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Low-Temperature Ultraviolet Photolysis and Its Application to the Synthesis of Novel and Known NF_4^+ Salts

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Low-temperature uv photolysis was used to synthesize the novel NF_4^+ salts NF_4PF_6 and NF_4GeF_5 and the known salts NF_4BF_4 and NF_4AsF_6. This technique offers the first convenient, simple, and high-yield synthesis for NF_4BF_4. The NF_4PF_6 and NF_4GeF_5 salts were also prepared from NF_4BF_4 by displacement reactions with PF_5 and GeF_4, respectively. Treatment of NF_4GeF_5 with anhydrous HF resulted in its conversion to $(NF_4)_2GeF_6$, and $(NF_4)_2GeF_6$ was quantitatively converted back to NF_4GeF_5 by treatment with an excess of GeF_4. The NF_4^+ salts were characterized by vibrational and ^{19}F NMR spectroscopy and x-ray powder data. A cis-fluorine-bridged polymeric structure is proposed for GeF_5^- in its NF_4^+ salt based on the spectroscopic data, its thermal stability, and lack of reaction with either liquid N_2F_4 or FNO_2. The applicability of low-temperature uv photolysis to other reactant systems was briefly studied. The hydrolysis of NF_4^+ salts was reinvestigated.

Introduction

The synthesis of NF_4^+ salts had been discouraged by the nonexistence of a stable NF_5 parent molecule and theoretical computations[1,2] showing that these salts should be thermodynamically unstable. Once the principle was recognized[3,4] that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of a suitable activation energy source, various synthetic approaches were discovered.

Low-temperature glow discharge was used for the synthesis of NF_4AsF_6[4,5] and NF_4BF_4.[6,7] High-pressure and thermal activation were employed[8,9] for the synthesis of the thermally very stable $NF_4SbF_6{\cdot}xSbF_5$. The latter method was also applied to the synthesis of NF_4AsF_6, but the reaction rates are low and metal salts are formed[10] as by-products. Low-temperature γ irradiation was used[11] to prepare NF_4BF_4, but it requires special equipment (3-MeV bremsstrahlung) and cannot easily be scaled up. Impure NF_4BF_4 can be prepared by metathesis[12,13] from the readily accessible[9] $NF_4SbF_6{\cdot}xSbF_5$; however, product purification is difficult. A novel method[14] involving uv photolysis was recently reported for the synthesis of NF_4BF_4, NF_4AsF_6, and $NF_4SbF_6{\cdot}xSbF_5$; however, the yields obtained for the BF_4^- and the AsF_6^- salt were discouragingly low.

In view of the general interest in NF_4^+ salts and the importance of NF_4BF_4 for chemical HF–DF lasers, we were interested in improved methods for synthesizing pure NF_4^+ salts and in the synthesis of novel salts. The results of this study are summarized in this paper.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in well-passivated (with ClF_3) stainless steel or Monel vacuum lines equipped with Teflon FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Arsenic pentafluoride, PF_5, and GeF_4 (Ozark Mahoning), NF_3 and F_2 (Rocketdyne), BF_3 and Kr (Matheson), and OF_2 (Allied Chemical) were purified by fractional condensation prior to their use. The CF_3NF_2 was prepared by uv photolysis of a mixture of $(CF_3CO)_2O$ and N_2F_4.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl or AgBr windows in the form of pressed disks. The pressing operation was carried out using a Wilks minipellet press. Raman spectra were recorded on a Cary Model 83 double monochromator using the 4880-Å exciting line, a Claassen filter[15] for the elimination of plasma lines, and quartz or Teflon FEP tubes as sample containers. The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian Model DA-60 high-resolution NMR spectrometer. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm relative to the external standard $CFCl_3$. Anhydrous HF[16] was used as a solvent and Teflon FEP tubes (Wilmad Glass Co.) were used as sample containers. The thermal decomposition of NF_4^+ salts was examined with a Perkin-Elmer differential scanning calorimeter (Model DSC-1B) using crimp-seal aluminum pans as sample containers and heating rates of 5°/min at atmospheric pressure. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel-filtered copper Kα radiation. Quartz capillaries (~0.5-mm o.d.) were used as sample containers.

The low-temperature uv-photolysis reactions were carried out in either a quartz or a stainless steel–sapphire reaction vessel. The quartz reactor had a pan-shaped bottom and a flat top consisting of a 3-in. diameter optical grade quartz window. The vessel had a side arm connected by a Teflon O ring to a Fischer-Porter Teflon valve to facilitate removal of solid reaction products. The depth of the reactor was about 1.5 in. and its volume was 135 ml. The steel–sapphire reactor was constructed from a 3 in. long, 1.75 in. wide (volume 120 ml) 347 stainless steel cylindrical body provided with a 2-in. diameter sapphire flat sealed to the cell body by means of a flange and a Teflon O-ring. A side arm closed by a steel valve was attached to the cell body. The uv source consisted of a 900-W air-cooled high-pressure mercury arc (General Electric Model B-H6) and was positioned 1.5 in. above the flat reactor surface. The bottom of the reactors was kept cold by immersion in liquid N_2. Dry, gaseous N_2 was used as a purge gas to prevent condensation of atmospheric moisture on the flat top of the reactor. As a heat shield a 0.25 in. thick quartz plate was positioned between the uv source and the top of the reactor.

Syntheses of NF_4^+ Salts by Uv Photolysis. In a typical experiment, premixed NF_3 and BF_3 (27 mmol of each) were condensed into the cold (−196 °C) bottom of the pan-shaped quartz reactor. Fluorine (9 mmol) was added and the mixture was photolyzed at −196 °C for 1 h with a 900-W high-pressure Hg arc in the manner described above. After termination of the photolysis, volatile material was pumped out of the reactor during its warm-up to room temperature. The nonvolatile white solid product consisted of NF_4BF_4 (1.0 g) which was shown by vibrational spectroscopy and elemental analysis to contain no detectable impurities.

The uv photolyses of other systems were carried out in the same manner and the results are summarized in Table I.

Syntheses of NF_4^+ Salts by Displacement Reactions without Solvent. In a typical experiment, pure NF_4BF_4 (2.07 mmol) was combined at −196 °C with an excess of PF_5 (40.01 mmol) in a passivated (with ClF_3) 10-ml 316 stainless steel cylinder. The mixture was kept at 25 °C for 64 h. The volatile materials were removed in vacuo and separated by fractional condensation. They consisted of BF_3 (2.05 mmol) and unreacted PF_5 (37.93 mmol). The white solid residue had gained 120 mg in weight. Based on the above material balance, the conversion of NF_4BF_4 to NF_4PF_6 was essentially complete. This was further confirmed by vibrational spectroscopy which showed the solid to be NF_4PF_6 containing no detectable amounts of NF_4BF_4.

