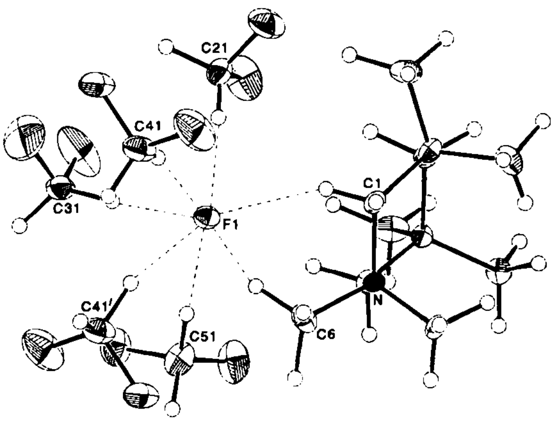

Fig. 2. The environment of F$^-$ in the crystal structure of pip$^+$F$^-\cdot$4CH$_2$F$_2$ (ellipsoids at the 50% probability level). Solid circle = nitrogen atom; dashed lines = H$\cdots$F contacts of less than 220 pm.

The ability of CH$_2$F$_2$ to act as an electron accepting ligand through hydrogen bonds is certainly novel. It was recently reported that HCCl$_3$ acts as a weak acceptor ligand towards a formal triple bond in an ethine complex.[12] In contrast, CH$_2$Cl$_2$ and CH$_2$Br$_2$ have been described as donor ligands, for example, in [Ag(CH$_2$Cl$_2$)$_3$]$^+$ and [Ag(CH$_2$Br$_2$)$_3$]$^+$,[13] in which Ag$\cdots$Cl–C and Ag$\cdots$Br–C bridges are observed.

Clearly, the presence of weakly acidic hydrogen atoms is essential for a good solubility. To our knowledge, the pK_s value of CH$_2$F$_2$ is not known, but it is not surprising that pip$^+$F$^-$ does not dissolve in CH$_3$F or hydrocarbons. Solutions in CH$_2$F$_2$ should react with all systems that are more acidic than CH$_2$F$_2$.

Hexafluoroselenate(VI) (SeF$_6^{2-}$): In the first reported synthesis of SeF$_6^{2-}$ (see below), we made use of the extremely high reactivity of pip$^+$F$^-$. For a long time it remained an open question, why SF$_6^{2-}$, SeF$_6^{2-}$, and TeF$_6^{2-}$ could not be synthesized, in contrast to SeCl$_6^{2-}$ and TeCl$_6^{2-}$, which have been known for many decades. The reaction of SF$_4$ and its higher homologues SeF$_4$ and TeF$_4$ with F$^-$ afford SF$_5^-$, SeF$_5^-$, and TeF$_5^-$. These pentafluorochalcogenates(IV) have a square-pyramidal structure and have been investigated very thoroughly.[14] Occasional reports of the existence of hexafluorochalcogenates have not been substantiated.[15]

The fact that these anions were seemingly nonexistent was interpreted in terms of a duodecet rule, that is, by assuming that nonmetal elements of the second and third row of the periodic table can accommodate only 12 electrons in their valence shell, and only elements of the fourth row are able to accommodate more (IF$_7$, XeF$_6$, XeF$_8^{2-}$). This rule was never completely valid, since BrF$_6^-$ has been known for a long time.[16] Even ClF$_6^-$ is now known.[17] A careful examination of the solid state structures of SeF$_4$[18] and TeF$_4$[19] revealed a surprising behavior for SeF$_4$: Both compounds show molecular units with additional weaker fluorine bridging bonds, in contrast to SeCl$_4$ and TeCl$_4$ that are ionic tetramers (SeCl$_3^+$Cl$^-$)$_4$.[20] TeF$_4$ adopts a square-pyramidal geometry, if the one additional contact is taken into account. SeF$_4$, however, has two contacts, so that the overall geometry of a given selenium unit is a distorted octahedron. SeF$_5^-$ and TeF$_5^-$[14] both have additional anionic–anionic contacts through fluorine bridging, so that the coordination number of the central atom may be counted as seven, including the nonbonding electron pair. However, these bridging bonds are surprisingly short in SeF$_5^-$ compared to those in TeF$_5^-$, and even shorter than in SF$_5^-$.[14] Therefore it seems that SeF$_5^-$ may be the best candidate to accommodate one more fluoride ion. Also, the established reaction (a) indicates a higher fluoride ion affinity for the third row element than for the fourth row element.[21]

