RESEARCH STUDIES IN NF₄⁺ SALTS

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This report describes the results of a 3-year program in basic research studies in \( \text{NF}_4^+ \) chemistry. The mechanism of \( \text{NF}_4^+ \) salt formation and decomposition was determined and the decomposition kinetics of \( \text{NF}_4\text{AsF}_6 \) and \( \text{NF}_4\text{BF}_4 \) were measured. The formation of \( \text{NF}_3^+ \) salt intermediates, both in the formation and decomposition of \( \text{NF}_4^+ \) salts, was established, and the \( \text{NF}_3^+ \) radical cation was thoroughly...
19. Key Words (Continued)

Computations, Trifluoroammonium Radical Anion, Trifluorodiazonium Salts, Thermo-
dynamic Properties, Crystal Structure, Elemental Analysis, Metathesis, Anhydrous
Hydrofluoric Acid Solvent System.

20. Abstract (Continued)

-characterized by ESR spectroscopy. Improved synthetic methods were developed
for $\text{NF}_4\text{SbF}_6$ and its metathesis to other $\text{NF}_4^+$ salts. A new method was developed
for the synthesis of $\text{NF}_4^+$ salts derived from polymeric Lewis acids which
do not form HF soluble cesium salts. The following new $\text{NF}_4^+$ salts were synthe-
sized and thoroughly characterized: $(\text{NF}_4)_2\text{MnF}_6$, $\text{NF}_4\text{HF}_2$, $\text{FF}_4\text{UF}_5\text{O}$, $\text{NF}_4\text{ClO}_4$
and $\text{NF}_4\text{SO}_3\text{F}$. In addition, the novel $\text{N}_2\text{F}_3\text{SnF}_5$ and $\text{N}_2\text{F}_3\text{SbF}_6$ salts, which are
useful burning rate modifiers in solid propellant $\text{NF}_3\text{F}_2$ gas generator formula-
tions, were prepared and characterized. Unsuccessful attempts were made to
prepare $\text{NF}_4\text{NO}_3$, $\text{NF}_4\text{ClF}_4\text{O}$, $\text{NF}_4\text{BrF}_4\text{O}$, $\text{NF}_4\text{BrO}_4$ and $\text{NF}_4^+$ salts of several transition
metal fluoride anions. Crystal structure determinations of $\text{NF}_4\text{BF}_4$ and $\text{NF}_4\text{SbF}_6$,
and the measurement of thermodynamic data on $\text{NF}_4\text{BF}_4$, $\text{NF}_4\text{PF}_6$, $\text{NF}_4\text{AsF}_6$, and
$\text{NF}_4\text{SbF}_6$ are in progress. The vibrational spectra of $^{14}\text{NF}_4$ and $^{15}\text{NF}_4$ were
recorded and the measured isotopic shifts were used for the computation of a
General Valence Force Field. Reliable methods were developed for the analyses
of $\text{NF}_4^+$ salts.
FOREWORD

The research reported herein was supported by the U.S. Army Research Office under Contract No. DAAG29-77-C-0007, with Dr. B. Spielvogel as Scientific Officer. This is the final report for this contract and covers the period 1 April 1977 through 31 March 1980. The responsible scientist for this program was Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, W. W. Wilson, I. B. Goldberg, M. D. Lind, and Mr. R. D. Wilson, R. Rushworth and H. R. Crowe. The program was administered by Drs. K. O. Christe and L. R. Grant. Profs. R. Peacock, D. Russell and Dr. J. Fawcett of the University of Leicester, England, also contributed to the scientific effort.
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INTRODUCTION

This is the final report under Contract No. DAAG29-77-C-0007 and covers a 3-year period. It describes research related to $\text{NF}_4^+$ chemistry carried out in support of the Army's $\text{NF}_3\text{F}_2$ gas generator programs. These $\text{NF}_3\text{F}_2$ gas generators are based on solid propellant formulations, containing $\text{NF}_4^+$ salts as the principal ingredient, and are used for HF-DF chemical lasers. The objectives of this program included:

1. A study of the general formation and decomposition mechanism of $\text{NF}_4^+$ salts
2. The investigation of improved methods for the synthesis of known $\text{NF}_4^+$ salts
3. The synthesis of novel $\text{NF}_4^+$ salts
4. The characterization of known and novel $\text{NF}_4^+$ salts
5. The determination of the thermodynamic and structural properties of these salts

All of these objectives have been completed or, at least, partially accomplished and the results are summarized in this report. Because the bulk of the results have been summarized in the form of manuscripts, copies of which are given as Appendices to this report, the Technical Discussion is limited to a brief review of the major accomplishments.

It should be pointed out that most of the presently known $\text{NF}_4^+$ salts were discovered under ONR sponsorship (Ref. 1) resulting in a certain degree of overlap between these two programs.
PUBLICATIONS OF DATA GENERATED UNDER THIS CONTRACT

PAPERS PUBLISHED


PAPERS IN PRESS

7. "Synthesis and Properties of \( \text{NF}_4^+\text{ClO}_4^- \) and \( \text{NF}_4^+\text{HF}_2\cdot \text{nHF} \) and Some Reaction Chemistry of \( \text{NF}_4^+ \) Salts," by K. O. Christe, W. W. Wilson, and R. D. Wilson, Inorg. Chem.


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PAPERS PRESENTED AT MEETINGS


17. "Synthesis and Characterization of $\text{NF}_4\text{ClO}_4$, $\text{NF}_4\text{HF}_2(\times\text{HF})$ and cis- and trans-$\text{OIF}_4\text{OF},$" by K. O. Christe, W. W. Wilson, and R. D. Wilson, 9th International Symposium on Fluorine Chemistry, Avignon, France (September 1979), and 178th National ACS Meeting, Washington, D.C., September 1979.

19. An invited seminar on our research was given at the University of Southern California, 1979.
DISCUSSION

A. STATE OF THE ART OF NF$_3$-F$_2$ GAS GENERATORS

For a long time, nitrogen fluorides have been of great interest as advanced oxidizers for rocket propulsion. Of these, nitrogen trifluoride is the most important compound because it combines a high fluorine and energy content with a remarkable inertness. Its only major drawback is its low boiling point of -129°C. Therefore, the conversion of NF$_3$ into stable storable solids without significant loss in energy was highly desirable. The first step in this direction was undertaken in 1965 when one of us (Ref. 2) discovered the existence of the stable NF$_4$AsF$_6$ salt. However, it was not until 1971 when, with the advent of HF-DF chemical lasers, the interest in storable NF$_3$-F$_2$ sources was renewed.

It became rapidly obvious that NF$_4^+$ salts were the most promising oxidizers for solid propellant NF$_3$-F$_2$ gas generators. The concept of such a gas generator was conceived (Ref. 3) and, to a large extent (Ref. 4 through 11), developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers.

In an HF-DF chemical laser, F atoms are generated by burning F$_2$ in a precombustor with a fuel, such as hydrogen:

\[ F_2 + H^* \rightarrow HF + F^* \]

The F atoms are subsequently reacted with a cavity fuel, such as D$_2$, to produce vibrationally excited DF as the active lasing species:

\[ F^* + D_2 \rightarrow DF^* + D^* \]

In the original solid F atom generator concept (Ref. 3), the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need of a precombustor. This concept is demonstrated in the following equation for NF$_4$BF$_4$ with a small percentage of Teflon serving both as a fuel and a binder.

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The heat of reaction \( Q \) is sufficient to dissociate most of the \( \text{NF}_3 \) and \( F_2 \) to \( F \) atoms and \( N_2 \):

\[
\text{NF}_4\text{BF}_4 + (\text{CF}_2)_n \rightarrow \text{CF}_4 + \text{BF}_3 + \text{NF}_3 + Q
\]

\[
2\text{NF}_3 + Q \rightarrow N_2 + 6F^*
\]

From a practical point of view, however, such a direct generation of \( F \) atoms is not desirable, since it does not allow the necessary flow controls and flexibility required for operation. Consequently, the concept was modified to that of an \( \text{NF}_3-F_2 \) molecule generator, using a gas catch tank. Further modification of this concept became necessary when system analysis data revealed that gaseous byproducts of high molecular weight and low \( C_p/C_v \) significantly degraded the performance of a laser. Consequently, an \( \text{NF}_3-F_2 \) gas generator was desired that would produce no gases other than \( \text{NF}_3 \) and \( F_2 \). The latter objective can be achieved by a so-called clinker system in which the \( \text{BF}_3 \) byproduct is converted by an alkali metal fluoride to a nonvolatile \( \text{BF}_4 \) salt:

\[
\text{NF}_4\text{BF}_4 + \text{KF} \rightarrow \text{KBF}_4 + \text{NF}_3 + F_2
\]

Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of \( \text{KF} \) lowers the \( \text{NF}_3-F_2 \) yield per pound of solid propellant and the possibility always exists of having incomplete clinkering.

