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Synthesis and Properties of $NF_4^+ClO_4^-$ and $NF_4^+HF_2^-\cdot nHF$ and Some Reaction Chemistry of NF_4^+ Salts

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The possibility of synthesizing $NF_4^+XO_4^-$ (X = Cl, Br, I) salts by metathesis between NF_4SbF_6 and $CsXO_4$ in anhydrous HF solution at −78 °C was studied. Of these NF_4XO_4 salts, NF_4ClO_4 was isolated and characterized by vibrational and ^{19}F NMR spectroscopy. It is an unstable white solid decomposing at 25 °C to give NF_3 and $FOClO_3$ in high yield. The NF_4BrO_4 salt is of marginal stability in HF solution and decomposes to NF_3, O_2, and $FBrO_2$. Attempts to isolate NF_4BrO_4 as a solid resulted in explosions. The NF_4IO_4 salt could not be prepared due to the facile fluorination of IO_4^- to $IF_4O_2^-$ by either HF or BrF_5. Attempts to prepare $NF_4^+XF_4O^-$ (X = Cl, Br) salts by metathesis between NF_4SbF_6 and $CsXF_4O$ in BrF_5 solution at 25 °C were unsuccessful; with BrF_4O^-, fluoride abstraction occurred, resulting in the formation of NF_3, F_2, and BrF_3O, whereas $CsClF_4O$ underwent a displacement reaction with BrF_5 to give $CsBrF_6$ and ClF_3O. The metathetical synthesis of NF_4NO_3 could not be studied in HF due to the reaction of NO_3^- with HF to give NO_2^+, H_2O, and HF_2^-. The metathesis between NF_4SbF_6 and CsF in HF at −78 °C did not produce $NF_4^+F^-$ but produced an unstable white solid of the composition $NF_4^+HF_2^-\cdot nHF$. The composition, thermal stability, spectroscopic properties, and decomposition products of this solid were studied. The $NF_4^+HF_2^-$ salt is stable in HF solution at 25 °C, and the synthetic usefulness of these solutions for the synthesis of other NF_4^+ salts is briefly discussed. Attempts to prepare NCl_4^+ and NCl_2O^+ salts by F–Cl exchange between BCl_3 and NF_4^+ and NF_2O^+ were unsuccessful.

Introduction

The first report on the successful syntheses of NF_4^+ salts were published[1,2] in 1966. Since then, numerous NF_4^+ salts have been prepared and characterized which contain as counterions BF_4^-,[3-10] XF_5^- (X = Ge, Ti, Sn), XF_6^-[10-12] (X = P, As, Sb, Bi),[1,2,7,8,10,13,14-18] or XF_6^{2-} (X = Ge, Sn, Ti, Ni).[10-12,19] All these anions are derived from strong perfluorinated Lewis acids. It was therefore interesting to investigate the possible synthesis of salts derived from either the simplest anion F^- or oxygen containing anions. Although in 1968 Tolberg and co-workers found evidence for the existence of unstable NF_4^+ salts probably containing the HF_2^- or the ClO_4^- anion,[4] these salts were not well characterized, and no data were published. In this paper, we describe the synthesis and characterization of $NF_4^+HF_2^-\cdot nHF$ and $NF_4^+ClO_4^-$ and the attempted syntheses of $NF_4^+BrO_4^-$, $NF_4^+BrF_4O^-$, NF_4^+-

ClF_4O^-, and $NF_4^+NO_3^-$. Since the existence of a stable $NOCl_2^+SbCl_6^-$ salt has recently been reported,[20] it appeared interesting to study the possibility of exchanging chlorine for fluorine in either NF_4^+ or NF_2O^+ salts by using BCl_3.

Experimental Section

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[7] NF_2OSbF_6,[21] $CsClF_4O$,[22] and $CsBrF_4O$.[23] The BrF_5 (Matheson) was treated with 35 atm of F_2 at 200 °C for 24 h and then purified by fractional condensation through traps kept at −64 and −95 °C, with the material retained in the latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_5 to remove the last traces of H_2O.[18] The CsF (American Potash) was fused in a platinum crucible and ground in the drybox. The $CsClO_4$ (ROC/RIC) was used as received. The $CsNO_3$ was prepared from aqueous Cs_2CO_3 and HNO_3 by using a pH electrode for end point detection. It was purified by recrystallization from H_2O and dried in an oven at 100 °C for 24 h. The BCl_3 (Matheson) was treated with Hg and purified by fractional condensation prior to use.