$$\mathrm{BrF_5 + IF_6^- \longrightarrow BrF_6^- + IF_5} \qquad \text{(a)}$$

Indeed, SeF$_4$ reacted with two mols of pip$^+$F$^-$ to give SeF$_6^{2-}$. The principal problem with doubly charged anions is their low solubility in organic solvents, which makes it difficult to obtain single crystals. Nevertheless, (pip$^+$)$_2$SeF$_6^{2-}$ was obtained as a pale yellow-brown, stable material. The important question of whether the anion SeF$_6^{2-}$ is octahedral or nonoctahedral could only be solved by single-crystal structure determination. IR and Raman spectra of this compound show the vast number of vibrations due to the cation, and from the few remaining bands that can be attributed to the anion no conclusions about the structure can be drawn. Furthermore, the compound fluoresces very strongly in the Raman spectra, obscuring the entire spectra. Also, the ^{19}F and ^{77}Se NMR spectra gives no indication about the structure. A single line at $\delta = 13.38$ without ^{77}Se satellite lines is observed, which is shifted to higher values upon addition of SeF_5^- and to lower values upon addition of F^-; this indicates that rapid intermolecular fluorine exchange is taking place between SeF_5^-, SeF_6^{2-}, and F^-.

The crystal structure of $(pip^+)_2SeF_6^{2-}$ shows discrete cations and anions. The geometry of the cations needs no further discussion. The anion appears as a doubly disordered entity with respect to all fluorine positions, where the disorder is generated by the inversion center (Fig. 3, top). In spite of the fact that pairs of fluorine atoms with site occupation factors 0.5 are close, they could be differentiated without difficulty and refined anisotropically. R_w values (0.034), the reflection/parameter ratio (20:1), and the estimated standard deviations indicate a reliable crystal structure determination. It is immediately obvious that SeF_6^{2-} is nonoctahedral. The Se–F bond lengths fall in two categories, namely, shorter (three bonds of approximately 185 pm) and longer (three bonds of approximately 200 pm). Since the angles between the shorter Se–F bonds are less than 90° and those between the longer Se–F bonds are greater than 90°, it is clear that the ion has C_{3v} symmetry (Fig. 3, bottom). On closer inspection, the structure shows a distortion towards C_{2v} symmetry: one of the angles between the longer bonds is somewhat smaller, one of the bonds in the longer category is somewhat shorter, and one of the bonds in the shorter category is somewhat longer. It should be noted that for isoelectronic gaseous XeF_6 such a stereochemical nonrigid C_{3v}/C_{2v} model was predicted[21] and later shown to be consistent with all experimental data.[22]

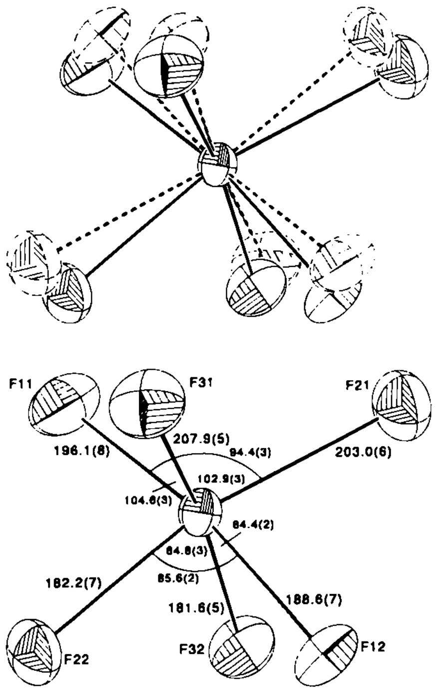

Fig. 3. Top: The SeF_6^{2-} anion in $(pip^+)_2SeF_6^{2-}$ (ellipsoids at the 50% probability level). Dashed atoms indicate the second orientation created by the inversion center. Bottom: Bond lengths [pm] and angles [°] in one orientation of the SeF_6^{2-} anion.