Realizing these limitations, we have searched for novel \( \text{NF}_4^+ \) salts derived from nonvolatile Lewis acids. Further improvements in fluorine yields were achieved by the synthesis of salts containing more than one \( \text{NF}_4^+ \) cation per anion, i.e., salts containing multiply charged anions, and by the use of lighter anions which preferably were also oxidizers of their own, thereby contributing to the fluorine yields. The presently known \( \text{NF}_4^+ \) salts and their theoretical usable fluorine contents are summarized in Table 1.
**TABLE 1. COMPARISON OF THE FLUORINE YIELDS OF PRESENTLY KNOWN NF₃–F₂ GAS GENERATOR SYSTEMS**

<table>
<thead>
<tr>
<th>RANK</th>
<th>SYSTEM</th>
<th>THEORETICAL F, WT. PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(NF₄)₂NiF₆</td>
<td>64.6</td>
</tr>
<tr>
<td>2</td>
<td>(NF₄)₂MnF₆</td>
<td>59.9</td>
</tr>
<tr>
<td>3</td>
<td>(NF₄)₂TiF₆**</td>
<td>55.6</td>
</tr>
<tr>
<td>4</td>
<td>(NF₄)₂SnF₆</td>
<td>46.0</td>
</tr>
<tr>
<td>5</td>
<td>(NF₄)₂TiF₆·2.4KF</td>
<td>39.5</td>
</tr>
<tr>
<td>6</td>
<td>NF₄BF₄·1.2KF</td>
<td>38.5</td>
</tr>
<tr>
<td>7</td>
<td>(NF₄)₂GeF₆·2.4KF</td>
<td>37.6</td>
</tr>
<tr>
<td>8</td>
<td>NF₄SnF₅</td>
<td>31.3</td>
</tr>
<tr>
<td>9</td>
<td>NF₄PF₆·1.2KF</td>
<td>31.2</td>
</tr>
<tr>
<td>10</td>
<td>NF₄GeF₅·1.2KF</td>
<td>29.0</td>
</tr>
<tr>
<td>11</td>
<td>NF₄AsF₆·1.2KF</td>
<td>27.3</td>
</tr>
<tr>
<td>12</td>
<td>NF₄SbF₆·1.2KF</td>
<td>24.0</td>
</tr>
<tr>
<td>13</td>
<td>NF₄BiF₆·1.2KF</td>
<td>19.7</td>
</tr>
</tbody>
</table>

*The molar ratio of KF to NF₄⁺ salt is based on experimental data for NF₄BF₄ formulations. A 20 molar percent excess of KF is required to clinker BF₃ efficiently. *(NF₄)₂TiF₆ might require clinkering with KF which would drop its fluorine yield below that of (NF₄)₂SnF₆.

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Obviously, there were many problems associated with the development of this class of compounds, and the purpose of this program was to provide some of the required basic information. The following paragraphs summarize the results of our studies.

B. MECHANISM OF \( \text{NF}_4^+ \) FORMATION AND DECOMPOSITION

In order to develop improved and efficient methods for the synthesis of known and novel \( \text{NF}_4^+ \) salts, it was very important to gain a better understanding of the \( \text{NF}_4^+ \) formation mechanism. We have used ESR spectroscopy to show that the \( \text{NF}_3^+ \) radical cation is formed as an intermediate, not only in the \( \gamma \)-irradiation induced decomposition (Ref. 12) of \( \text{NF}_4^+ \) salts, but also in the UV photolyzed formation of \( \text{NF}_4^+ \) salts (Appendix A). Furthermore, we have measured the decomposition kinetics of \( \text{NF}_4^+ \text{BF}_4 \) and \( \text{NF}_4^+ \text{AsF}_6 \) (Appendix E), and found from the observed rate suppression data that both the formation and the decomposition of \( \text{NF}_4^+ \) salts are best explained by the following reversible mechanism given for \( \text{NF}_4^+ \text{AsF}_6 \).

\[
\begin{align*}
\text{F}_2 & \rightarrow 2\text{F} \\
\text{F} + \text{NF}_3^- & \rightarrow \text{NF}_4^- \\
\text{NF}_4^- + \text{AsF}_5^- & \rightarrow \text{NF}_3^- + \text{AsF}_6^- \\
\text{NF}_3^+ \text{AsF}_6^- + \text{F} & \rightarrow \text{NF}_4^+ \text{AsF}_6^- 
\end{align*}
\]

C. IMPROVED AND NOVEL SYNTHETIC METHODS

Because most of the advanced \( \text{NF}_4^+ \) salts are accessible only by metathetical methods, it was important to determine the most favorable reaction conditions. It was found that for the general process

\[
\text{NF}_4^+\text{A}^- + \text{M}^+\text{X}^- \overset{\text{solvent}}{\rightarrow} \text{NF}_4^+\text{X}^- + \text{MA} 
\]

the best product yields and purities are obtained when \( \text{A} = \text{SbF}_6^- \), \( \text{M}^+ = \text{Cs}^+ \), solvent = HF and the temperature of the filtration step is -78 C (Appendix B).

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Improvements in the synthesis of the NF$_4$SbF$_6$ starting material were also made. It was found (Appendix F) that the compound can be prepared directly from the low-cost and readily available SbF$_3$ starting material according to:

$$\text{SbF}_3 + 2\text{F}_2 + \text{NF}_3 \xrightarrow{250 \degree C, 30-70 \text{ atm}} \text{NF}_4^+\text{SbF}_6^-$$

A novel synthetic method was developed for NF$_4^+$ salts derived from nonvolatile polymeric Lewis acids which do not possess an HF soluble cesium salt. This method involves the reaction of the Lewis acid with an excess of NF$_4$HF$_2$ and was successfully demonstrated for NF$_4^+$UF$_5$O$^-$ (Appendix I) according to:

$$\text{NF}_4\text{HF}_2 + \text{UF}_4 \xrightarrow{4 \text{ atm}} \text{NF}_4^+\text{UF}_5\text{O}^- + \text{HF}$$

D. SYNTHESIS OF NOVEL NF$_4^+$ SALTS

Several novel NF$_4^+$ salts were synthesized. These included (NF$_4$)$_2$MnF$_6$ (Appendix J), NF$_4$UF$_5$O (Appendix I), NF$_4$SO$_3$F (Appendix H), NF$_4$HF$_2$ and NF$_4$ClO$_4$ (Appendix G). The (NF$_4$)$_2$MnF$_6$ salt is, at the present time, the most promising candidate for a solid propellant NF$_3$-F$_2$ gas generator. Although its usable fluorine yield is not quite as high as that of (NF$_4$)$_2$NiF$_6$ (Table 1), its thermal stability is considerably higher, thus making it more useful. The low-temperature metathetical CsSbF$_6$ based process

$$\text{Cs}^+\text{X}^- + \text{NF}_4^+\text{SbF}_6^- \xrightarrow{\text{HF}, -78 \degree C} \text{CsSbF}_6^+ + \text{NF}_4^+\text{X}^-$$

was used for the syntheses of (NF$_4$)$_2$MnF$_6$, NF$_4$SO$_3$F, NF$_4$ClO$_4$ and NF$_4$HF$_2$. The NF$_4$UF$_5$O salt was prepared from NF$_4$HF$_2$ and UF$_4$O (see above). Theoretically, the NF$_4$ClO$_4$ salt would be of great interest as an ingredient in explosives, but unfortunately its thermal stability is too low for practical applications. Efforts were also made to prepare NF$_4^+$ salts containing the following anions, NO$_3^-$, ClF$_4$O$^-$, BrF$_4$O$^-$, IF$_6$O$_2^-$, BrO$_4^-$, and IO$_4^-$ (Appendix G), and MF$_6^{2-}$ or MF$_6^{3-}$ anions derived from third row transition metal fluorides (Appendix J). Unfortunately, none of these salts was stable enough to permit their isolation.
The novel salts $\text{N}_2\text{F}_3\text{SbF}_6^+$ and $\text{N}_2\text{F}_3\text{SnF}_5^-$ were also prepared (Appendix G) according to:

$$\text{N}_2\text{F}_4^+ + \text{SbF}_5^- \xrightarrow{\text{HF}} \text{N}_2\text{F}_3\text{SbF}_6^+$$

and

$$2\text{N}_2\text{F}_3\text{SbF}_6^+ + \text{Cs}_2\text{SnF}_6^- \xrightarrow{\text{HF}} 2\text{CsSbF}_6^- + + \text{N}_2\text{F}_3\text{SnF}_5^- + \text{N}_2\text{F}_4^-$$

These salts are stable and are of interest as burning rate modifiers in solid propellant $\text{NF}_3-\text{F}_2$ gas generator formulations containing $\text{NF}_4^+$ salts (Ref. 13).

E. CHARACTERIZATION OF $\text{NF}_4^+$ SALTS

The reliable determination of the properties of $\text{NF}_4^+$ salts is very important for practical applications. For example, the thermochemistry and densities of the $\text{NF}_4^+$ salts must be known for theoretical performance calculations. The thermal stability and decomposition mode must be known to decide whether certain salts pass long term storability requirements, and methods must be developed for determining the purity of the salts.

All the novel salts, described in the preceding paragraph, were thoroughly characterized. The techniques applied included elemental analyses (Appendix L), $^{19}\text{F}$ NMR, infrared, Raman and ESR spectroscopy, X-ray diffraction, DSC, thermal decomposition, and calorimetry. The results of these studies are given in the appendices, except for the crystal structure and calorimetric studies which are still under progress and will be completed under a follow-on contract. Two crystal structure studies on $\text{NF}_4\text{BF}_4$ and $\text{NF}_4\text{SbF}_6^+$ turned out to be rather frustrating, due to partial disorder of the anions. Both studies, however, indicate that the N-F bond length in $\text{NF}_4^+$ is about 1.25Å, a value in excellent agreement with the results of our force field analysis (Appendix K). Attempts will be continued to refine these crystal structures. Thermodynamic data on $\text{NF}_4\text{BF}_4^+$, $\text{NF}_4\text{PF}_6^+$, $\text{NF}_4\text{AsF}_6^+$, and $\text{NF}_4\text{SbF}_6^+$ have been obtained by Prof. Peacock of the University of Leicester by measuring the heats of hydrolysis of these salts.
The results of these measurements will be crosschecked by Prof. Margrave of Rice University using a different technique.