A displacement reaction between NF_4BF_4 and GeF_4 was carried out in a similar manner and resulted in a 65 mol % conversion of NF_4BF_4 to NF_4GeF_5. When this step was repeated two more times, the conversion of NF_4BF_4 to NF_4GeF_5 was complete as shown by the observed material balance, the absence of BF_4^- bands in the vibrational spectra, and elemental analysis.

For the elemental analysis, NF_4GeF_5 (0.339 mmol) was hydrolyzed in a Teflon FEP U-trap with 2 ml of distilled water. The formed O_2 (0.114 mmol) was distilled off at −196 °C and the NF_3 (0.336 mmol)

Table I. Comparative Yields of Products Formed by Uv Photolysis[a] at −196 °C

Reactants	Solid Product	Rate of formn of solid, mg/h
NF_3, BF_3, F_2	NF_4BF_4	1000
NF_3, AsF_5, F_2	NF_4AsF_6	1145
NF_3, PF_5, F_2	NF_4PF_6	10
NF_3, GeF_4, F_2	NF_4GeF_5	25
NF_3, SiF_4, F_2		
N_2, AsF_5, F_2		
CF_3NF_2, AsF_5, F_2	AsF_6^- salts of NF_4^+, $N_2F_3^+$, N_2F^+	1051
OF_2, AsF_5, F_2	O_2AsF_6	130

[a] The uv source was a 900-W (GE B-H6) mercury arc without backing mirror. The mole ratio of the reactants was 3:3:1. All reactions were carried out in the pan-shaped quartz reactor with unfiltered radiation and a radiation time of 1 h without reactant surface renewal. For these reasons the given formation rates do not represent maximum attainable values but are given for comparative purposes.

at −126 °C. They were identified by mass and infrared spectroscopy. The aqueous solution was analyzed by x-ray fluorescence for Ge (calcd for NF_4GeF_5, 28.2; found, 28.6) and for hydrolyzable F^- with an Orion specific ion fluoride electrode (calcd, 44.3; found, 43.7). The presence of H_2O_2 in the hydrolysate was established by its ability to oxidize iodide to free iodine and manganese(II) to manganese(IV) and to reduce MnO_4^-.

Syntheses of NF_4^+ Salts by Displacement Reactions in HF Solution. In a typical experiment pure NF_4BF_4 (2.6 mmol) were placed into a passivated 30-ml Teflon FEP ampule and liquid HF (3 ml) and GeF_4 (3.59 mmol) were added at −196 °C. Upon warm-up of the mixture to room temperature bubbling and foaming was noticed. The contents of the ampule were agitated at 25 °C for several hours on a mechanical shaker. The volatile material was pumped off and based on the observed material balance and spectroscopic and elemental analyses of the solid product, the conversion of NF_4BF_4 to a mixture of NF_4GeF_5 and $(NF_4)_2GeF_6$ was 33 mol %. After repeating this procedure for three more times, the conversion of NF_4BF_4 was 85 mol % and the mole ratio between NF_4GeF_5 and $(NF_4)_2GeF_6$ was about 1.3:1.

Similar exposure of NF_4BF_4 to an excess of PF_5 in HF solution resulted for a single and triple treatment in a conversion of NF_4BF_4 to NF_4PF_6 of 8 and 17 mol %, respectively. However, treatment of NF_4AsF_6 with GeF_4 in HF solution did not produce any detectable amounts of GeF_6^{2-} or GeF_5^- salts.

Interconversion of NF_4GeF_5 and $(NF_4)_2GeF_6$. A sample of pure NF_4GeF_5 was dissolved in a large excess of anhydrous HF in a Teflon FEP ampule. After keeping this solution at 25 °C for 6 h, the volatile products were pumped off at 25 °C. This procedure was repeated three more times and the progress of the reaction was followed by determining the weight change of the solid residue and spectroscopic and elemental analyses of the solid. After the fourth HF treatment, the conversion of NF_4GeF_5 to $(NF_4)_2GeF_6$ was essentially complete. Anal. Calcd: Ge, 19.8; NF_3, 38.7; hydrolyzable F, 41.5. Found: Ge, 19.9; NF_3, 38.5; hydrolyzable F, 41.1.

A sample of pure $(NF_4)_2GeF_6$ was treated at 25 °C with a tenfold excess of liquid GeF_4 for 20 h. The unreacted GeF_4 was pumped off at 40 °C. Based on the observed material balance and spectroscopic and elemental analyses of the solid product, the $(NF_4)_2GeF_6$ was quantitatively converted to NF_4GeF_5.

Interaction of NF_4GeF_5 with N_2F_4 and FNO_2. A sample of NF_4GeF_5 was treated at −78 °C for several hours with a large excess of either liquid N_2F_4 or FNO_2. Based on the observed material balances and spectroscopic analyses of the product, very little reaction occurred. The main product was unreacted NF_4GeF_5 containing some GeF_6^{2-} salt.

Results and Discussion

Syntheses of NF_4^+ Salts by Uv Photolysis. The difficulty of synthesizing NF_4^+ salts from NF_3, F_2, and a Lewis acid increases with decreasing strength of the Lewis acid. Whereas the $SbF_6^- \cdot xSbF_5$ salt can readily be prepared using thermal activation[8,9] or room-temperature uv photolysis,[14] these methods are of only marginal feasibility for the AsF_6^- salt and of little or no use for the BF_4^- salt. Since no simple methods existed for the convenient synthesis of the interesting compound $NF_4^+BF_4^-$ in high purity and yield, we have searched for novel synthetic approaches.

It was found that low-temperature uv photolysis is ideally suited for preparing NF_4BF_4. A large number of reaction parameters were studied[17] to maximize the yield. Maximum yields of NF_4BF_4 were obtained close to liquid nitrogen temperature (−196 °C) using unfiltered uv radiation, a short path length to avoid recombination of F atoms to molecular F_2,[14] and periodic addition of fresh starting materials to the uv cell to avoid coating of the surface of the condensed reactants by solid NF_4BF_4. The highest yield of NF_4BF_4 achieved to date in our laboratory with a 900-W mercury arc was in excess of 3 g/h and was achieved with a semiautomated steel–sapphire cell with a vertical cold surface and a periodic feed and product removal system.[18]

Both types of reactors, stainless steel–sapphire and quartz, yield NF_4BF_4 of very high purity showing no detectable impurities, although the quartz reactor is slowly attacked (weight loss of ~1 mg/h of operation) by the F atoms with SiF_4 and O_2^+ formation. However, the possibility of photolytic O_2BF_4 formation[19] does not present a problem since O_2BF_4 is thermally unstable and is removed from NF_4BF_4 by pumping at 25 °C during product workup.