Apparatus. Volatile materials used in this work were handled either in a Monel–Teflon FEP, a stainless steel–Teflon FEP, or a Teflon PFA vacuum line. The latter was constructed exclusively from injection-molded PFA fittings and valves (Fluoroware, Inc.). The anhydrous HF was preferentially handled in the PFA or Monel line, whereas the halogen fluorides were handled mainly in a steel line. All lines were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in either HF or BrF_5 solution by using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref 12). For NMR or low-temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4-mm Teflon FEP or thin-walled Kel-F tube.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Room-temperature spectra of solids were obtained by using dry powders pressed between AgCl disks. Low-temperature spectra were obtained by placing the chilled powder between cold AgCl disks and striking the disks with a hammer. The resulting AgCl sandwich was held in a liquid N_2 cooled

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sample holder of a low-temperature infrared cell[24] with external CsI windows. Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[25] for the elimination of plasma lines. Sealed quartz, Teflon FEP, or Kel-tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded by using a previously described[26] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[25] Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external CFCl$_3$.

Preparation and Properties of NF$_4$$^+ClO_4$$^-$. The compatibility of the ClO$_4$$^-$ anion with HF was established by dissolving CsClO$_4$ in HF and recording the Raman spectra of the solution and of the solid residue recovered after removal of the solvent. Both spectra showed exclusively the bands characteristic for ClO$_4$$^-$. In a typical preparation of NF$_4$ClO$_4$, NF$_4$SbF$_6$ (10.03 mmol) and CsClO$_4$ (10.02 mmol) were placed into the $^3/_4$-in. o.d. Teflon FEP bottom U-trap of the metathesis apparatus. Anhydrous HF (8.56 g) was added at −196 °C. The mixture was kept at −78 °C for 15 h and then for 2 h at −45 °C with agitation. The entire metathesis apparatus was cooled to −78 °C and inverted to separate the CsSbF$_6$ precipitate from the NF$_4$$^+ClO_4$$^-$ solution. Dry N$_2$ (2 atm) was used to pressurize the solution during this filtration step. The HF solvent was pumped off at −78 and −45 °C for 7 days. The resulting white solid residue was allowed to warm to ambient temperature, and the gaseous decomposition products were separated in a dynamic vacuum by fractional condensation through a series of traps kept at −112, −186, and −210 °C. The −210 °C trap contained 8.0 mmol of NF$_3$ and the −186 °C trap had 8.0 mmol of FOClO$_3$ which were identified by infrared, Raman, and ^{19}F NMR spectroscopy.[27] The filter cake (3.60 g, weight calculated for 10 mmol of CsSbF$_6$ 3.69 g) was shown by infrared and Raman spectroscopy to be CsSbF$_6$ and did not contain any detectable impurities. A small amount (80 mg) of a white stable solid residue was left behind after the thermal decomposition of the NF$_4$ClO$_4$ which, on the basis of its vibrational spectra, consisted of a mixture of NF$_4$SbF$_6$ and CsSbF$_6$. The 20% of NF$_4$ClO$_4$ unaccounted for by the above material balance corresponds to the amount of product in the mother liquor typically retained by the CsSbF$_6$ filter cake in similar metathetical reactions. It is decomposed and pumped off during the HF removal step in which the filter cake is allowed to warm to ambient temperature. On the basis of the above material balance, the NF$_4$ClO$_4$ prepared in this manner had a purity of 95 wt %.

For the spectroscopic identification of NF$_4$ClO$_4$ and the determination of its thermal stability, reactions were carried out on a 1–2-mmol scale by using 4-mm o.d. Teflon FEP NMR or thin-walled Kel-F tubes as receivers. The ^{19}F NMR spectrum of an NF$_4$$^+ClO_4$$^-$ solution in anhydrous HF at −40 °C showed the signals characteristic of NF$_4$$^+$ (triplet of equal intensity at ϕ −214.8 with J_{NF} = 229.3 Hz and a line width of less than 3 Hz),[10] FOClO$_3$ (singlet at ϕ −219.4),[27] and NF$_3$ (broad triplet of equal intensity at ϕ −142 with J_{NF} = 150 Hz).[28,29] When the solution was kept at 20 °C and continuously monitored by NMR, the signal due to NF$_4$$^+$ was found to steadily decrease, and those due to FOClO$_3$ and NF$_3$ were found to correspondingly increase in relative intensity. A solution containing 40 mol % of NF$_4$$^+$ and 60 mol % FOClO$_3$ was found to change within 16 h at 20 °C to 17 mol % of NF$_4$$^+$ and 83 mol % of FOClO$_3$. The decomposition of NF$_4$ClO$_4$ in HF solution at ambient temperature was also followed by Raman spectroscopy which showed the bands due to FOClO$_3$[27] to grow with time at the expense of those due to NF$_4$$^+$ and ClO$_4$$^-$. Due to its low boiling point and low solubility in HF, NF$_3$ could not be detected in the HF solution by Raman spectroscopy.