F. CONCLUSION

This program has significantly advanced our knowledge of NF$_4^+$ chemistry. It has provided us with new synthetic methods, novel NF$_4^+$ salts and chemical, physical, structural, kinetic and thermodynamic data which have been and are extremely useful for the ongoing development work of solid propellant NF$_3$-F$_2$ gas generators.
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ESR EVIDENCE FOR THE FORMATION OF THE NF$_3^+$ RADICAL CATION AS AN INTERMEDIATE IN THE SYNTHESIS OF NF$_4^-$ SALTS BY LOW-TEMPERATURE UV PHOTOLYSIS

Karl O. Christe* and Ira B. Goldberg

Received July 18, 1977

The mechanism of the formation of NF$_3^+$ salts is of significant practical and theoretical interest. From a practical point of view, a better understanding of this mechanism would permit optimization of the reaction conditions for the direct syntheses of NF$_3^+$ salts, such as NF$_3$BF$_4$, NF$_3$PF$_6$, or NF$_3$GeF$_6$. From a theoretical point of view, the formation of the NF$_3^+$ cation is intriguing because its parent molecule NF$_3$ does not exist as a stable species. Since under the conditions used for most of the syntheses of NF$_3^+$ salts an F$^-$ cation should be extremely difficult, if not impossible, to prepare by chemical means, the following mechanism has previously been proposed.

$\text{F}_3^+ \rightarrow 2\text{F}^- + \text{A}_3^+$

(1)

$\text{F}^- + \text{AsF}_5 \rightarrow \text{AsF}_4^+$

(2)

$\text{AsF}_4^- + \text{NF}_3 \rightarrow \text{NF}_3^+ + \text{AsF}_4^-$

(3)

$\text{NF}_3^+ + \text{F}^- + \text{AsF}_4^+ \rightarrow \text{F}_3^+ + \text{AsF}_4^+$

(4)

In good agreement with the known experimental facts, this mechanism requires only a moderate activation energy ($D^0(\text{F}) = 36.8 \text{ kcal mol}^{-1}$). The two critical intermediates are the AsF$_5^-$ radical and the NF$_3^+$ radical cation. Whereas the AsF$_5^-$ radical is unknown, the NF$_3^+$ radical cation was shown to form during γ irradiation of NF$_3^+$ salts at $196^\circ C$. Although this observation of the NF$_3^+$ cation demonstrated its possible existence at low temperature, it remained to be shown that the NF$_3^+$ radical cation is indeed formed in an intermediate in the syntheses of NF$_3^+$ salts. We have now succeeded in observing experimentally the NF$_3^+$ radical cation by ESR spectroscopy as an intermediate in the low-temperature UV photolyses of both the NF$_3^-$ and F$_3$ AsF$_5$ and the NF$_3^-$ and F$_3$ BF$_4$ systems. The results and implications derived from the observations are given in this paper.

EXPERIMENTAL SECTION

Binary and ternary mixtures of the starting materials were prepared for both the NF$_3^-$ and F$_3$ AsF$_5$ and the NF$_3^-$ and F$_3$ BF$_4$ systems in a stainless-steel Pyrex HP vacuum system. The sample tubes consisted of flamed-out quartz tubes of 4-mm o.d., 10-cm long, with a ballast volume of about 150 mL attached at the top. The starting materials were condensed into these tubes at $-210^\circ C$ and the tubes were flame sealed. The NF$_3$ (Rockedyne) was used without further purification. F$_3$ (Rockedyne) passed through a Na$_2$O scrubber for HF removal, and BF$_3$ (Matheson) and AsF$_5$ (Ozark Mahoning) were purified by fractional condensation prior to use. About 300 cm$^3$ of gas mixture was used for each sample in the following mole ratios: NF$_3$F$_2$ = 1:10; BF$_3$:F$_3$ = 1:10; AsF$_5$:F$_3$ = 1:10; NF$_3$:BF$_3$ = 1:1; NF$_3$:AsF$_5$ = 1:1; NF$_3$:BF$_3$:F$_3$ = 1:4:1 and 1:2:1; NF$_3$:F$_3$:AsF$_5$ = 1:4:1.

The ESR spectra were recorded as previously described.$^*$ Variable-temperature control over the temperature range 4 to 300 K was achieved with an Air Products liquid-helium-transfer refrigerator. A Model LTD-110. For the photolyses, an Oriel Model 6240 arc lamp with 200-W Hg lamp was used. In some of the experiments, the starting materials were condensed at $196^\circ C$ into the tip of the ESR tube and were irradiated for 10-30 min while inserted in a liquid-nitrogen-filled unsilvered Dewar. The ESR tube was then quickly transferred to the precooled ESR spectrometer. In other experiments, the sample tubes were irradiated at various temperatures inside the ESR cavity.

RESULTS AND DISCUSSION

UV photolyses of both the NF$_3$:F$_3$:AsF$_5$ and the NF$_3$:F$_3$:BF$_4$ systems produced an intensely violet species which exhibited the ESR signal shown in Figure 1, traces A and B. Comparison with the previously published anisotropic spectrum of the NF$_3^+$ cation (trace C, Figure 1) establishes beyond doubt the presence of NF$_3^+$ in our samples. The spectra are assigned on the basis of anisotropic hyperfine coupling to three fluorine atoms ($I = 1/2$) and approximately isotropic hyperfine coupling to one nitrogen atom ($I = 1$). The g matrix is isotropic to within the line width. The spectra thus appear as a quartet of triplets as shown in Figure 1. The broader line widths observed in the spectra of UV-irradiated NF$_3^-$:At$_3$ and NF$_3$:F$_3$:BF$_4$ mixtures than in γ-irradiated NF$_3$:SbF$_5$ may be the result of exchange or of dipolar interactions of materials on the surfaces of the solid components of the mixtures.

The observation of identical signals for both the BF$_3$ and the AsF$_5$-containing system proves that the signal must be due to a species not containing boron or arsenic. By carrying out irradiation experiments of the sample within the ESR cavity at $196^\circ C$, it was shown that the signal strength increased during irradiation but did not decrease when the lamp was turned off. The thermal stability of the signal in the absence of UV radiation depended on the strength of the Lewis acid used. For the stronger Lewis acid AsF$_5$, the signal did not change significantly up to about $105^\circ C$, whereas for BF$_3$, decomposition started at about $155^\circ C$. When the sample tubes were warmed to ambient temperature, they contained white stable solids which were identified by Raman spectroscopy as NF$_3$:AsF$_5$ and NF$_3$:BF$_4$, respectively.$^{1,78}$ Irradiation of all possible binary mixtures, i.e., NF$_3$, Lewis acid F$_3$, Lewis acid AsF$_5$, and NF$_3$: Lewis acid, under comparable conditions did not produce any ESR signal attributable to NF$_3^+$.

A positive identification of the proposed AsF$_5^+$ or BF$_4^+$ radical intermediates was not possible in the above experi-

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combination with a fluorine radical dealing with polymeric solid AsF₆ or BF₆ phases which on structure. The line width of the resulting signal would depend on the corresponding anions is possible which would destroy hyperfine lattice, rapid electron exchange between the radicals and the we assume the existence of an strongly temperature-dependent line width. Furthermore, if we assume the existence of an AsF₆⁻ or BF₆⁻ radical in an ionic lattice, rapid electron exchange between the radicals and the corresponding anions is possible which would destroy hyperfine structure. The line width of the resulting signal would depend on the rate of exchange. Finally, in our experiments we were dealing with polymeric solid AsF₆ or BF₆ phases which on combination with a fluorine radical are not likely to result in an isolated AsF₆⁻ or BF₆⁻ radical. In our experiments, several ESR signals were observed in addition to NF₆⁺. However, in the absence of observable hyperfine structure we prefer not to make any assignments.

On the basis of our results, the following conclusions can be reached concerning the formation mechanism of NF₆⁺ salts. (i) The NF₆⁺ radical cation is indeed an important intermediate. (ii) The requirement of UV activation and of both F₂ and a Lewis acid for the synthesis of NF₆⁺ is in agreement with steps 1 and 2 of the given mechanism. (iii) The strength of the Lewis acid determines the thermal stability and lifetime of the intermediate NF₆⁺ salt formed. This can account for the low-temperature conditions required for the synthesis of the NF₆⁺ salts of weaker Lewis acids. (iv) In the absence of UV irradiation, the NF₆⁺ salts do not spontaneously react with the large excess of liquid F₂ present. This indicates that in the absence of an activation energy source the thermodynamically feasible chain-propagation step NF₆⁺AsF₆⁻ + F₂ - NF₆⁺AsF₆⁻ + F does not play an important role. Possibly, the conversion of NF₆⁺AsF₆⁻ to NF₆⁺AsF₆ may require F⁻ atoms according to

\[ \text{NF}_6^+\text{AsF}_6^- + F^- \rightarrow \text{NF}_6^+\text{AsF}_6^- \]  

Since the intermediate NF₆⁺ salt is an ionic solid, its reaction with a fluorine atom might well be a heterogeneous diffusion-controlled reaction and step 5 might be the rate-determining step in the mechanism. It was shown that at temperatures above -196 °C, where a given NF₆⁺ salt is still stable in the absence of light, UV irradiation causes a rapid decay of the NF₆⁺ ESR signal. However, it was not possible to distinguish whether this decay was caused by photodecomposition of the intermediate NF₆⁺ salt or by the reaction of the latter with the generated F atoms according to step 5.

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Registry No. NF₆⁺, 54384-83-7; NF₆AsF₆⁻, 16871-75-3; NF₆BF₆⁻, 15640-93-4.

References and Notes

APPENDIX B

ON THE SYNTHESES AND PROPERTIES OF SOME HEXAFLUOROBISMUTHATE (V) SALTS AND THEIR USE IN THE METATHETICAL SYNTHESSES OF NF₄⁺ SALTS

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SUMMARY

The salts LiBiF₆, NaBiF₆, KBiF₆, CsBiF₆ and NF₄BiF₆ were prepared and characterized. Differences in the observed numbers and relative intensities of some of the Raman bands of these salts are explained by crystal effects. Solubilities of these salts in anhydrous HF at -78°C were determined and compared to those of the corresponding SbF₆ salts. It was shown that, contrary to a previous report, CsBiF₆ does not exhibit any unusual properties such as forming a mushy volatile HF adduct. The potential of NF₄BiF₆ based metathetical processes for the production of other NF₄⁺ salts was evaluated. The novel H₃O⁺BiF₆⁻ salt was prepared and characterized. The usefulness of BiF₅ for water removal from HF is briefly discussed.