Using estimates for the amount of uv radiation entering the cell (80% for the experiments using a parabolic backing mirror for the uv source) and being absorbed by F_2 (12%), the quantum yield for the formation of NF_4BF_4 at a rate of 3 g/h was calculated to be about 0.015. Since this value is much smaller than unity, it does not provide any experimental proof for a previously suggested[14] gas-phase chain reaction. Since the BF_3 starting material is frozen out as a solid during the reaction, a diffusion-controlled mechanism in the solid (BF_3)–liquid (F_2, NF_3) phase appears more plausible and can account for the low observed quantum yield.

In agreement with our previous report,[14] we found that the rate of NF_4BF_4 formation in the gas phase at room temperature is extremely slow. Contrary to our original statement,[14] we believe that this is not caused by window coating but is due to the low thermal stability[13] of some of the intermediate products.[14] The fact that $NF_4SbF_6 \cdot xSbF_5$ can be readily produced by uv photolysis at room temperature[13] indicates that the stability of these intermediates is influenced by the strength of the Lewis acid used.

The reaction conditions found most suitable for the synthesis of NF_4BF_4 were also tested for the syntheses of the known NF_4AsF_6[3,5,8,9] and the novel PF_6^-, GeF_5^-, SiF_5^-, GeF_6^{2-}, and SiF_6^{2-} salts. The results from these experiments are summarized in Table I and the product formation rates are compared to those obtained for NF_4BF_4 under similar reaction conditions. The NF_4AsF_6 salt can be prepared by our method at a rate comparable to that of NF_4BF_4 and yields a very pure product. This makes low-temperature uv photolysis also the most attractive method presently known for the preparation of high-purity NF_4AsF_6. The novel salts NF_4PF_6 and NF_4GeF_5 were also successfully synthesized by our method although their rate of formation was lower than those of the BF_4^- and AsF_6^- salts. Attempts to synthesize the corresponding SiF_5^- salt were unsuccessful and did not produce any solid stable at −78 °C or above.

Syntheses of Other Salts by Uv Photolysis. Based on our success with NF_4^+ salts, it was interesting to test the applicability of low-temperature uv photolysis to other reactant systems. The results are summarized in Table I.

In the case of CF_3NF_2 no evidence for the formation of the unknown $CF_3NF_3^+$ cation was obtained. Instead, all of the

CF_3NF_2 starting material underwent C–N bond breakage resulting in the formation of a mixture of NF_4^+, $N_2F_3^+$,[20-22] and N_2F^+ [20,23-26] salts. The use of a Vycor (Hanovia 7910)–nickel oxide (Hanovia 9863) filter (transmitting only between 2300 and 4200 Å) to avoid C–N bond breakage did not significantly change the composition of the solid reaction products. Attempts to convert N_2 to either N_2F^+, $N_2F_3^+$, or NF_4^+ salts were unsuccessful.

Photolysis of an OF_2–F_2–AsF_5 mixture gave no evidence for the novel $OF_3^+AsF_6^-$ but produced the known $O_2^+AsF_6^-$.[27] This is not surprising since O_2AsF_6 has previously been prepared by room-temperature uv photolysis[28] or thermal activation[29] of AsF_5 with either OF_2 or $O_2 + F_2$.

The uv photolysis of an equimolar mixture of Kr, F_2, and AsF_5 in the steel–sapphire reactor at −196 °C produced 49 mg/h of an unstable KrF_2–AsF_5 adduct[30,31] which decomposed before it could be transferred out of the reactor for further identification. For NF_4^+ salts the yields in this steel reactor generally were about one-third of those listed in Table I for the quartz reactor. These results are in good agreement with a recent report[32] that KrF_2 can be prepared by uv photolysis of a liquid mixture of Kr and F_2 at −196 °C.

Syntheses of NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ by Displacement Reactions. In view of the relatively slow formation rates of NF_4PF_6 and NF_4GeF_5 during uv photolysis, alternate routes to these salts were sought. Since NF_4BF_4 is more readily available, displacement reactions between NF_4BF_4 and PF_5 or GeF_4 were studied. It was found that essentially pure NF_4PF_6 or NF_4GeF_5 can be obtained by treating NF_4BF_4 with a large excess of liquid PF_5 or GeF_4, respectively, at room temperature. The observed material balances confirm the reactions

$$NF_4BF_4 + PF_5 \rightarrow NF_4PF_6 + BF_3$$

$$NF_4BF_4 + GeF_4 \rightarrow NF_4GeF_5 + BF_3$$

These displacement reactions represent at the present time the most convenient syntheses for larger amounts of NF_4PF_6 and NF_4GeF_5. For NF_4GeF_5, repeated treatment of the NF_4BF_4 starting material with GeF_4 was required to obtain a quantitative conversion.

The usefulness of anhydrous HF as a common solvent in these displacement reactions was studied. The conversions of NF_4BF_4 were found to be lower in HF solution, compared to those in the absence of HF, and even multiple treatments with the HF–Lewis acid mixtures did not result in quantitative conversions. This indicates that HF may act not only as a solvent in these reactions but may participate as a third component in the chemical equilibria involved. Treatment of NF_4AsF_6 with GeF_4 in HF solution did not result in any detectable displacement of AsF_6^-. This shows that, as expected, AsF_5 is a significantly stronger Lewis acid than GeF_4 but that BF_3, PF_5, and GeF_4 are of comparable acid strength.

Another interesting observation was made for the displacement reaction between NF_4BF_4 and GeF_4 in HF. The material balances and the spectroscopic and elemental analyses showed that, in addition to NF_4GeF_5, some $(NF_4)_2GeF_6$ was also formed. This observation suggested the possibility of converting NF_4GeF_5 to $(NF_4)_2GeF_6$ by treatment with HF. Examination of the NF_4GeF_5–HF system indeed revealed that in HF solution NF_4GeF_5 could be quantitatively converted to $(NF_4)_2GeF_6$. The Raman spectra of these solutions (see below) showed the presence of GeF_6^{2-}, indicating a reaction sequence such as

$$2NF_4GeF_5 + 4HF \xrightarrow{HF} 2NF_4^+ + 2GeF_6^{2-} + 2H_2F^+$$

$$2H_2F^+ + GeF_6^{2-} \rightleftarrows 4HF + GeF_4$$

$$2NF_4^+ + GeF_6^{2-} \rightarrow (NF_4)_2GeF_6$$

Removal of the GeF_4 product and repeated treatment with fresh HF were required to obtain a quantitative conversion to $(NF_4)_2GeF_6$ in agreement with the above postulated equilibrium reaction. The above synthesis of $(NF_4)_2GeF_6$ was of particular interest since it afforded the first known example of a NF_4^+ salt containing a multiply charged anion.