Hexafluorobromate(v) (BrF_6^-): The structure of BrF_6^- has been established by X-ray crystallography of $Cs^+BrF_6^-$ and by vibrational spectroscopy of $(CH_3)_4N^+BrF_6^-$ [23, 24] and was found to be octahedral. Also, the unstable ion ClF_6^- is reported to be octahedral, according to IR and Raman spectra.[17] For BrF_6^- there remained the doubt that the octahedral structure is enforced by its site symmetry $\bar{3}$ in the highly symmetric lattice. In order to investigate the structure of BrF_6^- in a lattice of low symmetry, $pip^+BrF_6^-$ was prepared in a metathesis reaction [Eq. (b)]. This type of reaction avoids the direct contact between

$$Cs^+BrF_6^- + pip^+F^- \longrightarrow pip^+BrF_6^- + CsF \qquad (b)$$

extremely strong oxidizing agent BrF_5 and organic substrates. IR and Raman spectra of BrF_6^- are comparable to those reported earlier; the same is true of the chemical shift in the ^{19}F NMR spectrum.[24] With the latter method the slow overall reaction can be monitored. But in contrast to the ^{19}F NMR data in ref. [24], we observe a signal with fine structure for BrF_6^- (Fig. 4). The appearance of two over lapping 1:1:1:1 quartet spectra is a result of $^{19}F-^{79/81}Br$ scalar coupling with coupling constants of 1570.6 and 1694.9 Hz. The ratio of these coupling constants (0.9267) is identical to the ratio of the gyromagnetic factors of ^{79}Br and ^{81}Br (0.9277). The fine structure is another qualitative proof that the BrF_6^- is very close to or fully octahedral, since deviation from this symmetry would give a partial or full collapse of the coupling, due to the high electric quadrupole moments of ^{79}Br and ^{81}Br. A scalar $^{19}F-^{79}Br/^{81}Br$ coupling has also been observed for octahedral BrF_6^+. The coupling constants are very similar, but the chemical shift is very different.[25] According to conventional theory, this would indicate a similar s character in the BrF bonding in BrF_6^- and BrF_6^+.

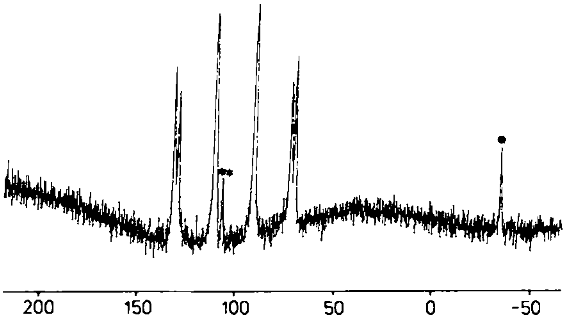

Fig. 4. ^{19}F NMR spectrum of the BrF_6^- anion in CH_3CN solution, −40 °C. * = BrF_4^- impurity, ** = $BrOF_4^-$ impurity.

The crystal structure determination of $pip^+BrF_6^-$ (Fig. 5) is hampered by large-amplitude vibrations of four of the six fluorine atoms. The interactions between large cation and large anion are quite weak. In the rather asymmetric cation the ionic charge seems to be focused on α-hydrogen atoms, and a fully ordered cation thus results. In contrast, the close to symmetric shape of SeF_6^{2-} and BrF_6^- with delocalization of the negative charge over the entire sphere of fluorine atoms allows a variety of dynamic

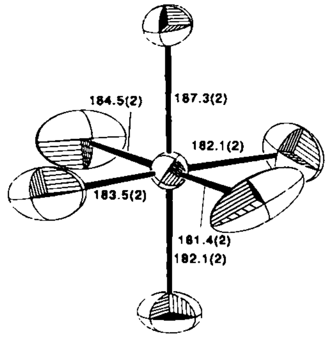

Fig. 5. The BrF_6^- anion in $pip^+BrF_6^-$ (bond lengths in pm).

or static disorder in the crystal. The overall symmetry of BrF_6^- is, however, evident since in all cases opposing fluorine atoms and the central bromine atom form nearly linear arrays (178.2, 179.5, 177.5°). The entire picture is therefore that of an octahedron that is librating to a certain extent around the F1-Br-F2 axis. Considering that the positions of four of the six fluorine atoms are certainly less accurate than the estimated standard deviations indicate, it remains an open question whether the deviations of maximum 2.5° from the ideal 180° angle are meaningful at all. So, in going from the highly symmetric $Cs^+BrF_6^-$ to $pip^+BrF_6^-$ the quality of the crystal structure determination suffers, but there is no indication of a nonoctahedral geometry.