INTRODUCTION

In the course of our work on oxonium salts [1] and metathetical NF₄⁺ salt processes [2-6], we became interested in pentavalent bismuth compounds as possible replacements for the corresponding antimony compounds. For example, the use of the less volatile BiF₅ has been proposed [1], but has never been tested, as an alternative to SbF₅.
for removal of small amounts of water from HF. Because $\text{NF}_4\text{BiF}_6$ has become readily accessible by direct thermal synthesis from $\text{NF}_3$, $\text{F}_2$, and $\text{BiF}_5$ [7], it holds potential as a starting material in meta-

thetical processes for the production of other less accessible $\text{NF}_4$ salts. However, its usefulness in such a process depends on the relative solubilities of its salts in a suitable solvent, such as anhydrous HF. Although $\text{BiF}_6^-$ salts have been known [8] since 1950, only a small number of papers [7, 9-18] dealing with $\text{BiF}_6^-$ salts have been reported since then, and some of the reported data are very much open to question. For example, Surles and coworkers reported [13] that HF formed a stable adduct with $\text{CsBiF}_6$ and that this adduct readily sublimed on heating. Consequently, a more systematic study of $\text{BiF}_6^-$ salts was necessary in order to be able to properly evaluate the potential of $\text{BiF}_6^-$ salts in the above applications.

EXPERIMENTAL

Materials and Apparatus

The apparatus, handling procedures, and the method used for the HF drying have previously been described [1,6]. Bismuth pentafluoride (Ozark Mahoning Co.) did not contain any detectable impurities and was used as received. Antimony pentafluoride (Ozark Mahoning Co.) was distilled prior to use. Lithium fluoride (Baker, A. R.) and NaF (MCB, Reagent grade) were used as received. Potassium fluoride (Allied, Reagent grade) and CsF (KBI) were dried by fusion in a platinum crucible and powdered in the drybox. The syntheses of $\text{NF}_4\text{BiF}_6$ [7] and $\text{NF}_4\text{SbF}_6$ [4] have previously been described. Except for NaBF$_4$ which was obtained from H$_3$BO$_3$ and Na$_2$CO$_3$ in concentrated aqueous HF solution, all the alkali metal tetrafluoroborates were prepared by introducing a slight excess of gaseous BF$_3$ into stirred solutions of the corresponding alkali metal fluorides in anhydrous HF at 20°, followed by removal of the volatile products.

Syntheses of $\text{BiF}_6^-$ and $\text{SbF}_6^-$ Salts

For the syntheses of the alkali metal hexafluorobismuthates, equimolar amounts of finely powdered alkali metal fluoride and $\text{BiF}_5$ were heated in a Monel cylinder for several days to 280° under 2 atm
of $F_2$. The vibrational spectra of the resulting products showed no evidence for the presence of either unreacted $\text{BiF}_5$ [19] or polybismuthate salts [7]. When these reactions were carried out at 150°, however, the products contained some polybismuthate salts. The alkali metal hexa-
fluoroantimonates were prepared in a similar manner by heating equimolar mixtures of $\text{SbF}_6$ and the corresponding alkali metal fluoride in a $F_2$ atmosphere to 280°. Again, vibrational spectra of the solid products showed no evidence for the presence of polyantimonates.

Spectra

Infrared spectra of solids were recorded as dry powders between pressed AgCl or AgBr disks on a Perkin Elmer Model 283 spectrometer. Raman spectra were recorded in glass melting point, quartz or Kel-F capillaries on a Cary Model 83 spectrophotometer using the 4880A exciting line of an Argon ion laser. Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel filtered copper Kα radiation and quartz capillaries as sample containers. The thermal decomposition of salts was examined with a Perkin Elmer differential scanning calorimeter (Model DSC-1B) using crimp-sealed aluminum pans as sample containers and a heating rate of 2.5°/min at atmospheric pressure.

Solubility Measurements

Solubilities of the salts in anhydrous HF at -78° were measured in an apparatus similar to that previously described [6] for metathetical reactions, except for eliminating trap 1. Saturated solutions were prepared at -78° and separated from excess undissolved salt by filtration at -78°. The HF solvent was pumped off at ambient temperature, and the amount of HF used and of the solid residues obtained after HF removal were determined by weighing.

Metathetical Reactions

Metathetical reactions between $\text{NF}_4\text{BiF}_6$ or $\text{NF}_4\text{SbF}_6$ and different alkali metal tetrafluoroborates in anhydrous HF solution were carried out as previously described [4,6].
Synthesis of $\text{H}_3\text{OBiF}_6$

Bismuth pentafluoride (10.08 mmol) was transferred into the glove box into a passivated (with $\text{ClF}_3$ Teflon FEP ampule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10.12 g) which had been stored over $\text{BiF}_5$ was condensed into the ampule at $-196^\circ$. The mixture was warmed to room temperature, and the Raman spectrum of the resulting clear solution was recorded. It showed bands similar, but not identical, to those expected for either $\text{BiF}_6^-$ (see below) or solid $\text{BiF}_5$ [16, 19]. The ampule was cooled to $-196^\circ$, and distilled $\text{H}_2\text{O}$ (10 mmol) was syringed into the ampule. On warm up to ambient temperature, a copious white precipitate was formed. The mixture was stirred for ten hours at 25°. The Raman spectrum of the clear solution above the white solid precipitate showed the bands characteristic for $\text{BiF}_-$ (see below). Removal of the HF solvent in a dynamic vacuum at $-45^\circ$ resulted in the formation of a white solid (3.469g, weight calc'd for 10.08 mmol of $\text{H}_3\text{OBiF}_6 = 3.447$g) which was identified by Raman and infrared spectroscopy as $\text{H}_3\text{O}^+\text{BiF}_6^-$. This solid was stable at ambient temperature only under an HF pressure of about 20mm. On evacuation of the ampule, the white solid would immediately turn dark brown. When the valve of the ampule was closed to allow the pressure to build up again, the white color of the sample was restored. Complete decomposition of $\text{H}_3\text{OBiF}_6$ in a dynamic vacuum at 35°for 3 days resulted in a light cream colored solid. Based on its weight, physical properties (nonhygroscopic, insoluble in $\text{H}_2\text{O}$ and aqueous $\text{HCl}$, sublimation at the softening point of glass), and elemental analysis (found: Bi, 77.2; F, 23.3; O, 0.2; calc'd for $\text{BiF}_3$: Bi, 78.57; F, 21.43; O, 0) this solid appeared to be mainly $\text{BiF}_3$. The vibrational spectra of the solid decomposition product did not show any evidence for the presence of either $\text{H}_3\text{O}^+$ or $\text{BiF}_6^-$. 

RESULTS AND DISCUSSION

Syntheses and Properties of Hexafluorobismuthates

The alkali metal hexafluorobismuthates were prepared from equimolar amounts of $\text{BiF}_5$ and the corresponding alkali metal fluoride by heating to 280° in a Monel cylinder. Fluorine was added to the
cylinder to suppress possible decomposition of BiF₅ to BiF₃ and F₂. This synthesis is similar to that [9] previously reported, except for using a significantly higher temperature. Using the previously reported [9] temperature conditions (85-150°), the product always contained some polybismuthate salt. For the syntheses of the alkali metal hexafluorobismuthates, similar reaction conditions were required to suppress the formation of polyantimonates.

The rather unusual properties previously reported [13] for CsBiF₆ could not be confirmed. Thus, CsBiF₆ was quantitatively recovered from HF solutions by pumping at ambient temperature, without any evidence for the formation of a stable CsBiF₆·xFHF adduct. Furthermore, no evidence was found for sublimation without decomposition for either HF treated or untreated CsBiF₆. DSC data obtained for CsBiF₆ showed a small reversible endotherm at 190°, attributed to a phase change, and the onset of a large endotherm at 308°, attributed to decomposition. Thermal decomposition of CsBiF₆ around 300° was confirmed by visual observation of samples sealed in melting point capillaries. At this temperature, sublimation of BiF₅ to the colder parts of the capillary occurred. For comparison, DSC data were also recorded for CsSbF₆. They showed a small reversible endotherm (phase change) at 187° and the onset of endothermic decomposition at 296°. These data show that the thermal stabilities of CsSbF₆ and CsBiF₆ are similar, with the bismuth salt being slightly more stable.

The vibrational spectra of the alkali metal hexafluorobismuthates were also recorded and showed some remarkable differences (see Figure 1). Particularly, the Raman active deformation mode exhibited different numbers of bands and intensity ratios. In order to determine whether the observed splittings were caused by the simultaneous presence of more than one crystal modification, the Debye-Scherrer powder patterns of these compounds were recorded. In excellent agreement with a previous report [10], it was found that LiBiF₆ and NaBiF₆ were rhombohedral (LiSbF₆ type), KBiF₆ was cubic (low-temperature modification), and CsBiF₆ was rhombohedral (KOsF₆ type). No evidence was found for the presence of other modifications in either the thermally prepared (200°) or the HF recrystallized (-78°) samples. The observed splittings can be readily explained, however, by solid state effects. In the rhombohedral compounds (space group R3-C₃₁, Nr. 146, 1 molecule per Bravais cell [10]), the site symmetry of BiF₆ is C₃₁.
Figure 1.
Infrared spectrum of CsBiF₆ and Raman spectra of CsBiF₆, KBF₆, NaBiF₆, and LiBiF₆. The infrared spectrum was recorded as a dry powder between pressed AgCl disks. The broken line is due to absorption by the window material.
TABLE I.