Table II. Relative Thermal Stability and Solid-State Transition Temperatures

Sample	Temp of rapid decompn (mp capillary), °C	Temp of reversible endotherm (DSC), °C
NF_4GeF_5[a]	249	129
NF_4PF_6[a]	245	125
NF_4BF_4[b]	330	234
NF_4AsF_6[c]	365	133
$(NF_4)_2GeF_6$	238	d

[a] First visual signs of shrinking of sample were observed at about 115 °C. The melting was relatively sharp and was accompanied by gas evolution. [b] Starts to decompose at about 250 °C (thermogram[6]) or 285 °C (DSC[11]) or 200 °C (slow gas evolution in vacuo[11]). [c] Starts to decompose at about 270 °C (DSC[5]) or 175 °C (slow gas evolution in vacuo[33]). [d] Not recorded.

The postulate that GeF_5^- is in equilibrium with GeF_6^{2-} and GeF_4 was experimentally confirmed. When $(NF_4)_2GeF_6$ was treated with a large excess of liquid GeF_4 at 25 °C, it was quantitatively converted back to NF_4GeF_5. Thus the formation of either NF_4GeF_5 or $(NF_4)_2GeF_6$ or mixtures of both depends on the exact reaction conditions

$$2NF_4GeF_5 \underset{\text{in } GeF_4}{\overset{\text{in HF}}{\rightleftharpoons}} (NF_4)_2GeF_6 + GeF_4$$

Since NF_4GeF_5 and $(NF_4)_2GeF_6$ have very different vibrational spectra and x-ray powder patterns (see below), they can be readily distinguished from each other.

In view of the above described tendency of GeF_5^- to interact with HF with GeF_6^{2-} formation, it seemed interesting to examine the reactions of NF_4GeF_5 with other fluoride ion donors. For this purpose, a relatively weak (N_2F_4) and a relatively strong (FNO_2) F^- donor were chosen, and the reactions were studied at −78 °C using a large excess of the donor as the liquid phase. For N_2F_4 no interaction was observed as might be expected from the fact[33] that N_2F_4 and GeF_4 do not form an adduct. However for FNO_2 which is capable of forming a stable GeF_6^{2-} salt, again no complexing was observed. This might be explained either by low solubility of NF_4GeF_5 in FNO_2 or by the probable polymeric nature (see below) of the GeF_5^- anion in NF_4GeF_5 which renders it a rather weak Lewis acid.

Properties of NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$. All three compounds are white, crystalline, hygroscopic solids stable at ambient temperature. The thermal stability of the NF_4^+ salts (see Table II) was examined by both DSC in crimped aluminum pans and visual examination in sealed glass melting point capillaries. Whereas DSC was suitable accurately to observe solid-state transitions (see Table II), both methods do not permit the accurate determination of the onset of thermal decomposition. This is caused by the slow decomposition rates of NF_4^+ salts and their suppression by the pressure buildup of the gaseous decomposition products.[34] Consequently, the thermal decomposition of the NF_4^+ salts results in a slow, smooth, and gradual increase of the slope of the DSC curve. For the melting point capillaries, slow gradual shrinkage of the solid can be observed long before rapid decomposition occurs. This behavior also explains the large discrepancies in thermal decomposition temperatures previously reported[6,11] for NF_4BF_4. Obviously, different techniques and experimental conditions can result in vastly different values. As can be seen from Table II, NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ are all

Table III. Crystallographic Data of NF_4^+ Salts[a]

	Unit cell dimensions				Vol per F, Å^3	Calcd density, g/cm^3
	a, Å	*c*, Å	*V*, Å^3	*Z*		
NF_4BF_4	9.944	5.229	517.04	4	16.16	2.27
NF_4PF_6	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[b]	7.70	5.73	339.73	2	16.99	2.72
$(NF_4)_2GeF_6$	10.627	11.114	1255.14	16/3	16.81	2.59

[a] All compounds crystallize in the tetragonal system. [b] Reference 5.

of good thermal stability. The $NF_4Sb_2F_{11}$ salt did not show a solid-state transition but melted at 178 °C. The melt showed a freezing point of 161 °C. The chemical properties of NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ are analogous to those[5,6,9–11] previously reported for other NF_4^+ salts.

Hydrolysis of NF_4^+ Salts. The hydrolysis of NF_4^+ salts was quantitatively studied[9] by Tolberg and co-workers. According to their results the hydrolysis follows the equation

$$NF_4^+ + H_2O \rightarrow NF_3 + H_2F^+ + {}^1/_2O_2$$

This hydrolysis reaction should therefore offer a convenient way to analyze NF_4^+ salts since NF_3 does not hydrolyze in water. A large number of NF_4^+ salts have been analyzed on a routine basis in our laboratory. Whereas quantitative NF_3 evolution was always observed, the amount of oxygen evolved was consistently less than that expected for the above equation. Examination of the hydrolysate showed that the balance of the oxygen was present as H_2O_2, the formation of which can readily be explained by the initial formation of HOF as an unstable[35] intermediate

$$NF_4^+ + OH^- \rightarrow NF_3 + HOF$$

The HOF intermediate can either decompose according to

$$2HOF \rightarrow 2HF + O_2$$

or react in a competing reaction with water according to

$$HOF + HOH \rightarrow HF + HOOH$$

The ratio between H_2O_2 and O_2 varied from experiment to experiment and seemed to depend strongly on the exact reaction conditions.

X-Ray Powder Data. The x-ray powder pattern of NF_4PF_6 is given as supplementary material. The tetragonal unit cell (see Table III) is very similar and, as expected, slightly smaller than that previously reported[5] for NF_4AsF_6. No nonindexable lines were observed for NF_4PF_6 indicating little or no crystalline impurities. Based on the lack of characteristic absences of certain diffraction lines, the most probable space group for NF_4PF_6 is *P*4/*m*.

The powder pattern of NF_4GeF_5 (see supplementary material) was too complex to allow indexing, but the pattern of $(NF_4)_2GeF_6$ (see supplementary material) could be indexed for a tetragonal unit cell (see Table III). The unusual value of $Z = 16/3$ for $(NF_4)_2GeF_6$ requires some comment. Assuming $Z = 5$ would result in an unacceptably high (17.93 Å^3) and $Z = 6$ would result in an unacceptably low (14.94 Å^3) average volume per fluorine atom. By comparison with the known crystal structures of other NF_4^+ salts (see Table III), for $(NF_4)_2GeF_6$ this value should be larger than that (16.16 Å^3) of NF_4BF_4 but smaller than that (16.99 Å^3) of NF_4AsF_6. A plausible value of 16.81 Å^3 can, however, be obtained by assuming a structure derived from that[36] of α-K_2UF_6 but with a tetragonally distorted fourfold unit cell. For α-K_2UF_6 a value of 4/3 was found for *Z* and explained by assuming a statistical distribution of the anions and cations among the calcium positions of a CaF_2-like structure.