The thermal stability of solid NF$_4$$^+ClO_4$$^-$ was studied by pumping on a sample at a given temperature for 1 h and measuring the amount of NF$_3$ and FOClO$_3$ evolved. Whereas at −13 °C NF$_4$ClO$_4$ essentially is still stable, slow decomposition was observed at 0 °C which became rather rapid at 25 °C, giving the sample the appearance of a fluidized sand bath. *Caution!* Since the thermal decomposition of NF$_4$ClO$_4$ yields the very shock-sensitive[30] FOClO$_3$ in high yield, one should take appropriate safety precautions when working with this compound.

Reaction of NF$_4$SbF$_6$ with CsBrO$_4$. The compatibility of CsBrO$_4$ with HF was established in the same manner as described above for CsClO$_4$. The solubility of CsBrO$_4$ in HF at 25 °C was in excess of 1 g/g of HF. For the metathetical reaction, NF$_4$SbF$_6$ and CsBrO$_4$ (1.0 mmol each) in HF (2 mL) were stirred at 20 °C for 1.5 h, then half of the solvent was pumped off, and the mixture was cooled to −78 °C and filtered at this temperature into a Teflon FEP NMR tube. The NMR tube was sealed off, and the filter cake was pumped to dryness and shown by vibrational spectroscopy to consist of CsSbF$_6$. The Raman spectrum of the solution, which showed signs of gas evolution (O$_2$), exhibited the bands characteristic for NF$_4$$^+$, BrO$_4$$^-$,[31] and FBrO$_2$[32] with the intensity of the FBrO$_2$ bands growing with time at the expense of those of NF$_4$$^+$ and BrO$_4$$^-$. The ^{19}F NMR spectrum showed resonances characteristic of NF$_4$$^+$ (sharp triplet of equal intensity at ϕ −217 with J_{NF} = 227 Hz) and NF$_3$ (broad triplet of equal intensity at ϕ −143 with J_{NF} = 150 Hz) and a broad line at ϕ 186 attributed to HF (ϕ 196) undergoing rapid exchange with FBrO$_2$ (ϕ −205).[33] *Caution!* Explosions occurred when attempts were made to isolate solid NF$_4$BrO$_4$ from an HF solution which had never been warmed above −78 °C.

Reaction of CsNO$_3$ with HF. Cesium nitrate was dissolved in anhydrous HF. The Raman spectrum of the solution did not show the bands characteristic of NO$_3$$^-$ but did show only one band at 1411 cm^{-1} which is characteristic[34] for NO$_2$$^+$. The solid residue obtained by pumping the solution to dryness was shown by Raman spectroscopy to consist again of CsNO$_3$.

Reaction of NF$_4$SbF$_6$ with CsBrF$_4$O in BrF$_5$. In a drybox a mixture of NF$_4$SbF$_6$ (0.536 mmol) and CsBrF$_4$O (0.449 mmol) was placed into a $^3/_4$-in. o.d. Teflon FEP ampule, and BrF$_5$ (4 mL, liquid) was added at −196 °C by using the vacuum line. The contents of the ampule were warmed to 20 °C and stirred with a magnetic stirring bar for 2.5 h. The ampule was cooled to −196 °C, and the noncondensable material (0.42 mmol of F$_2$) was distilled off. The material volatile at −95 °C was distilled off and consisted of 0.48 mmol of NF$_3$. The material volatile at 20 °C was separated by fractional condensation through a series of traps kept at −64, −78, and −196 °C. The −64 °C trap contained BrF$_3$O (0.43 mmol), in addition to some BrF$_5$. The two colder traps contained the bulk of the BrF$_5$. The solid nonvolatile reaction product (205 mg, weight calculated for 0.449 mmol CsSbF$_6$ and 0.087 mmol NF$_4$SbF$_6$ 194 mg) was shown by vibrational spectroscopy to consist mainly of CsSbF$_6$ containing some NF$_4$SbF$_6$.