Conclusion

The structures of BrF_6^-, IF_6^-, and SeF_6^{2-} can be compared by defining a distortion parameter from octahedral symmetry. Since IF_6^- and SeF_6^{2-} are closest to C_{3v} symmetry, a simplified distortion parameter is the angle between the bonds to opposing fluorine atoms (Fig. 6). This parameter (as an average of three angles) is 178–180° for BrF_6^-, 172° for SeF_6^{2-}, and 164° for IF_6^-. A simple explanation can be found for these results: The nonbonding electron pair will only play a directional, sterically active role if the size of the central atom allows it. The large iodine atom can accommodate more than six fluorine ligands (e.g., IF_7), the smaller bromine atom only six. The rather long Br–F bonds in BrF_6^- indicate the presence of a centrosymmetric nonbonding electron pair. SeF_6^{2-} is a borderline case; selenium is just large enough that some directional steric influence of the nonbonding electron pair is visible. Thus, the valence-shell electron-pair repulsion model, which has overall been quite successful, needs to be redefined in this sense.[26]

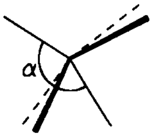

Fig. 6. A simple definition of the distortion from octahedral towards C_{3v} symmetry.

While we have stated above that SeF_6^{2-} is the most likely candidate for a successful synthesis, we do not rule out that the preparation of both SF_6^{2-} and TeF_6^{2-} might also be possible. In the light of the above model SF_6^{2-} should be octahedral, and TeF_6^{2-} at least as distorted as IF_6^-, if not more.

The situation in the corresponding chloride, bromide, and iodide analogues is more complicated. Depending on the symmetry of cation and space group, $SeCl_6^{2-}$, $SeBr_6^{2-}$, $TeCl_6^{2-}$, $TeBr_6^{2-}$, and TeI_6^{2-} turn out to be octahedral or strongly distorted.[27] Regular octahedral symmetry is enforced by high lattice symmetry. However, even at low temperatures, the vibrational amplitudes of the chlorine atoms have been interpreted in terms of overlapping close-lying positions of nonoctahedral $TeCl_6^{2-}$ ions. However, in contrast to the fluorine atoms in SeF_6^{2-}, the chlorine atoms in octahedral $TeCl_6^{2-}$ cannot be differentiated as occupying separate positions. Characteristic differences in the IR spectra, particular in the Te–Cl deformation region, are indicative of dynamic behavior in the solid state.

Experimental Procedure

General: NMR spectra: Jeol FX90Q spectrometer, TMS or $CFCl_3$ external standard. Raman spectra: Cary Instruments model 82, argon gas laser excitation. IR spectra: Perkin Elmer 983. X-ray: Enraf Nonius CAD4 four-circle diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator. Moisture-sensitive materials were handled in a dry box with less than 0.1 ppm of H_2O. Elemental analyses were performed by Beller Co., Göttingen. SeF_4 (from SeO_2 and SF_4) and $CsBrF_6$ (from CsF and BrF_5) were prepared according to literature procedures [16,28].

$[(CH_3)C\text{-}CH_2\text{-}N(CH_3)_3]^+F^-$: $(CH_3)C\text{-}COCl$ in Et_2O at room temperature was treated with gaseous $(CH_3)_2NH$ until no further amine was absorbed. After filtration and distillation $(CH_3)_3C\text{-}CO\text{-}N(CH_3)_2$ was obtained in 90% yield as a colorless liquid: B.p. 183 °C; ^1H NMR: $\delta = 1.09$ (9H), 2.62 (6H). $(CH_3)_3C\text{-}CO\text{-}N(CH_3)_2$ was treated in Et_2O with a slight excess $LiAlH_4$. After hydrolysis, separation of the organic phase, and distillation, $(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_2$ was obtained as colorless liquid in 75% yield: B.p. 96–97 °C; ^1H NMR: $\delta = 0.88$ (9H), 1.81 (2H), 2.16 (6H). $(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_2$ was quaternized with a 3:1 excess of CH_3I in CH_3CN by refluxing for 12 h. After filtration and drying in vacuum $[(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_3]^+I^-$ was obtained as white powder in 90% yield: ^1H NMR (CD_3CN): $\delta = 1.40$ (9H), 3.51 (6H), 3.70 (2H). $AgNO_3$ (0.2 mol) and KOH (0.21 mmol) were combined in aqueous solution. The resulting silver oxide/hydroxide mixture was washed until free of NO_3^- and OH^- and suspended in water. A solution of $[(CH_3)_3C\text{-}CH_2\text{-}N(CH_3)_3]^+I^-$ (0.05 mmol) in water was then added dropwise. After 1 h stirring the silver salts were filtered off and washed until the filtrate was neutral. The combined filtrate was then titrated with aqueous HF in a polyethylene container to neutrality. The titration was monitored with a potentiometer (glass electrode). The solution was quickly evaporated to dryness. The solid residue was dried under high vacuum: the temperature was slowly increased to 130 °C and maintained at this temperature for several days; at various intervals during the heating process the solid was ground into smaller pieces. A colorless crystalline powder, stable to 145 °C, was obtained in 98% yield: ^1H NMR (CD_3CN): $\delta = 1.37$ (9H), 3.61 (9H) 3.67 (2H); ^{19}F NMR (CD_3CN): $\delta = -71.2$; IR (KBr): $\tilde{\nu} = 2950, 1500, 1485, 970\ cm^{-1}$; Raman (solid): $\tilde{\nu} = 2996, 2914, 748\ cm^{-1}$ (only strong bands); $C_8H_{20}NF$ (149.27): calcd C 64.43, H 13.52, N 9.38, F 12.73; found C 64.23, H 13.95, N 9.18, F 13.10.