Correlation Table for Isolated $\text{BiF}^-$ of Point Group $O_h$ and for Site Symmetry $C_{3i}$

<table>
<thead>
<tr>
<th>$\nu_n$</th>
<th>$\tilde{s}_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$A_g$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$E_g$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>$A_g + E_g$</td>
</tr>
<tr>
<td>$E_{1u}$</td>
<td>$A_u + E_u$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$A_u + F_u$</td>
</tr>
</tbody>
</table>

Therefore, from Table I only the $F_{2g}$ mode in the Raman and the $E_{1u}$ modes in the infrared are expected to be split into two components. For cubic $\text{KBiF}_6$ (space group $Ia3$, Nr. 206) the site symmetry of $\text{BiF}_6^-$ is again $C_{3i}$, but since the Bravais cell contains four molecules, factor group splitting can further cause the doubly degenerate $E_g$ modes to split into two components. These predictions are in good agreement with our observations (see Figure 1), except for $\text{NaNiF}_6$ which exhibits only one Raman band in the $\text{BiF}_6^-$ deformation region. This lack of splitting for $\text{NaNiF}_6$ is attributed to a coincidence of the frequencies of the $A_g$ and the $E_g$ components of $\nu_6$. This is plausible since the weaker (probably the $E_g$) component has a higher frequency in $\text{LiSiF}_6$ and a lower frequency in $\text{CsBiF}_6$ than the more intense (probably the $A_g$) component. The frequency separation of the two components in $\text{NaNiF}_6$ must be rather small since, even at a spectral slit width of 1 cm$^{-1}$, we could not resolve the band into two components.

The infrared spectrum of $\text{CsBiF}_6$ (see Figure 1) shows a very intense and broad band for the antisymmetric $\text{BiF}_6^-$ stretching mode $\nu_3$ ($F_{1u}$) at 570 cm$^{-1}$. It exhibits a pronounced shoulder at 590 cm$^{-1}$ which probably represents the second component of $\nu_3$ predicted for $C_{3i}$ symmetry (see Table I). In addition, several infrared allowed combination bands were observed (see Figure 1). From these, the frequencies of the two remaining deformation modes can be derived as: $\nu_6(F_{3u}) = 277$ and $\nu_6(F_{2u}) = 147$ cm$^{-1}$. It should be noted that the combination bands involving $\nu_3$ show splittings of about 20 cm$^{-1}$, analogous to that exhibited by $\nu_3$ itself. This lends further support to the above assignments.

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B-7
The previously reported \[16\] Raman spectrum of NOBiF\(_6\) exhibits the same splittings and intensity pattern as \(\alpha\)-KBiF\(_6\), indicating that the two compounds are probably isotypic. Of the six frequency values reported by Bougon and coworkers \[14\] for BiF\(_6\), \(\nu_4\) and \(\nu_5\) appear too low and should be revised. In agreement with a previous report \[7\], it was found that infrared spectroscopy is well suited for the detection of polybismuthate impurities in BiF\(_6^-\) salts. The polyanions result in an intense infrared band at around 440 cm\(^{-1}\).

Solubility Measurements

The metathetical production of NF\(_4^+\) salts is based on the following principle. A readily available and highly soluble NF\(_4^+\) salt, such as NF\(_4^+\)SbF\(_6\), is reacted in a suitable solvent, such as anhydrous HF, with an alkali metal salt containing the desired anion. If the alkali metal is chosen in such a manner that the starting materials and the desired NF\(_4^+\) salt product are highly soluble and the resulting alkali metal SbF\(_6^-\) salt, for example, is of very low solubility, the following general equilibrium, where \(X=Sb\), can be shifted far to the right hand side:

\[
MY + NF_4XF_6 \xrightarrow{HF} MXF_6 + NF_4Y
\]

The principle has been demonstrated for salts where \(Y = BF_6^-\) \[2-4\], SnF\(_6^-\) \[6\], TiF\(_6^-\) \[5\], and NiF\(_6^-\) \[20\]. Prior to now, \(X\) had always been Sb; but the case where \(X\) could be Bi had not been tested. Since NF\(_4^+\)BiF\(_6\) has recently become readily available by direct synthesis \[7\], and since an extrapolation of crude solubility data, previously measured \[2\] for alkali metal XBF\(_6^-\) salts (X=As, Sb) in HF at room temperature, indicated that LiBiF\(_6\) might possess the lowest solubility of any MXF\(_6^-\) salt, quantitative solubility data for MXF\(_6^-\) salts in anhydrous HF were desired. These data should allow to determine whether a BiF\(_6^-\) based process would offer any significant advantages over one based on SbF\(_6^-\).

The solubilities of NF\(_4^+\) and of several alkali metal BF\(_6^-\) and SbF\(_6^-\) salts were measured in anhydrous HF at -78\(^\circ\). The low temperature was chosen based on our past experience \[4\]. The results of our measurements are summarized in Table II. As can be seen, the measured solubilities clearly favor a process based on a cesium rather than a
lithium salt. Furthermore, the solubility of CsBiF$_6$ is only slightly lower than that of CsSbF$_6$, thus not compensating for the significantly lower solubility of the NF$_4$BiF$_6$ starting material in HF and its less favorable formation rate [7], compared to those of NF$_4$SbF$_6$ [4]. Consequently, based on all the presently available experimental data, a CsSbF$_6$ based process appears to be the most attractive method for the metathetical preparation of other NF$_4$ salts.

TABLE II

Solubilities of Various BiF$_6^-$ and SbF$_6^-$ Salts in Anhydrous HF at -78°

<table>
<thead>
<tr>
<th>Anion</th>
<th>SbF$_6^-$</th>
<th>BiF$_6^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>NF$_4^+$</td>
<td>259.0</td>
<td>0.7951</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>9.21</td>
<td>0.0379</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>7.48</td>
<td>0.0289</td>
</tr>
<tr>
<td>K$^+$</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>1.80</td>
<td>0.00488</td>
</tr>
</tbody>
</table>

a) in mg of solute per g of HF
b) in mole of solute per 1000g of HF
c) not measured

Metathetical NF$_4$BF$_4$ Production

Since in the metathetical production of NF$_4$BF$_4$ highly concentrated HF solutions are used, the activity coefficients of the ions are expected to differ significantly from those of the more dilute solutions of the solubility measurements. Consequently, the knowledge of solubility data is insufficient to predict accurately the product composition obtainable from metathetical experiments.
Metathetical $\text{NF}_4\text{BF}_4$ production runs using different $\text{MBF}_4$ and $\text{NF}_4\text{XF}_6$ salts in HF were carried out. Typical results from such experiments are shown in Table III. As can be seen, the data of Tables II and III are only in qualitative, but not quantitative, agreement. As expected, the solubilities of the alkali metal hexafluoro-antimonates and bismuthates are much higher in the concentrated solutions of the metathetical runs. Furthermore, Table III shows that a cesium salt-based process results in the best product purity. The extremely low yield of $\text{NF}_4\text{BF}_4$ for the $\text{KBF}_4 - \text{NF}_4\text{BF}_6$ system is caused by $\text{KBF}_4$ being less soluble in HF than $\text{KSbF}_6$. Keeping the difference in the stoichiometry of the used starting materials in mind, (see footnote of Table III) the results obtained for the $\text{LiBF}_4 - \text{NF}_4\text{SF}_6$ and the $\text{LiBF}_4 - \text{NF}_4\text{BiF}_6$ system are roughly comparable.

**TABLE III.**

Comparison of the Composition of the Crude Products Obtained by the Metatheses of NF$_4$ Salts with Different Alkali Metal Tetra-fluoroborates in HF at -78°

<table>
<thead>
<tr>
<th>System</th>
<th>Composition of Product (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LiBF}_4 - \text{NF}_4\text{BF}_4$</td>
<td>81.7 8.4 9.9</td>
</tr>
<tr>
<td>$\text{LiBF}_4 - \text{NF}_4\text{BiF}_6$</td>
<td>86.7 5.9 7.4</td>
</tr>
<tr>
<td>$\text{NaBF}_4 - \text{NF}_4\text{BF}_6$</td>
<td>86.3 12.6 19.1</td>
</tr>
<tr>
<td>$\text{KBF}_4 - \text{NF}_4\text{SF}_6$</td>
<td>85.3 79.6 5.1</td>
</tr>
<tr>
<td>$\text{CsBF}_4 - \text{NF}_4\text{SF}_6$</td>
<td>85.4 13.3 1.3</td>
</tr>
</tbody>
</table>

(a) A 5 mole excess of the NF$_4$ salt was used in all runs, except for the $\text{LiBF}_4 - \text{NF}_4\text{SF}_6$ system, where approximately stoichiometric amounts of starting materials were used.

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B-10
Oxonium Hexafluorobismuthate

Our interest in the possible existence of $\text{H}_2\text{O}^+\text{BiF}_6^-$ was twofold. The salt has previously been proposed \cite{1} as a potential candidate for the removal of traces of water from HF. Furthermore, its possible formation in wet HF solutions of $\text{BiF}_5$ might interfere with metathetical experiments, or result in undesired by-products, particularly when $\text{BiF}_6$ salts are prepared from $\text{BiF}_5$ and alkali metal fluorides in HF solution \cite{13}.

It was found that, contrary to a previous literature report \cite{13}, $\text{BiF}_5$ is quite soluble in anhydrous HF and has a solubility in excess of 300 mg of $\text{BiF}_5$ per g of HF at 22°C. The Raman spectrum of this solution (Figure 2, trace A) significantly differs in the deformation region from those of the $\text{BIF}_6^-$ anion in HF solution (Figure 2, trace B) and of solid $\text{BiF}_5$ \cite{16,19}, but is not unreasonable for an associated hexacoordinated bismuth fluoride.