For NF_4BF_4, two different powder patterns have previously been reported. Sinel'nikov and Rosolovskii reported a cubic ($a = 7.53$ Å) structure,[6] whereas Goetschel et al. found[11] a tetragonal unit cell similar to those of the MF_6^- salts. Since both of these and our NF_4BF_4 sample had been prepared under similar conditions at −196 °C, their crystal structures might be expected to be identical. Consequently, we have also recorded the powder pattern of NF_4BF_4 (see supplementary material). Our results closely agreed with those[11] of Goetschel et al. Furthermore, only the tetragonal unit cell results in plausible trends (see Table III) for the density and the average volume per F atom (ignoring contributions from the central atoms).[37] Many of the diffraction lines reported by Sinel'nikov are similar to those reported[38] for NO_2BF_4, a likely impurity in samples prepared by glow-discharge techniques in glass apparatus.[39]

The powder pattern of NF_4BF_4 was indexed[11] by Goetschel et al. on the basis of a tetragonal unit cell with $Z = 2$. However, eight reflections could not be indexed and were tentatively attributed to an impurity. We have also observed these reflections with similar intensities and found that they belong to NF_4BF_4. They can be readily indexed if the volume of the unit cell, proposed by Goetschel, is doubled ($Z = 4$). The questionable diffraction line at $d = 3.126$ Å, reported by Goetschel,[11] was not observed during our study and therefore is attributed to an impurity in Goetschel's sample. The indexing of the NF_4BF_4 powder pattern for $Z = 4$ is given in the supplementary material. The space group *P*4/*nmm* suggested by[11] Goetschel et al. is unlikely since the extinction rule $hk0 = 0$ unless $h + k = 2n$ is not obeyed. Space group *P*4/*m* appears more likely based on the apparent lack of any characteristic absences.

NMR Spectra. The ^{19}F NMR spectra of NF_4PF_6 and $(NF_4)_2GeF_6$ in HF solution showed for NF_4^+ a triplet of equal intensity with $J_{NF} = 230$ Hz at −217.0 and −213.5 ppm, respectively, from external $CFCl_3$, and a common line for the rapidly exchanging solvent and the anions. These values are in excellent agreement with those previously reported for NF_4SbF_6[9] and NF_4AsF_6[40] in HF.

Since NF_4GeF_5 is converted to $(NF_4)_2GeF_6$ by HF and since HF rapidly exchanges with the anion, the NMR spectrum of NF_4GeF_5 was recorded in the inert solvent BrF_5. The spectrum showed in addition to the solvent lines (quintet at ϕ −272 and doublet at ϕ −134) and the characteristic[9,40] NF_4^+ triplet (ϕ −220.1, $J_{NF} = 230$ Hz) a broad unresolved resonance at ϕ 151. Its chemical shift significantly deviates from that (ϕ 123) found[41] for GeF_6^{2-} in H_2O and occurs in the region predicted for GeF_5^-. Attempts to obtain a well-resolved anion spectrum failed owing to the sharp decrease in the solubility of the salt in BrF_5 with decreasing temperature and to the relatively high melting point (−61 °C) of BrF_5. The failure to observe a sharp resonance for the anion might be explained either by a discrete trigonal-bipyramidal GeF_5^- undergoing rapid intramolecular exchange or by a polymeric anion (see below) undergoing rapid intermolecular exchange. Since the BrF_5 signal was well resolved, interaction between BrF_5 and GeF_5^- can be ruled out. The Raman spectrum of this NF_4GeF_5–BrF_5 solution was also recorded. It showed the lines due to NF_4^+ (see below), but unfortunately the solubility of NF_4GeF_5 in BrF_5 is relatively low and the region of the anion bands was masked by strong BrF_5 bands.

Vibrational Spectra. The vibrational spectra of NF_4GeF_5, $(NF_4)_2GeF_6$, NF_4PF_6, and $NF_4Sb_2F_{11}$ are shown in Figures 1–3, respectively. In view of the high purity of our samples and of the resultant good quality of their spectra, the spectra of NF_4AsF_6[10,40] and NF_4BF_4[6,11] are also given for comparison. The observed frequencies and their assignments are summarized in Tables IV–VI. Whereas the assignment of the

Table IV. Vibrational Frequencies[a] and Assignments for Tetrahedral NF_4^+ and BF_4^-

Assignments for NF_4^+, BF_4^- (T_d)	Obsd freq, cm^{-1}, and rel intens[b]														
	NF_4^+													BF_4^-	
	NF_4BF_4		NF_4PF_6		NF_4AsF_6		$NF_4Sb_2F_{11}$		$(NF_4)_2GeF_6$			NF_4GeF_5		NF_4BF_4	
	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Raman, HF soln	Ir	Raman	Ir	Raman
$2\nu_3(A_1 + E + F_2) =$ 2320, 2114			2380 vw		2380 vw							2380 vw			
	2320 vw		2320 w		2320 w		2320 vw		2320 vw			2320 w		2120 vw	
$\nu_1 + \nu_3(F_2) = 2008, 1829$	2000 w		2005 w		2000 w		2010 w		2010 w			2010 w		1830 vw	
$\nu_3 + \nu_4(A_1 + E + F_2) =$ 1769, 1582	1762 vw		1765 w		1762 w		1768 vw		1765 w			1766 w			
$\nu_2 + \nu_3(F_1 + F_2) = 1600, 1407$														1405 vw	
$\nu_1 + \nu_4(F_2) = 1457, 1297$												1465 w			
	1455 w		1457 w		1455 w		1457 w		1462 w			1456 vw		1298 ms	
$2\nu_4(A_1 + E + F_2) =$ 1218, 1050	1222 mw		1221 mw		1222 mw		1221 m		1222 mw			1221 mw			
$\nu_3(F_2)$	1180 sh	1179 (0.6)	1166 vs	1168 (1.5)	1161 vs	1162 (1.0)	1161 vs	1160 (0.2)	1161 vs	1159 (1.2)	1162 (0.4) dp		1168 (0.8)	1120 sh	1130 (0+)
	1162 vs			1150 (0.8)		1151 (0.6)						1160 vs	1159 (0.8)	1057 vs	1055 (0.2)
		1148 (0.6)	1135 vw		1135 vw		1135 w						1149 (0.9)		
$\nu_2 + \nu_4(F_1 + F_2) = 1049, 875$			1056 vw		1052 vw		1049 vw					1055 w		882 vw	
$2\nu_2(A_1 + A_2 + E) = 880, 700$		884 (0+)		880 (0.2)		880 (0+)		879 (0+)		881 (0+)	882 (0.2) p		881 (0+)		
$\nu_1(A_1)$		844 (10)		849 (8.2)		848 (7.3)		848 (2.6)		850 (8.1)	850 (10) p		848 (10)	772 w	772 (3.2)
$\nu_4(F_2)$			611 m		610 sh							613 m	615 (0.8)	525 sh	
	609 s	609 (6.3)		609 (7.4)		609 (5.2)	608 s	608 (1.6)	610 s	609 (10)[c]	609 (3.9) dp	604 m	604 (3.2)		524 (0.4)
			608 m		607 m							593 m	594 (2.6)	522 s	
$\nu_2(E)$		443 (2.6)		441 (2.9)		440 (2.0)		438 (0.5)		441 (3.2)	439 (1.7) dp		440 (2.6)		350 (0.9)
													431 (2.2)		