1,1,3,3,5,5-Hexamethylpiperidinium fluoride (pip^+F^-): The following reaction is a variation of a literature procedure, which guarantees reliable yields of more than 75%: 3,5,5-trimethyl-2-cyclohexen-1-one (52.6 mL, isophorone) was added dropwise to a solution of CH_3MgBr (140 mL, 3 M in diethyl ether) containing $CuCl_2$ (0.42 g); the temperature was maintained between 0 and +10 °C (otherwise largely 1,2-addition was observed). The solution was stirred for 2 h and stored overnight at room temperature before pouring it on ice (230 g) containing acetic acid (28 g). The organic layer was diluted with diethyl ether, separated, and washed with an aqueous $NaHCO_3$ solution, water, and saturated NaCl solution until it was neutral. After drying and evaporation of the ether, the crude product was distilled in vacuo at 82 °C/34 mbar and 40.5 g (75 °C) of 3,3,5,5,-tetramethylcyclopentanone was isolated. This product was transformed into 1,1,3,3,5,5-hexamethylpiperidinium iodide by applying literature procedures [9,10]. The iodide was then treated with silver oxide/hydroxide, and the aqueous solution of the hydroxide was titrated with aqueous HF as described above. During the drying procedure under high vacuum the temperature was kept below 120 °C. pip^+F^- was obtained as a colorless crystalline powder in over 98% yield, based on the iodide, and in an overall yield of 14%, based on isophorone: ^1H NMR (CD_3CN): $\delta = 1.18$ (12H), 1,51 (2H), 1,99 (4H), 3.77 (6H); $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta = 29.0, 30.1, 44.7, 55.3, 70.1$; ^{19}F NMR (CH_3CN): $\delta = -70.7$; the amount of the impurity HF_2^- can be deduced by the characteristic doublet $\delta = -146.4$ ($^1J = 122$ Hz) in the ^{19}F NMR; IR (Nujol): $\tilde{\nu} = 1506, 1258, 1142, 1050, 991, 972, 937, 920, 902, 886, 787, 722, 477, 441\ cm^{-1}$; Raman (solid): $\tilde{\nu} = 147.5, 144.0, 1355.5, 1263.5, 1234.5, 1195.0, 1149.0, 1109.5, 1054.5, 1019.5, 956.5, 971.0, 939.0, 912.0, 904.5, 787.0, 574.5, 500.5, 387.0, 356.5, 340.0, 317.0\ cm^{-1}$. $C_{11}H_{24}NF$ (189.32): calcd C 69.78, H 12.78, N 7.40, F 10.04; found C 68.66, H 12.72, N 7.19, F 10.2.