On addition of water to this solution a copious white precipitate formed. The formation of this less soluble solid in the presence of small amounts of water could explain the previous report \cite{13} on the low solubility of $\text{BiF}_5$ in supposedly anhydrous HF. The Raman spectrum (Figure 2, trace B) of the HF solution above the white solid showed one polarized (591 cm$^{-1}$) and two depolarized bands (520 and 220 cm$^{-1}$), in agreement with our expectations for octahedral $\text{BIF}_6^-$. These frequency values are similar to those observed for the alkali metal $\text{BIF}_6^-$ salts in the solid state (see above). The Raman spectrum of the precipitate was also recorded and was similar to that of the liquid phase. These observations show that water addition converts HF dissolved $\text{BiF}_5$ into a $\text{BIF}_6^-$ salt.

Further identification of the formed precipitate was achieved by pumping off the HF solvent at -45°C. Based on the observed material balance and vibrational spectra, the following reaction occurred

$$\text{H}_2\text{O} + \text{HF} + \text{BiF}_5 \rightarrow \text{H}_2\text{O}^+\text{BiF}_6^-$$

The Raman spectra of the solid product (Figure 2, traces C) showed the presence of the bands characteristic for $\text{BIF}_6^-$ (see above) and $\text{H}_2\text{O}^+$ \cite{1}. The presence of these ions was further confirmed by infrared spectroscopy at -196°C which showed a strong band at 3240 cm$^{-1}$ with a shoulder at 3000 cm$^{-1}$ due to $\text{H}_2\text{O}^+$ stretching and a very intense
Figure 2. Raman spectra of a 1 molar solution of BiF$_5$ in HF (trace A), a saturated solution of BiF$_6^{3-}$ in HF (trace B), and of solid H$_2$O$^+BiF_6$ (trace C). All spectra were recorded at room temperature. P and DP indicates polarized and depolarized lines, respectively.
broad band with maxima at 598, 566 and 538 cm$^{-1}$ due to BiF$_6^-$ stretching. The splittings for the BiF$_6^-$ stretching mode is not surprising since at the low temperature rotational motions of the ions in the crystal lattice are frozen out [1] causing symmetry lowering due to strong anion-cation interactions. The same temperature effect was observed for the Raman spectra. At -100°, the 594 cm$^{-1}$ band was observed to split into the following bands: 595 vs., 586 s, 574 mw, 562 w, 555 sh.

An interesting behavior was observed for solid H$_3$OBiF$_6$. At ambient temperature, H$_3$OBiF$_6$ appears to be stable only under an HF pressure of about 20 torr. When the HF is pumped off, the compound turns instantly dark brown indicating hydrolysis of BiF$_5$ [9]. When the HF pressure is restored, the solid turns white again. The nature of the decomposition product was established by allowing a sample of H$_3$OBiF$_6$ to completely decompose in a dynamic vacuum for 3 days at 35°. The solid residue was found to be mainly BiF$_3$, as expected from the known [9] hydrolysis of BiF$_5$. Based on these observations, it appears that H$_3$OBiF$_6$ first undergoes a reversible dissociation according to

\[ H_3\text{OBiF}_6 \rightleftharpoons cH_2O + HF + BiF_5 \]

followed by the irreversible hydrolysis

\[ BiF_5 + H_2O \rightarrow BiF_3 + 2HF + 1/2O_2 \]

with the first step being strongly suppressed by HF.

Although the thermal stability of H$_3$OBiF$_6$ appears to be lower than that [1] of H$_3$OSbF$_6$, the following reaction cycle might offer a convenient method for drying HF:

\[ BiF_5 + H_2O + HF \rightarrow H_3\text{OBiF}_6 \]

\[ H_3\text{OBiF}_6 \rightarrow BiF_3 + 3HF + 1/2O_2 \]

\[ BiF_3 + F_2 \rightarrow BiF_5 \]

\[ H_2O + F_2 \rightarrow 2HF + 1/2O_2 \]
The advantage of this cycle over one using SbF$_5$ would be that BiF$_5$ is a nonvolatile solid which is easier to handle. As shown by the above equations, the proposed cycle amounts to a fluorination of water to yield HF and oxygen. Although this objective can also be achieved by a direct treatment of wet HF with high pressure fluorine with agitation [1], the proposed cycle could offer practical advantages. For example, in the proposed cycle the fluorination step could be limited to a relatively small amount of BiF$_3$ instead of treating the bulk of the HF with a large excess of high pressure fluorine which has to be recovered.

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Chemistry and Structure of $N_2F^+$ Salts

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The novel $N_2I^+$ salt $N_2I_SbI_4$ was prepared from $N_2I_4$ and SbI$_4$ in anhydrous HF solution. A metathetical reaction between $N_2I_SbI_4$ and $C_2SbI_4$ in HF produced $N_2F_4$ and the novel salt $N_2I_SbI_4$. It was shown that $N_2I_4$ and BF$_3$ do not form a stable adduct at temperatures as low as -78°C. The vibrational and $^1$H NMR spectra of the $N_2F^+$ cation were reexamined. All the experimental data are consistent with a planar structure of symmetry $C_2v$ for $N_2F^+$. The previously reported vibrational assignments made on the basis of a nonplanar structure of symmetry $C_1$, are revised for six fundamental frequencies.

Introduction

The first report on the formation of a stable adduct between $N_2I_4$ and a Lewis acid was published in 1965 by Ruff. He showed that SbF$_5$, when treated with an excess of $N_2I_4$ in AsF$_5$ solution, produced, depending on the pressure of $N_2I_4$, either the 1:2 adduct $N_2I_4$SbF$_5$, or the 1:3 adduct $N_2I_4$SbF$_6$. On the basis of the observed $^1$H NMR spectrum, and an incomplete infrared spectrum, he assigned to $N_2I_4$SbF$_5$, the ionic structure $N_2F^+$SbF$_5$ with hindered rotation around the $N-N$ bond in $N_2F^+$. In 1967, Young and Moy published...
the syntheses of adducts between N$_2$F$_4$ and AsF$_5$. At -78 °C and ambient temperature, the AsF$_5$N$_2$F$_4$ combination ratios were reported to be 2.3 and 1.3 ± 0.2, respectively. In addition to an incomplete infrared spectrum and an unresolved $^{19}$F NMR spectrum, the strongest lines of an X-ray powder diffraction pattern were given which was indexed on the basis of a cubic unit cell with $a = 10.8$ Å. In the same year, Lawless published a better resolved infrared spectrum of N$_2$F$_3$AsF$_5$, but no assignments were offered. In 1970, Qureshi and Aubke published a paper dealing with the infrared and Raman spectra of solid N$_2$F$_3$AsF$_5$ and N$_2$F$_3$SbF$_5$. With the exception of the N–N torsional mode, they observed and tentatively assigned all fundamental vibrations of N$_2$F$_3^+$ as a nonplanar structure of symmetry C$_2v$.

Since N$_2$F$_3^+$ salts are of interest as burning aids in solid propellant N$_2$F$_3$ gas generator formulations, we have studied (i) the synthesis of N$_2$F$_3$SbF$_6$, (ii) the possibility of converting N$_2$F$_3$SbF$_6$ into "self-clinker" N$_2$F$_3^+$ salts by metathetical reactions, and (iii) the vibrational spectra and structure of the N$_2$F$_3^+$ cation. The results of this study are summarized in this paper.

**Experimental Section**

**Materials and Apparatus.** Volatile materials were manipulated in a well-passivated (with Cl$_2$F) Monel vacuum line equipped with Teflon-FEP U-tubes and diaphragm valves. Pressures were measured with either a Heise Bourdon tube-type gauge (0-1500 mm 0.1% accuracy) or a Valdyne Model DM 56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox. Arsenic pentafluoride and SbF$_5$ (Ozark Mahoning), N$_2$F$_3$ (Air Products), and BF$_3$ and SO$_3$F$_2$ (Matheson) were purified by fractional condensation prior to use. The BF$_3$ (Matheson) was treated with 30% H$_2$SO$_4$ and then treated with 200°C by fractional condensation. HF was dried as previously described. The SnF$_4$ (Ozark Mahoning) was used as received. The preparation of CsSbF$_6$ has previously been described.

The infrared spectra were recorded on a Perkin-Elmer Model 38 spectrophotometer as dry powders pressed between AgCl or AgBr or AgClI disks in a Wilks mupinilet press. Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-A exciting line and a Claassen filter$^{11}$ for the elimination of plasma lines. Polarization no solvent was required and the yield was quantitative:

$$\text{N}_2\text{F}_4 + \text{SbF}_5 \rightarrow \text{N}_2\text{F}_3\text{SbF}_6$$

Similarly, no difficulty was encountered in preparing a well-defined 1:1 adduct between N$_2$F$_4$ and AsF$_5$. In this case, no solvent was required and the yield was quantitative:

$$\text{N}_2\text{F}_4 + \text{AsF}_5 \rightarrow \text{N}_2\text{F}_3\text{AsF}_5$$

According to a previous report by Young and Moyer on the same system, the averaged composition of their adduct was N$_2$F$_4$:1.3AsF$_5$, and, in the presence of HF as a solvent, the yield was only about 65%.

Boron trifluoride, which is a weaker Lewis acid than SbF$_5$ and AsF$_5$ does not form a stable adduct with N$_2$F$_4$ at temperatures as low as -78 °C. Our attempts also failed to directly synthesize an N$_2$F$_3^+$ salt derived from SnF$_6$ by treatment of a SnF$_2$-HF suspension with N$_2$F$_4$. No N$_2$F$_4$ uptake occurred. This lack of reactivity cannot be due to insufficient acid strength of SnF$_6$ since metathesis in HF yields stable N$_2$F$_3$SnF$_3$ (see below). A more plausible explanation is that N$_2$F$_3$ is not a strong enough Lewis base to depolymerize SnF$_6$.