[a] Unless noted otherwise, the listed spectra are those of the solids. [b] Uncorrected Raman intensities. [c] Coincides with ν_1 of GeF_6^{2-}.

Table V. Vibrational Frequencies and Assignments for Octahedral MF_6 in $(NF_4)_nMF_6$

Assignments for $MF_6(O_h)$	Obsd freq, cm^{-1}, and rel intens[a]						
	NF_4PF_6		NF_4AsF_6		$(NF_4)_2GeF_6$		
	Ir	Raman	Ir	Raman	Ir	Raman	Raman, HF soln
$\nu_1 + \nu_3(F_{1u}) = 1590, 1403$	1590 w		1398 vw				
$\nu_2 + \nu_3(F_{1u} + F_{2u}) = 1413, 1294$	1414 w		1290 vw				
$\nu_1 + \nu_4(F_{1u}) = 1307, 1079$	1308 vw		1080 vvw				
$\nu_2 + \nu_4(F_{1u} + F_{2u}) = 1130, 970$			985 vvw				
$\nu_3(F_{1u})$	842 vs		720 vs				
		838 (1.5)		703 (1.5)	600 vs, br		
	789 w		699 w				
$\nu_1(A_{1g})$	749 w	748 (10)		688 (10)		609 (10)[b]	641 (1.6) p
$\nu_2(E_g)$		571 (0.8)	578 w	578 (1.2)	472 mw	480 (0+) vbr	470 (0+) dp
$\nu_4(F_{1u})$	559 s		396 s		348 vs	350 (0+) br	
$\nu_5(F_{2g})$	474 vw						
		469 (1.2)		369 (3.6)		325 (2.3)	320 (0+) br, dp

[a] Uncorrected Raman intensities; unless noted otherwise, the listed spectra are those of the solids. [b] Contains contribution from $\nu_4(F_2)$ of NF_4^+.

Table VI. Vibrational Frequencies and Assignments for the Anions in NF_4GeF_5 and $NF_4Sb_2F_{11}$

Obsd freq, cm^{-1}, and rel intens			Obsd freq, cm^{-1}, and rel intens		
NF_4GeF_5			$NF_4Sb_2F_{11}$		
Ir	Raman	Assignments for GeF_5^-	Ir	Raman	Assignments for $Sb_2F_{11}^-$
701 vs		Terminal Ge-F str modes	1360 vw		Combination bands
690 sh	689 (1.0)		1295 vw		
673 mw	672 (4.9)		975 vw		
630 vs				764 (0.1)	Sb-F str modes
	578 (1.6)		695 vs		
	490 (0+) br	ν(GeFGe) bridge		689 (3.1)	
474 mw			664 s	678 sh	
386 m		Def modes		649 (10)	
373 w	373 (0+) br			597 sh	
	343 (0+) br		540 w	572 (0+)	
335 m					
	321 (0.8)		497 s		ν(SbFSb) bridge
	281 (1.0)			289 (1.0)	Sb-F def modes
	249 (0.6)			273 (0.7)	
	212 (0.4)			221 (1.8)	
	152 (0.4)			125 (0.4)	Lattice vib

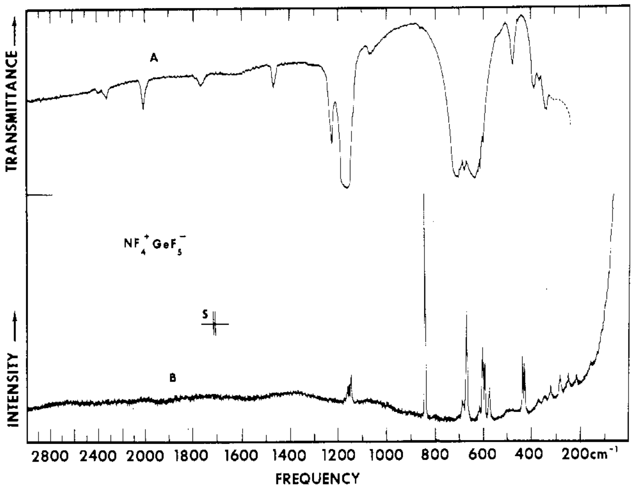

Figure 1. Vibrational spectra of solid NF_4GeF_5: Trace A, infrared spectrum of the dry powder in a silver bromide disk, the absorption below 300 cm^{-1} (broken line) being due to the AgBr windows; trace B, Raman spectrum, S indicating spectral slit width.

four fundamentals expected for tetrahedral NF_4^+ is well established,[10,11,37] the assignment of some combination bands has previously been questioned.[11] Furthermore, it seemed interesting to study the influence of solid-state effects on the vibrational spectra of these highly symmetric octahedral and tetrahedral ions.

Inspection of Figures 1–3 and of Table IV establishes beyond doubt the presence of approximately tetrahedral NF_4^+ ions in these salts. However, for several salts solid-state effects are observed. For the GeF_5^- salt, for example, the degeneracy of the E and the two F_2 modes is completely lifted and a splitting into two and three components, respectively, was observed. This is not surprising since the site symmetry of NF_4^+ in these salts is bound to be lower than T_d. However, since the space groups of the NF_4^+ salts are not firmly established (see above), the assignments for NF_4^+ in Table IV were made assuming symmetry T_d.

Out of the ten possible binary combination bands of NF_4^+ of T_d symmetry seven should be infrared active. Of these, six have been observed in the infrared spectra thus lending further support to the assignment of the fundamentals. In addition, one of the infrared-inactive combination bands was observable at about 880 cm^{-1} in the Raman spectra, probably due to intensity enhancement by Fermi resonance with $\nu_1(A_1)$.