Reaction of CsClF$_4$O with BrF$_5$. In a sapphire reactor, CsClF$_4$O (1.234 mmol) and BrF$_5$ (15 mmol) were combined at −196 °C. The mixture was kept at 20 °C for 12 h. The volatile products were distilled off and consisted of BrF$_5$ and ClF$_3$O (1.2 mmol). The solid residue (405 mg, weight calculated for 1.234 mmol of CsBrF$_6$ 403 mg) was shown by vibrational spectroscopy to consist of CsBrF$_6$.[35]

Preparation and Properties of NF$_4$$^+HF_2$$^-$·$n$HF. In a typical experiment, NF$_4$SbF$_6$ and CsF (10.0 mmol each) were placed into the metathesis apparatus and HF (10 mL) was added at −196 °C. The mixture was stirred at 20 °C for 2 h, then cooled to −78 °C, and filtered. Most of the HF solvent was removed by pumping at −78 °C for 36 h, −64 °C for 12 h, −57 °C for 6 h, and −45 °C for 6 h. At −45 °C the residue was still liquid but, when cooled to −78 °C, changed its appearance to that of a wet solid. The pumped-off material consisted of HF. The sample was allowed to warm to ambient temperature, and the evolved volatile material was pumped off through traps kept at −126 and −210 °C. The amounts and mole ratios of HF (−126 °C trap) and NF$_3$ (−210 °C trap) were periodically

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measured while the sample was cooled back to −45 °C. Several hours of warming to ambient temperature and to 40 °C was required to achieve complete decomposition of the salt. A total of 8.32 mmol of NF_3 and 19.63 mmol of HF was collected with the $HF:NF_3$ mole ratio ranging from 10.1 at the start to 1.54 toward the end of the decomposition. A small amount (80 mg) of a stable white solid residue was left behind after completion of the decomposition which consisted mainly of NF_4SbF_6 and some $CsSbF_6$. The filter cake (3.5 g, weight calculated for 10.0 mmol of $CsSbF_6$ 3.687 g) consisted of $CsSbF_6$. The 15% of the NF_4^+ value unaccounted for by the above material balance is in line with the amount of material in the mother liquor generally retained by the $CsSbF_6$ filter cake in similar reactions (see NF_4ClO_4 preparation). On the basis of the above material balance, the purity of $NF_4HF_2 \cdot nHF$ obtained in this manner is about 97 mol % with the $CsSbF_6$ and NF_4SbF_6 impurities being caused by the slight solubility of $CsSbF_6$ in HF and a small excess of one reagent. During the above-described ambient-temperature decomposition of $NF_4HF_2 \cdot nHF$, the originally liquid sample first turned milky and pasty and then after being recooled to −45 °C had the appearance of a white dry solid which melted very slowly when warmed again to 20 °C. On melting, it started to bubble and foam.

For the determination of the spectroscopic properties, metathetical reactions were carried out as described above but on a 1-mmol scale. The ^{19}F NMR spectrum of the compound in HF solution showed the signal (triplet of equal intensity at ϕ −216.2 with J_{NF} = 230 Hz and a line width of less than 3 Hz) characteristic[13,14] of NF_4^+ and a broad line at ϕ 195 due to rapidly exchanging HF and HF_2^-. The solution appeared to be stable at ambient temperature, and no formation of the NF_3 decomposition product was detectable by NMR.
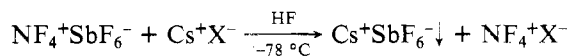
Raman spectra were recorded for the HF solutions at different concentration stages. In all cases, only the characteristic NF_4^+ bands at 1170, 859, 617, and 448 cm^{-1} were observed. For the most dilute solution also a very broad solvent band centered at about 3300 cm^{-1} was observed. After removal of most of the solvent at −57 °C, the solvent band had disappeared. When this sample was frozen at −110 °C, numerous intense bands in the 1400–1700- and the 650–850-cm^{-1} region appeared. However, on further removal of HF, the spectrum of the solid at −110 °C showed again only bands due to NF_4^+.

Reactions of NF_4SbF_6 and NF_2OSbF_6 with BCl_3. A sample of NF_4SbF_6 (1.85 mmol) was treated in a Teflon FEP ampule with a 10-fold excess of BCl_3 for 3 h at 20 °C. The volatile products were separated by fractional condensation and shown to consist of NF_3 and mixed BF_xCl_{3-x}-type compounds. A small amount of solid residue (60 mg) was identified by vibrational spectroscopy as $NO^+SbCl_6^-$.

A sample of NF_2OSbF_6 was similarly treated with BCl_3. The volatile products consisted again of mixed BF_xCl_{3-x}-type compounds, but $NO^+SbF_6^-$ was formed in almost quantitative yield as a nonvolatile residue.
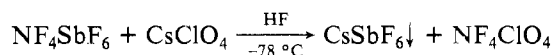
Results and Discussion

The general usefulness of the metathetical reaction

$$NF_4^+SbF_6^- + Cs^+X^- \xrightarrow[-78\ °C]{HF} Cs^+SbF_6^-\downarrow + NF_4^+X^-$$

for the syntheses of otherwise inaccessible $NF_4^+X^-$ salts has previously been demonstrated[7,11,12,18,19] for a number of perfluorinated anions. In this study this approach was extended to oxygen-containing anions, such as the perhalates and tetrafluorohalates.