Bis(1,1,3,3,5,5-hexamethylpiperidinium) hexafluoroselenate(IV) ($(pip^+)_2SeF_6^{2-}$): pip^+F^- (5 mmol) was placed in a Teflon FEP (fluorinated ethylene-poly(propylene) resin) tube (length = 15 cm, diameter = 0.8 cm), which was then attached to a vacuum line. Carefully purified [29] CH_3CN (3 mL) and SeF_4 (0.25 mmol) were condensed onto the fluoride. The tube was sealed off and briefly warmed to room temperature. A solid precipitate was formed immediately. This precipitate was centrifuged to one end of the tube. The tube over was tipped over, and a clear, slightly yellow liquid was obtained at the other end of the tube. The tube was maintained at −15 °C for several weeks. Slowly yellow-brown crystals were formed in 25% yield: ^{19}F NMR (CH_3CN): $\delta = 13.38$; IR (Nujol): $\tilde{\nu} = 1256, 1129, 1040, 988, 968, 940, 900, 671\ cm^{-1}$. Raman (solid): $\tilde{\nu} = 1467, 943, 903, 787, 670, 572.5\ cm^{-1}$. $C_{22}H_{48}N_2F_6Se$ (533.57): calcd C 49.52, H 9.06, N 5.25; found C 47.94, H 9.51, N 5.36.

1,1,3,3,5,5-Hexamethylpiperidinium hexafluorobromate(V) ($pip^+BrF_6^-$): pip^+F^- (0.66 mmol) and $CsBrF_6$ (0.70 mmol) were placed in a Teflon FEP tube. CH_3CN (2 mL) was condensed onto the mixture. After the tube had been sealed, the progress of the reaction was monitored by ^{19}F NMR spectroscopy at −20 °C. When the BrF_6^- signal was no longer observed to increase in intensity, the insoluble components were separated by centrifugation and tipping the tube. The clear colorless solution was cooled slowly to −40 °C, and colorless crystals were formed (98% yield): ^{19}F NMR (CH_3CN): $\delta = 100.6$ ($^1J(^{79}Br\text{–}F) = 1570.6$ Hz, $^1J(^{81}Br\text{–}F) = 1694.9$ Hz); single lines at $\delta = 106.2$ and -34.2 indicate the formation of $BrOF_4^-$ and BrF_4^- [23]; IR (Nujol): $\tilde{\nu} = 472\ cm^{-1}$; Raman (solid): $\tilde{\nu} = 561, 445, 241\ cm^{-1}$ (only anion bands); lines at 522 and 445 cm^{-1} indicate the presence of BrF_4^-.

Crystal structure determinations: Suitable crystals were taken directly out of the mother liquor and transferred to the goniometer head with the help of a special

Table 1. Crystallographic details of the pip$^+$ salts described in this paper.

	pip$^+$F$^-$	pip$^+$F$^-$ $\cdot 4CH_2F_2$	(pip$^+$)$_2$SeF$_6^{2-}$	pip$^+$BrF$_6^-$
size [mm]	$0.5 \times 0.3 \times 0.2$	$0.4 \times 0.4 \times 0.4$	$0.4 \times 0.3 \times 0.2$	$0.3 \times 0.3 \times 0.2$
a [pm]	1083.1(2)	1509.0(4)	791.3(1)	747.7(1)
b [pm]	979.9(2)	874.6(6)	827.4(1)	835.8(2)
c [pm]	1088.9(1)	1544.2(4)	1178.0(1)	1269.2(2)
α [°]	90	90	83.08(1)	86.50(1)
β [°]	95.84(1)	93.88(2)	77.51(1)	73.55(1)
γ [°]	90	90	60.72(1)	80.29(1)
V [10^6 pm^3]	1150.8(3)	2033(1)	656.8(2)	776.8(2)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	4	4	1	2
$2\theta_{max}$ [°]	50	50	70	60
T [°C]	−143	−163	−143	−143
Reflections				
measured	2272	4351	5773	4498
independent	1720	2690	5441	4212
$I \geq 3\sigma(F)$	1445	1998	4964	3853
Parameters	191	323	242	245
R	0.059	0.073	0.041	0.043
R_w	0.048	0.054	0.035	0.038
Residual electron density [10^{-6} e$^-$ pm^{-3}]	0.3 (C1, 89 pm)	0.4 (C31, 149 pm)	0.9 (Se, 107 pm)	0.6 (Br, 90 pm)

cooling device [30]. The quality of the crystals was checked by rotating crystal polaroid photos. Lattice constants were determined with 25 reflections, usually with θ angles of between 18 and 22°. Intensity measurements were obtained by ω–2θ scans, by allowing 1/4 of the scan time for background measurements. Corrections for decay, Lorentz polarization, and absorption in case of the SeF$_6^{2-}$ and BrF$_6^-$ [31] were applied. The structures were solved by direct methods [32] and refined towards F[33] by the SHELXS procedures. Other experimental details are found in Table 1. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58848.

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