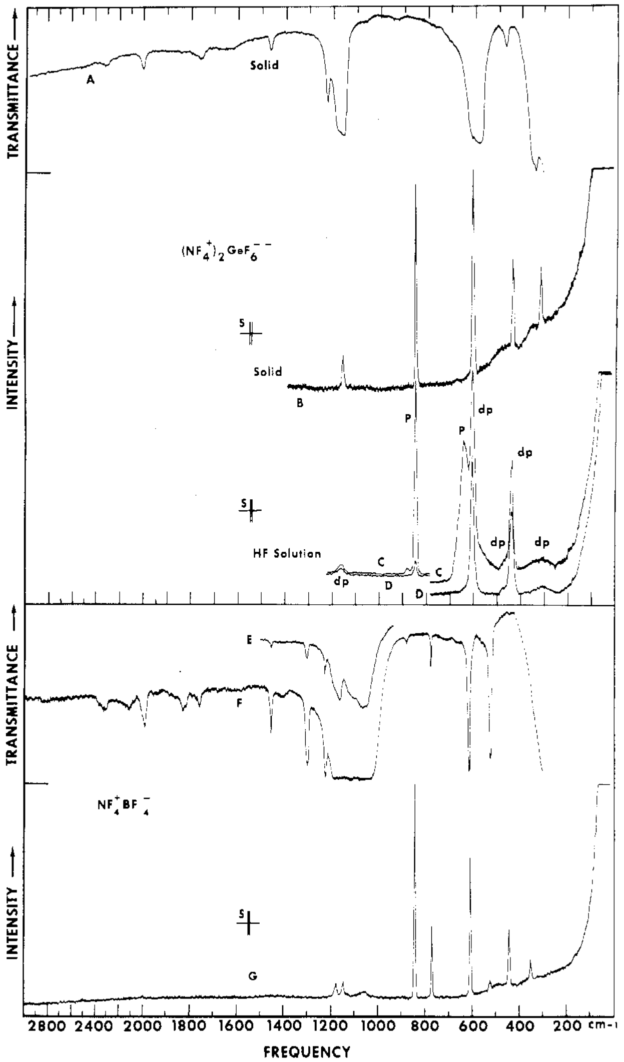

Figure 2. Vibrational spectra of $(NF_4)_2GeF_6$ compared to those of NF_4BF_4: trace A, infrared spectrum of solid $(NF_4)_2GeF_6$ as dry powder in a silver chloride disk; trace B, Raman spectrum of solid $(NF_4)_2GeF_6$; traces C and D, Raman spectra of $(NF_4)_2GeF_6$ in HF solution at two different recorder voltages with incident polarization parallel and perpendicular, respectively [p and dp stand for polarized and depolarized bands, respectively]; traces E and F, infrared spectrum of solid NF_4BF_4 at two different concentrations; trace G, Raman spectrum of solid NF_4BF_4.

The frequency of $\nu_1(A_1)$ of NF_4^+ varies by several cm^{-1} for the different NF_4^+ salts, and, owing to its narrow line width, this band is well suited to monitor quantitatively by Raman spectroscopy the progress of anion displacement reactions.

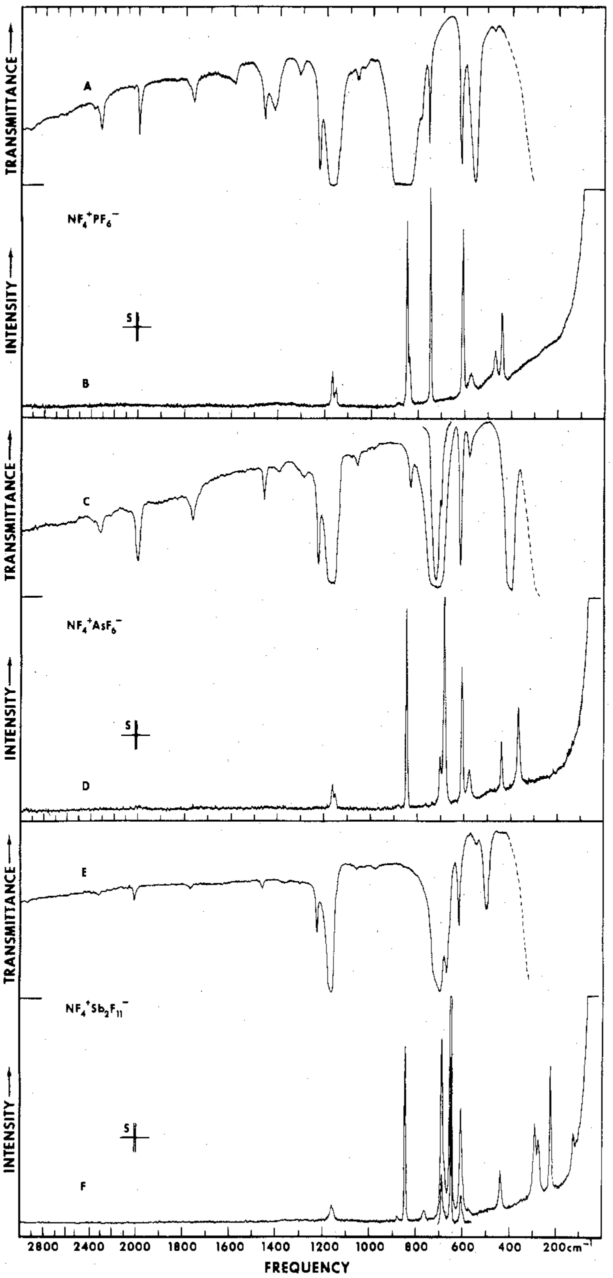

Figure 3. Vibrational spectra of NF_4PF_6, NF_4AsF_6, and $NF_4Sb_2F_{11}$: traces A and B, infrared and Raman spectra, respectively, of solid NF_4PF_6; traces C and D, infrared and Raman spectra, respectively of solid NF_4AsF_6; traces E and F, infrared and Raman (at two different recorder voltages) spectra, respectively, of solid $NF_4Sb_2F_{11}$.

The vibrational spectra of the anions also show solid-state effects. The spectrum of BF_4^- is analogous to that of NF_4^+ and consequently was assigned for point group T_d (see Table IV). The spectra of PF_6^- and AsF_6^- deviate somewhat from the O_h selection rules by showing splittings for the triply degenerate $\nu_3(F_{1u})$ mode and by not strictly following the rule of mutual exclusion. However, the deviations from O_h for these anions are relatively minor and, in the absence of exact knowledge of the space group, assignments (see Table V) were made for O_h. The observed frequencies agree well with those previously reported for other AsF_6^-,[42,43] PF_6^-,[43,44] and GeF_6^{2-} [43,45,46] salts. The spectrum of $Sb_2F_{11}^-$ in $NF_4Sb_2F_{11}$ (see Table VI) is in good agreement with that previously reported[47] for the anion in $O_2^+Sb_2F_{11}^-$, particularly if the pronounced changes observed for the $Sb_2F_{11}^-$ anion in different salts are kept in mind.