Synthesis and Properties of NF_4ClO_4. The ClO_4^- anion was found to be stable in HF solution. Therefore, NF_4ClO_4 was prepared according to

$$NF_4SbF_6 + CsClO_4 \xrightarrow[-78\ °C]{HF} CsSbF_6\downarrow + NF_4ClO_4$$

The reaction must be carried out at low temperature since, even in HF solution, NF_4ClO_4 undergoes decomposition at room temperature. The NF_4ClO_4 salt can be isolated as a white solid, stable up to about −13 °C. At 0 and 25 °C, respectively, slow and rapid decompositions of the solid were observed according to

$$NF_4ClO_4 \rightarrow NF_3 + FOClO_3$$
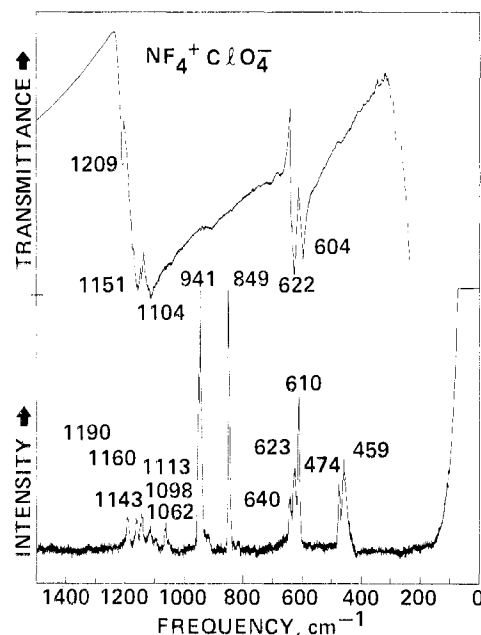
In HF solution the rate of decomposition is slower but follows

Figure 1. Low-temperature vibrational spectra of solid $NF_4^+ClO_4^-$. The infrared spectrum was recorded as a dry powder between AgCl disks at −196 °C. The broken line indicates absorption due to the AgCl window material. The Raman spectrum was recorded at −110 °C with a spectral slit width of 6 cm^{-1}.

Table I. Vibrational Spectra of Solid NF_4ClO_4

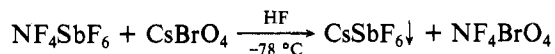| obsd freq, cm^{-1}, and rel intens[a]		assignt (point group)	
IR	Raman	NF_4^+ (T_d)	ClO_4^- (T_d)
1209 w		$2\nu_4$ $(A_1 + E + F_2)$	
	1190 (1.3)	}	
1151 s	1160 (1)	} ν_3 (F_2)	
	1143 (1.2)	}	
1104 vs	1113 (0.8)		}
	1098 (0.3)		} ν_3 (F_2)
	1062 (1)		}
	950 (6)		} ν_1 (A_1)
	941 (10)		}
	849 (10)	ν_1 (A_1)	
	640 (2)		}
622 s	623 (3)		} ν_4 (F_2)
604 s	610 (6)	ν_4 (F_2)	
	474 (2.5)		ν_2 (E)
	459 (3.5)	ν_2 (E)	

[a] Uncorrected Raman intensities.

the same path. The essentially quantitative formation of $FOClO_3$ is noteworthy and represents a new and convenient synthesis of $FOClO_3$. On the basis of the observed material balance, the yield of NF_4ClO_4 is high, and the only significant loss of material is due to the amount of mother liquor retained by the $CsSbF_6$ filter cake. The purity of the NF_4ClO_4 product is also high, and the impurities present are $CsSbF_6$, in an amount corresponding to its solubility in HF at −78 °C, and any slight excess of starting material used in the reaction.
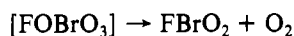
The ionic composition of NF_4ClO_4, in both HF solution and the solid state, was established by vibrational and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of $NF_4^+ClO_4^-$ in HF solution showed the signal characteristic[13,14] for tetrahedral NF_4^+. The Raman spectra (cm^{-1}) of this solution confirmed the presence of tetrahedral NF_4^+ (1170 (w, br), 855 (vs, p), 612 (m), 448 (mw))[10] and ClO_4^- (940 (s, p), 620 (w), 460 (w)).[34] The infrared and Raman spectra of solid $NF_4^+ClO_4^-$ are given in Figure 1. The observed frequencies and their assignments in point group T_d are summarized in Table I. As expected for a solid, splittings of bands into their degenerate

components and crystal splittings are observed. In addition $\nu_1(A_1)$ and $\nu_2(E)$ which ideally are infrared inactive were observed in the infrared spectrum as extremely weak bands. The pronounced Christiansen effect[36] observed for the infrared spectrum is due to the experimental difficulties in obtaining good pressing of AgCl windows at low temperature. The pressing was achieved by striking the sample sandwiched between the AgCl plates with a hammer. The sample did not detonate under these conditions, indicating that NF$_4$ClO$_4$ is considerably less sensitive than its decomposition product FOClO$_3$.[30]