Since the direct synthesis of an adduct between N$_2$F$_4$ and SnF$_6$ was not possible, a metathetical reaction between N$_2$F$_3$SbF$_6$ and Cs$_2$SnF$_6$ was carried out in hot solution. The following reaction occurred:

$$2\text{N}_2\text{F}_3\text{SbF}_6 + \text{Cs}_2\text{SnF}_6 \rightarrow \text{HF soln}$$

Similarly, no difficulty was encountered in preparing a well-defined 1:1 adduct between N$_2$F$_4$ and AsF$_5$. In this case, no solvent was required and the yield was quantitative:

$$\text{N}_2\text{F}_4 + \text{AsF}_5 \rightarrow \text{N}_2\text{F}_3\text{AsF}_5$$

According to a previous report by Young and Moyer on the same system, the averaged composition of their adduct was N$_2$F$_4$:1.3AsF$_5$, and, in the presence of HF as a solvent, the yield was only about 65%.

Boron trifluoride, which is a weaker Lewis acid than SbF$_5$ and AsF$_5$ does not form a stable adduct with N$_2$F$_4$ at temperatures as low as -78 °C. Our attempts also failed to directly synthesize an N$_2$F$_3^+$ salt derived from SnF$_6$ by treatment of a SnF$_2$-HF suspension with N$_2$F$_4$. No N$_2$F$_4$ uptake occurred. This lack of reactivity cannot be due to insufficient acid strength of SnF$_6$ since metathesis in HF yields stable N$_2$F$_3$SnF$_3$ (see below). A more plausible explanation is that N$_2$F$_3$ is not a strong enough Lewis base to depolymerize SnF$_6$.
caused by significant contributions from resonance structure II. The assignments previously made by Qureshi and Aubke for \( \text{N}_2\text{F}_3^+ \) were based on symmetry \( C_1 \), although structure II is energetically considerably less favorable than I (one nitrogen possesses only six valence electrons) and is in poor agreement with the published NMR data which show hindered rotation around the N=N bond up to at least 120 °C. Symmetry \( C_1 \) had previously been chosen because the highest Raman frequency observed for either solid \( \text{N}_2\text{F}_3\text{AsF}_6^+ \) or \( \text{N}_2\text{F}_3\text{SbF}_6^+ \) occurred at about 1310 cm\(^{-1}\). Since this frequency is considerably lower than expected for an N=N bond, significant contributions from II were assumed. As can be seen from Figures 1, 2, and 3, the highest Raman band observed for all three \( \text{N}_2\text{F}_3^+ \) salts occurs at about 1520 cm\(^{-1}\), thus confirming the original assignment of the strong 1520-cm\(^{-1}\) infrared band to the N=N stretching mode and eliminating the basis for Qureshi and Aubke's reassignment. The previous failure to observe the 1520-cm\(^{-1}\) Raman band can be explained by its relatively low intensity and the low signal to noise ratio in the reported spectrum. Having established the identity of the N=N stretching mode, we can now proceed to test if the rest of the \( \text{N}_2\text{F}_3^+ \) spectrum is consistent with symmetry \( C_1 \). For \( \text{N}_2\text{F}_3^+ \) of \( C_1 \) symmetry, a total of nine fundamental vibrations is expected of which six belong to species \( \Lambda \), three belong to \( \Lambda' \), and one to \( \Lambda'' \). An approximate description of these nine modes is given in Table...

![Figure 1](image1.png)

**Figure 1.** Vibrational spectra of \( \text{N}_2\text{F}_3\text{SbF}_6^+ \). Trace A, infrared spectrum of the solid as an AgBr disk, the broken line being due to absorption by the window material; traces B and C, Raman spectrum of the solid recorded at two different recorder voltages with spectral slit widths of 3 and 8 cm\(^{-1}\), respectively; traces D II, Raman spectra of an HF solution recorded at different recorder voltages and spectral slit widths (5 and 8 cm\(^{-1}\)) with incident polarization parallel and perpendicular (p and dp stand for polarized and depolarized bands, respectively).

![Figure 2](image2.png)

**Figure 2.** Vibrational spectra of \( \text{N}_2\text{F}_3\text{AsF}_6^+ \). For explanation, see caption of Figure 1.

![Figure 3](image3.png)

**Figure 3.** Raman spectrum of solid \( \text{N}_2\text{F}_3\text{SbF}_6^+ \) recorded at two different recorder voltages.
Table I. Vibrational Spectra of N\textsubscript{2}F\textsubscript{3}, AsF\textsubscript{3}, and N\textsubscript{2}F\textsubscript{2}SbF\textsubscript{3}

<table>
<thead>
<tr>
<th>assignments for (N_2F_3) in point group (C_2)</th>
<th>solid freq, cm(^{-1}), and rel. int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1 + v_2 (A') = 2829)</td>
<td>2825 vz</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 2649)</td>
<td>2647 vz</td>
</tr>
<tr>
<td>(2v_1 (A') = 2614)</td>
<td>2608 wv</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 2447)</td>
<td>2443 vz</td>
</tr>
<tr>
<td>(v_1 + 2v_1 (A') = 2339)</td>
<td>2343 vz</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 2232)</td>
<td>2227 wz</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 2052)</td>
<td>2050 sh</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 1978)</td>
<td>1976 w</td>
</tr>
<tr>
<td>(2v_2 (A') = 1450)</td>
<td>1485 vz</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 1430)</td>
<td>1397 vz</td>
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<tr>
<td>(v_1 + v_2 (A') = 1417)</td>
<td>1443 m</td>
</tr>
<tr>
<td>(2v_1 (A') = 1342)</td>
<td>1310 vs</td>
</tr>
<tr>
<td>(v_1 (A') = 1240)</td>
<td>1127 vs</td>
</tr>
<tr>
<td>(v_1 + v_2 (A') = 1187)</td>
<td>1189 vz</td>
</tr>
<tr>
<td>(v_1 (A') = 1127)</td>
<td>1120 vz</td>
</tr>
<tr>
<td>(v_1 (A') = 1103)</td>
<td>1032 vs</td>
</tr>
<tr>
<td>(v_1 (A') = 994)</td>
<td>996 m</td>
</tr>
<tr>
<td>(v_1 (A') = 925)</td>
<td>925 s</td>
</tr>
<tr>
<td>(v_1 (A') = 775)</td>
<td>775 mw</td>
</tr>
<tr>
<td>(v_1 (A') = 670)</td>
<td>670 l</td>
</tr>
<tr>
<td>(v_1 (A') = 604)</td>
<td>604 (10)</td>
</tr>
<tr>
<td>(v_1 (A') = 572)</td>
<td>572 (3)</td>
</tr>
<tr>
<td>(v_1 (A') = 492)</td>
<td>492 (1)</td>
</tr>
<tr>
<td>(v_1 (A') = 310)</td>
<td>310 (0.5)</td>
</tr>
<tr>
<td>(v_1 (A') = 280)</td>
<td>280 (2.4)</td>
</tr>
</tbody>
</table>

\(a\) Uncorrected Raman intensities.

Table II. Vibrational Spectra of Solid \(N_2F_3\), \(N_2F_2SbF_3\), and Their Assignment in Point Group \(C_{2v}\)

<table>
<thead>
<tr>
<th>assignments</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1 (A'))</td>
<td>1519 (0.1)</td>
<td>1519 s</td>
</tr>
<tr>
<td>(v_2 (A'))</td>
<td>1520 (0.2)</td>
<td>1520 (0.2)</td>
</tr>
<tr>
<td>(v_1 (A') + v_2 (A'))</td>
<td>1524 (0.2)</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 2829)</td>
<td>2825 vz</td>
<td></td>
</tr>
<tr>
<td>(v_2 (A') = 2649)</td>
<td>2647 vz</td>
<td></td>
</tr>
<tr>
<td>(2v_1 (A') = 2614)</td>
<td>2608 wv</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 2447)</td>
<td>2443 vz</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 2339)</td>
<td>2343 vz</td>
<td></td>
</tr>
<tr>
<td>(v_2 (A') = 2232)</td>
<td>2227 wz</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 2052)</td>
<td>2050 sh</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 1978)</td>
<td>1976 w</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 1342)</td>
<td>1310 vs</td>
<td></td>
</tr>
<tr>
<td>(v_2 (A') = 1240)</td>
<td>1127 vs</td>
<td></td>
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<tr>
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<td>1189 vz</td>
<td></td>
</tr>
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<td>(v_1 (A') = 1127)</td>
<td>1120 vz</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 994)</td>
<td>996 m</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 925)</td>
<td>925 s</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 775)</td>
<td>775 mw</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 670)</td>
<td>670 l</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 604)</td>
<td>604 (10)</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 572)</td>
<td>572 (3)</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 492)</td>
<td>492 (1)</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 310)</td>
<td>310 (0.5)</td>
<td></td>
</tr>
<tr>
<td>(v_1 (A') = 280)</td>
<td>280 (2.4)</td>
<td></td>
</tr>
</tbody>
</table>

Table III. Fundamental Frequencies (cm\(^{-1}\)) of \(N_2F_3\) and Their Assignment in Point Group \(C_{2v}\)

<table>
<thead>
<tr>
<th>freq assignment</th>
<th>approx. description of mode</th>
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<tr>
<td>(1522)</td>
<td>(\Delta v)</td>
</tr>
<tr>
<td>(1307)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(1127)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(925)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(516)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(310)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(671)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(497)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>(344)</td>
<td>(\nu)</td>
</tr>
</tbody>
</table>

\(\beta\) = sym \(N_{2}F_{3}\) str, \(\beta\) = asym \(N_{2}F_{3}\) str, \(\alpha\) = sym \(N_{2}F_{3}\) str, \(\alpha\) = asym \(N_{2}F_{3}\) str.