Assignments for GeF_5^- in NF_4GeF_5 are more difficult since this anion has not been well characterized. The existence of GeF_5^- salts was postulated[48] by Clark and Dixon and subsequently was established[49] by Wharf and Onyszchuk, who prepared several quaternary alkylammonium and arylarsonium salts. They attributed infrared bands at 690, 652, 343, and 317 cm⁻¹ to GeF_5^-. No further data on GeF_5^- could be found in the literature. Recently, $O_2^+GeF_5^-$ was synthesized and its vibrational spectrum was recorded which suggested[50] a polymeric cis-fluorine-bridged structure for GeF_5^-.

Although the general appearance of the GeF_5^- Raman bands in NF_4GeF_5 (see Table VI) is similar to those of GeF_5^- in O_2GeF_5, there are pronounced differences. By analogy with O_2GeF_5, the large number of observed anion bands and the occurrence of bands in the frequency region (450–550 cm⁻¹) expected for fluorine bridge stretching modes rule out the presence of discrete GeF_5^- anions in NF_4GeF_5. The frequencies of the NF_4^+ modes in NF_4GeF_5 are essentially identical with those in NF_4MF_6 salts. Consequently, fluorine bridging of GeF_5^- in NF_4GeF_5 must occur between the anions. Since the addition of an extra fluoride ligand to GeF_5^- results in a pseudooctahedral structure, two kinds of bridging, cis and trans, are possible[51] which should be distinguishable from their vibrational spectra.

For a trans-fluorine-bridged structure, the anion would possess a symmetry center and the four nonbridging fluorines and the central atom would form a square plane. This would result in a highly symmetric structure exhibiting a small number of infrared and Raman bands, which ideally would be mutually exclusive. A typical example for such a trans-fluorine-bridged polymeric XF_5 species is α-BiF_5.[52]

On the other hand, a cis-fluorine-bridged structure would be of lower symmetry and result in a more complex spectrum. The spectra due to the GeF_5^- part of NF_4GeF_5 show a frequency and intensity pattern similar to those observed for NF_4SnF_5[53] and solid TaF_5.[54] Since the structure of solid TaF_5 is known[55] to consist of cyclic cis-fluorine-bridged tetramers, such a cyclic tetramer is also plausible for GeF_5^-. A more detailed discussion of the GeF_5^- spectrum will be given elsewhere.[53] The formation of polymeric anions in NF_4GeF_5 is not surprising in view of the established[51] polymeric nature of CrF_5^{2-}, AlF_5^{2-}, FeF_5^{2-}, and MnF_5^{2-} salts. All of these salts form polymeric chains of MF_6 units with the nature (cis or trans bridges, linear, helical, or ramified) of the chains varying from salt to salt.

Summary

Uv photolysis is a useful and convenient technique for the synthesis of high oxidation state complex fluorides which are difficult to prepare by other methods. Low-temperature conditions may be required if either the final or one of the intermediate products formed by the interaction of the F atoms with the starting materials are thermally unstable. Typical examples are stable $O_2^+AsF_6^-$ which can be prepared at room temperature,[28] unstable $O_2^+BF_4^-$[13] and $O_2^+GeF_5^-$ [50] which can be prepared at −78 °C, or stable NF_4^+ salts which, depending on the anion, were prepared at either 25 or −196 °C. For the NF_4^+ salts the exact formation mechanism still remains to be established. If the formation of NF_4AsF_6 either by low-temperature uv photolysis or by thermal activation at high pressure[8] involves the same reaction mechanism, reaction kinetics might be more important than the thermal stability of the intermediates.

Three novel NF_4^+ salts, i.e. NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$, have been prepared by uv photolysis and displacement reactions and have been characterized. The $(NF_4)_2GeF_6$ salt is the first example of an NF_4^+ salt containing a multiply charged anion. Interesting equilibrium reactions were found which allow the interconversion of GeF_5^-

and GeF_6^{2-} salts. Vibrational spectra indicate that the GeF_5^- anion in NF_4GeF_5 has a cis-fluorine-bridged polymeric structure.

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Registry No. NF_4BF_4, 15640-93-4; NF_4PF_6, 58702-88-8; NF_4AsF_6, 16871-75-3; $NF_4Sb_2F_{11}$, 58702-89-9; $(NF_4)_2GeF_6$, 58702-87-7; NF_4GeF_5, 58702-86-6; NF_3, 7783-54-2; BF_3, 7637-07-2; AsF_5, 7784-36-3; PF_5, 7647-19-0; GeF_4, 7783-58-6; CF_3NF_2, 335-01-3; F_2, 7782-41-4.

Supplementary Material Available: Listings of the observed x-ray powder diffraction patterns of NF_4PF_6, NF_4GeF_5, $(NF_4)_2GeF_6$, and NF_4BF_4 (4 pages). Ordering information is given on any current masthead page.

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Reactions of $SnCl_2$ and PbF_2 with CO, NO, and N_2 and of $PbCl_2$, $PbBr_2$, and PbI_2 with CO in Argon Matrices

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The reactions between metal halides such as $SnCl_2$, PbF_2, $PbCl_2$, $PbBr_2$, and PbI_2 and the ligands such as CO, NO, or N_2 in argon matrices have been studied by infrared spectroscopy. It has been found that the ligand bands shift to higher whereas the metal halide bands shift to lower frequencies by complex formation. The magnitude of these shifts has been used as a measure of the extent of σ donation from the ligand to the metal. The effects of changing the ligand, halogen, and metal on σ donation have been discussed based on observed shifts.

Introduction

In 1971, DeKock[1] first succeeded in the preparation of unstable and transient metal carbonyls such as Ni(CO), $Ni(CO)_2$, and $Ni(CO)_3$ in argon matrices by treating metal vapor directly with CO and elucidated their structures by infrared spectroscopy. Since then, a large number of novel coordination compounds have been synthesized, and their structures have been studied in inert-gas matrices by infrared and Raman spectroscopy.[2] The reactivity of metal halides at matrix temperatures was first demonstrated by Bassler et al.,[3] who confirmed the reactions of SiF_2 with BF_3, CO, and NO by infrared spectroscopy. Recently, Van Leirsburg and DeKock[4] treated linear triatomic metal halides (MX_2) with ligands (L) in argon matrices and confirmed the formation