Reaction of NF$_4$SbF$_6$ with CsBrO$_4$. The BrO$_4^-$ anion was found to be stable in HF solution, thus allowing the metathetical reaction

$$NF_4SbF_6 + CsBrO_4 \xrightarrow[-78\ °C]{HF} CsSbF_6\downarrow + NF_4BrO_4$$

to be carried out. The presence of tetrahedral NF$_4^+$ [10,13,14] and BrO$_4^-$ [31] in the resulting HF solution was demonstrated by ^{19}F NMR and Raman spectroscopy. By analogy with NF$_4$ClO$_4$, slow decomposition of the NF$_4$BrO$_4$ solution occurred at room temperature. However, instead of the yet unknown FOBrO$_3$, only its expected[37] decomposition products, FBrO$_2$ and O$_2$, were obtained in addition to NF$_3$.

$$NF_4BrO_4 \rightarrow NF_3 + [FOBrO_3]$$

$$[FOBrO_3] \rightarrow FBrO_2 + O_2$$

Attempts to isolate solid NF$_4$BrO$_4$ from an HF solution, which had never been warmed above -78 °C, were unsuccessful due to a sharp detonation of the sample with flashing. Whether this was caused by NF$_4$BrO$_4$ itself or by possibly the presence of some FOBrO$_3$ could not be established.

The metathetical synthesis of NF$_4$IO$_4$ was not possible due to the fact that IO$_4^-$ interacts with either HF[27,38] or BrF$_5$[27] according to

$$IO_4^- + 4HF \rightarrow IF_4O_2^- \text{ (cis and trans isomers)} + 2H_2O$$

$$IF_4O_2^- + 2HF \rightarrow HF_2^- + HOIF_4O$$

$$IO_4^- + 2BrF_5 \rightarrow IF_4O_2^- \text{ (trans isomer mainly)} + 2BrF_3O$$
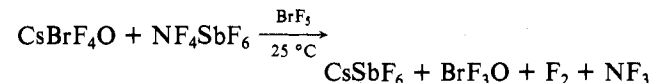
The metathesis between CsIF$_4$O$_2$ and NF$_4$SbF$_6$ in HF, followed by the thermal decomposition of the metathesis product, produces the novel compounds *cis*- and *trans*-OIF$_4$OF and will be reported in a separate paper.
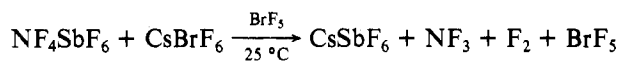
Reaction of NF$_4$SbF$_6$ with CsBrF$_4$O. Although CsBrF$_4$O reacts with HF[39] according to

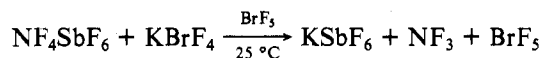$$CsBrF_4O + HF \rightarrow CsHF_2 + BrF_3O$$

BrF$_5$ does not interact with CsBrF$_4$O[23] and therefore is a suitable solvent for studying the reaction of NF$_4$SbF$_6$ with CsBrF$_4$O. The following reaction was observed:

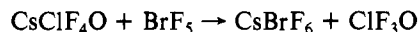$$CsBrF_4O + NF_4SbF_6 \xrightarrow[25\ °C]{BrF_5} CsSbF_6 + BrF_3O + F_2 + NF_3$$

The formation of these products indicates that the salt NF$_4^+$BrF$_4$O$^-$ is not stable under these conditions and that, contrary to the NF$_4^+$ClO$_4^-$ and NF$_4^+$IF$_4$O$_2^-$ reactions, fluoride abstraction from BrF$_4$O$^-$ is preferred over the fluorination of BrF$_4$O$^-$ to either BrF$_4$OF or BrF$_5$O. A similar fluoride abstraction has previously been observed[4] for BrF$_6^-$

$$NF_4SbF_6 + CsBrF_6 \xrightarrow[25\ °C]{BrF_5} CsSbF_6 + NF_3 + F_2 + BrF_5$$

but not for BrF$_4^-$ which was fluorinated[4] to BrF$_5$

$$NF_4SbF_6 + KBrF_4 \xrightarrow[25\ °C]{BrF_5} KSbF_6 + NF_3 + BrF_5$$

The corresponding metathesis between CsClF$_4$O and NF$_4$SbF$_6$ was not studied because it was found that CsClF$_4$O reacts with BrF$_5$ according to

$$CsClF_4O + BrF_5 \rightarrow CsBrF_6 + ClF_3O$$

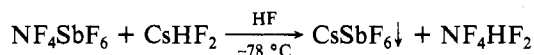The formed CsBrF$_6$ would be capable of undergoing with NF$_4$SbF$_6$ the above-given fluoride abstraction reaction.

Reaction of CsNO$_3$ with HF. The compatibility of CsNO$_3$ with HF was studied in order to explore the feasibility of synthesizing NF$_4$NO$_3$. Although CsNO$_3$ is quite soluble in HF and can be recovered as such from HF solutions, Raman spectra of these solutions showed the absence of NO$_3^-$ and the presence of NO$_2^+$ as the only nitrogen–oxygen-containing species. These results imply an equilibrium, such as

$$NO_3^- + 4HF \xrightleftharpoons{HF} NO_2^+ + H_2O + 2HF_2^-$$

which has previously been postulated[40] for these solutions. In view of the absence of NO$_3^-$ in the HF solution, no metathetical reactions between CsNO$_3$ and NF$_4$SbF$_6$ were attempted.

Preparation and Properties of NF$_4$HF$_2$·nHF. The NF$_4^+$F$^-$ salt, which has an active fluorine content in excess of 90 wt %, would be of extreme interest. However, previous attempts to prepare a stable salt from NF$_3$ and F$_2$ at -196 °C by either bremsstrahlung[3] or UV photolysis[10] were unsuccessful, indicating that the salt is unstable with regard to its decomposition to NF$_3$ and F$_2$. Since most of the metathetical reactions for the production of NF$_4^+$ salts are carried out in anhydrous HF, which is an acid, it was of interest to define the nature and stability of a possible NF$_4^+$HF$_2^-$ salt. A previous unpublished study[4] of the LiF–NF$_4$SbF$_6$ system in HF at ambient temperature had provided evidence that after removal of the precipitated LiSbF$_6$ a stable solution containing the NF$_4^+$ cation was obtained. All attempts to isolate a salt at temperatures of -44 °C and above from this solution resulted in decomposition to NF$_3$, F$_2$, and HF. Removal of the solvent at -78 °C resulted in a wet solid which was not characterized.

Since our previous studies[18] had shown that a low-temperature metathesis using a cesium salt is superior to a lithium salt based process, the following system was studied:

$$NF_4SbF_6 + CsHF_2 \xrightarrow[-78\ °C]{HF} CsSbF_6\downarrow + NF_4HF_2$$

On the basis of the observed material balance, the soluble product consisted of about 97 mol % NF$_4$HF$_2$ with the remainder being CsSbF$_6$ and excess of either starting material. In agreement with the previous observation,[4] NF$_4$HF$_2$ is stable in HF solution at ambient temperature and shows in the ^{19}F NMR spectrum the characteristic[13,14] NF$_4^+$ signal. The presence of the NF$_4^+$ cation and the virtual absence of anions other than those due to solvated F$^-$ was also demonstrated by Raman spectroscopy of solutions at different concentrations. As shown by trace A of Figure 2, these solutions exhibited only the four bands characteristic[10] of tetrahedral NF$_4^+$. The difficulty in observing bands due to solvated HF$_2^-$ is not surprising in view of HF being a weak scatterer and the ex-

(36) Lawless, E. W. *Anal. Lett.* **1967**, *1*, 153.
(37) Macheteau, Y.; Gillardeau, J. *Bull. Soc. Chim. Fr.* **1969**, 1819.
(38) Selig, H.; Elgad, U. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 91.
(39) Christe, K. O.; Curtis, E. C.; Bougon, R. *Inorg. Chem.* **1978**, *17*, 1533.

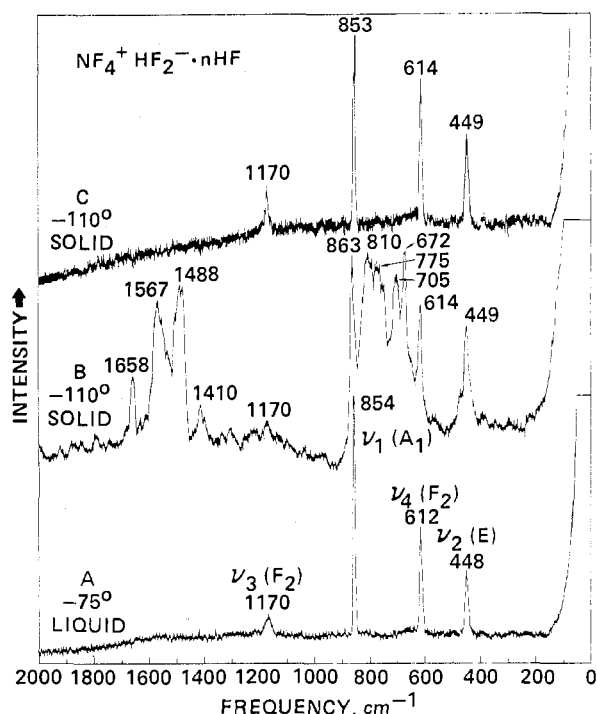(40) Clifford, A. F.; Beachell, H. C.; Jack, W. M. *J. Inorg. Nucl. Chem.* **1957**, *5*, 57.

Figure 2. Raman spectra of liquid and solid $NF_4^+HF_2^- \cdot nHF$ in a Kel-F capillary: trace A, spectrum of a concentrated HF solution at −75 °C (the given assignments are for tetrahedral NF_4^+); trace B, spectrum for the trace A sample cooled to −110 °C (in addition to the NF_4^+ bands, the spectrum shows bands attributed to $HF_2^- \cdot nHF$); trace C, spectrum of the solid at −110 °C containing only a small excess of HF. The sample of trace B was used after pumping off most of the HF and decomposing most of the sample at about −20 °C. All spectra were recorded with a spectral slit width of 8 cm⁻¹.

pected broadness of the lines of HF_2^- undergoing rapid exchange with the solvent HF.

Most of the solvent can be removed by pumping at −45 °C. The resulting residue is a clear liquid at −45 °C but solidifies at −78 °C to give the appearance of a wet solid. The composition of this residue was determined by studying its exhaustive dissociation at 25 °C according to

$$NF_4HF_2 \cdot nHF \rightarrow NF_3 + F_2 + (n + 1)HF$$

It was found that the mole ratio of NF_3:HF was about 10.1 at the beginning and 1.54 toward the end of this decomposition. These results demonstrate that complete removal of solvated HF from NF_4HF_2 is extremely difficult and is accompanied by decomposition of most of the NF_4^+ salt itself. The presence

of a solvated $HF_2^- \cdot nHF$ anion was also demonstrated by Raman spectroscopy (see trace B of Figure 2) which shows the presence of broad complex bands in the vicinity of the symmetric (600 cm⁻¹) and the antisymmetric (1455 cm⁻¹) stretching modes[34] of HF_2^-. Upon removal of most of the solvated HF, these bands lost intensity, resulting in a spectrum consisting exclusively of the NF_4^+ bands (see trace C of Figure 2).

It is also noteworthy that with decreasing HF content the melting point of $NF_4^+HF_2^- \cdot nHF$ increases and approaches room temperature for *n* approaching zero. The decomposition of $NF_4HF_2 \cdot nHF$ becomes rather slow for decreasing *n*, particularly in the presence of other stable fluorides. It appears that such fluorides can assume the function of stabilizing the HF_2^- anion. A typical example for such a fluoride is AlF_3 or AlF_4^-.[27] A careful analysis of such systems is therefore necessary to avoid the interpretation of such $(NF_4HF_2)_nMF_x$ in terms of $(NF_4)_nMF_{x+n}$ salts.

The possibility of preparing stable HF solutions of NF_4HF_2 renders them a very useful intermediate. By addition of a stronger or less volatile Lewis acid, the HF_2^- anion can be displaced and NF_4HF_2 can be converted into other NF_4^+ salts. This was first demonstrated[4] by reacting NF_4HF_2 solutions with BF_3 to form NF_4BF_4 and has recently been extended[41] to the formation of other salts, which due to the low solubility of their cesium salts are not amenable to direct metathetical reactions.

Halogen Exchange in NF_4^+ and NF_2O^+. In view of the existence of a stable $NCl_2O^+SbCl_6^-$ salt,[20] it was of interest to study the possibility of halogen exchange in either NF_4^+ or NF_2O^+ with BCl_3. For both salts, the observation of mixed BF_xCl_{3-x} products indicated that halogen exchange took place. For NF_4^+ the main product was gaseous NF_3, suggesting that the likely NF_3Cl^+ intermediate might be unstable toward decomposition under the given conditions. For $NF_2O^+SbF_6^-$, the main product was $NO^+SbF_6^-$ which could arise again from breaking of the rather weak N–Cl bonds in an NCl_2O^+ intermediate.

(41) Wilson, W. W.; Christe, K. O., unpublished results.