III. All nine modes should be infrared and Raman active, with a possible exception being the torsional mode \(\nu_4\) which is expected to be of very low Raman intensity. The three \(A'^{\prime}\) modes should result in depolarized Raman bands.

As can be seen from Table III, three NF stretching modes are expected all belonging to species \(A'\) and occurring in the frequency range 900 - 1300 cm\(^{-1}\). There are three very intense infrared bands in this region (see Figures 1 and 2), all of which have Raman counterparts. Of the three predicted NF stretching modes, the symmetric NF\(_3\) stretch \(\nu_3\) is expected to have the highest Raman intensity and the lowest depolarization ratio and, therefore, is assigned to the band at about 925 cm\(^{-1}\). The reverse should hold true for the antisymmetric NF\(_3\) stretching mode \(\nu_5\) which, therefore, is assigned to the band at about 1310 cm\(^{-1}\). This leaves the assignment of the band at about 1127 cm\(^{-1}\) to the unique NF stretching mode \(\nu_6\), the frequency of which is similar to that of the NF stretch in \(N_2F_3\). For the assignment of the five deformation modes, the following five frequencies are available: 671, 516, 497, 344, and 310 cm\(^{-1}\). Of these, the 516- and 310-cm\(^{-1}\) bands are clearly polarized in the Raman spectra and therefore must represent the two remaining \(A''\) modes. By comparison with
Our low-temperature spectra (-70 to -90 °C) in either BrF₅ (see Figure 4) or acidified HF solutions were much better resolved than those obtainable for the SO₂ solution and thus permitted a more accurate determination of the three coupling constants. The A signal consisted of a sharp doublet of doublets with \( J_{AB} = 317 \) Hz, \( J_{AX} = 78 \) Hz, and a line width of about 8 Hz. The B signal was again a doublet of doublets with \( J_{AB} = 317 \) Hz and \( J_{BX} = 78 \) Hz, but with significantly broader lines (line width of about 60 Hz). The X signal was a sharp 1:2:1 (\( J = 78 \) Hz) triplet indicating very similar values of \( J_{AX} \) and \( J_{BX} \). Our observed coupling constants significantly differ from those \( J_{AB} = 379 \) Hz, \( J_{AX} = 81 \) Hz, \( J_{BX} = 45 \) Hz) previously reported for a poorly resolved spectrum.

Assignment of ABX to the three fluorines in N₃F₅⁺ can be made based on the following arguments. The two nitrogen atoms in N₃F₅⁺ are not equivalent. The one possessing only one fluorine ligand is centered in \( t \), and it looks more symmetric, thus making 'N quadrupole relaxation more effective and causing line broadening. Consequently, the broadened B signal is assigned to the unique fluorine. Since for the related FN=N=NF, CF≡NF, and substituted fluorotoluenes the cis coupling constants were found to be always significantly smaller than the trans ones, \( J_{AB} = 317 \) Hz should be trans and \( X = 78 \) Hz should be cis with respect to B. The resulting structure is shown in Figure 4. The observed coupling constants are similar to those observed for cis FN≡NF (\( J = 99 \) Hz) and trans FN≡NF (\( J = 322 \) Hz). ²³

X-ray Powder Data. The X-ray powder patterns of N₃F₅AsF₅ and N₃F₅SbF₄ are given as supplementary material. Young and Moy have reported the three strongest lines for N₃F₅AsF₅, and stated that the pattern can be indexed for a cubic unit cell with \( a = 10.8 \) Å. Although our data confirm the three previously reported lines, our observed pattern cannot be indexed based on the previously given unit-cell dimensions. In view of the nonspherical geometry of N₃F₅⁺, a relatively small cubic cell would be very surprising for N₃F₅AsF₅.

Acknowledgment. We are indebted to Drs. L. R. Grant and W. W. Wilson for helpful discussions and to Mr. B. D. Wilson for experimental help. This work was supported in part by the Office of Naval Research and the U.S. Army Research Office.

Registry No. N₃F₅SbF₄, 67326-70-5; N₃F₅AsF₅, 67326-71-6; N₃F₅, 12234-91-0; N₃F₅AsF₅, 12234-91-0.

Supplementary Material Available: Table IV, listing the observed X-ray powder diffraction patterns of N₃F₅AsF₅ and N₃F₅SbF₄ (1 page). Ordering information is given on any current masthead page.

References and Notes


**APPENDIX D**

**ESR SPECTRA OF THE $^{14}\text{Ne}^+$ AND $^{15}\text{Ne}^+$ RADICAL CATIONS**

**Electron Spin Resonance Spectra of the $^{14}\text{Ne}^+$ and $^{15}\text{Ne}^+$ Radical Cations**

I. B. GOLDBERG,* H. R. CROWE, and K. O. CHRISTIE

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The ESR spectra of the $^{14}\text{Ne}^+$ and $^{15}\text{Ne}^+$ radical cations were observed over the temperature range 15–340 K. The radical cations were generated either by a 3-irradiation of $\text{NeCl}_3$ salts or by low-temperature UV photolysis of $\text{NeCl}_3$. Lewis acid mixtures. For $^{15}\text{Ne}^+$, two different types of spectra were observed. At the lower temperatures, a highly anisotropic spectrum was observed which is attributed to $^{15}\text{Ne}^+$ of axial symmetry. An analysis of the observed spectra was carried out and was supported by computer simulations and the observed $^{15}\text{N}$ isotopic data. It was found that the previously reported value of the isotopic spin hyperfine splitting is incorrect. The resulting spin density distributions indicate that $^{15}\text{Ne}^+$ is pyramidal, but that within the isoelectronic series $\text{He}^+, \text{C}^+, \text{N}^+$, the planarity of the radicals increases from $\text{He}^+$ toward $^{15}\text{Ne}^+$.

**Introduction**

Radicals and radical ions formed from first-row elements have been the subject of numerous studies. These species provide experimental data by which molecular orbital models can be tested and also define limits within which properties of isoelectronic species can be predicted. Electron spin resonance (ESR) provides a useful technique for studying the structure of these radicals since the spin distribution in $s$ and $p$ orbitals can be determined from hyperfine splittings (hfs) and limits can often be set on the energies of excited states through the $g$ factors.

This study was prompted by the following observations: (a) During a recent study of the synthesis of $^{15}\text{Ne}^+$ salts, ESR spectra were obtained which were substantially different from those previously reported. The radicals exhibiting these spectra were stable up to 250 K, depending upon the particular anion. The ESR spectra recorded at higher temperatures could not be reconciled with the parameters previously given by Mishra et al. (b) On the basis of the known isotropic fluorine hyperfine splittings ($g_{iso}$) of isoelectronic BI, $^{17}\text{F}$ (17.8 MHz) and $^{19}\text{F}$ (14.35 MHz), the value of 16.7 MHz previously reported of $^{15}\text{Ne}^+$ appeared to be too high if a monotonic trend in the values for $g_{iso}$ is assumed for the isoelectronic series. Since the values of the hyperfine splittings can be used to determine the structure of these radicals, a reexamination of the previously given analysis of the ESR spectra seemed necessary. For this purpose, it was also found necessary to study the isoelectronic labeled $^{14}\text{Ne}^+$ to permit unambiguous assignment of the nitrogen hfs.

In this paper we report the ESR spectra of $^{14}\text{Ne}^+$ and $^{15}\text{Ne}^+$, including a study of their temperature dependencies and a revised analysis of the hyperfine splittings.

**Experimental Section**

**Synthesis of $^{14}\text{Ne}^+$ and $^{15}\text{Ne}^+$ Salts**

The low-temperature UV photolysis experiments of $\text{Ne}^+$ and mixtures were carried out in quartz containers as previously described. The $\text{NeCl}_3$ used in these experiments was prepared by glow discharge of $\text{Ne}, \text{HCl}$, and $\text{Ne}$-Isotope Chemicals and $\text{I}_2$ (Rockefeller) mixtures according to the method of Mayne. The samples of $\text{N}_2\text{H}_4\cdot \text{BF}_4^-$ and $\text{N}_2\text{H}_4\cdot \text{AsF}_6^-$, used for the $^{15}\text{N}$ illumination experiments were prepared by low-temperature UV photolysis in a quartz reactor using a previously described method. The samples of $\text{N}_2\text{H}_4\cdot \text{BF}_4^-$ antimonate were prepared by heating mixtures of $\text{N}_2\text{H}_4$, $\text{BF}_3$, and $\text{BF}_3$, at elevated pressures in a Monel cylinder. These salts were recrystallized from amine solutions to remove impurities.

**Irradiation.** $\text{N}_2\text{H}_4\cdot \text{BF}_4^-$ and $\text{N}_2\text{H}_4\cdot \text{AsF}_6^-$ salts were transferred to a dry nitrogen at atmospheric pressure in a 4-mm quartz tube (T. J. Scanlon Co., Solon, Calif) which was flame-sealed under vacuum. Typically, samples of 100 mg of $\text{N}_2\text{H}_4\cdot \text{BF}_4^-$ salts were used while only 15 mg samples of $\text{N}_2\text{H}_4\cdot \text{AsF}_6^-$ salts were available. Samples were exposed to UV light at various temperatures between 15 and 340 K.

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**Results**

**ESR Spectra.** During a recent ESR study of the UV photolysis of mixtures of $\text{N}_2\text{H}_4$, $\text{BF}_3$, and $\text{AsF}_6^-$, spectra similar to that shown in Figure 4a were observed at ca. 77 K. However, as shown in Figure 1 of ref 3, these spectra were very poorly resolved. These spectra, which were attributed to an immobile $^{15}\text{Ne}^+$ radical cation in a matrix, are expected to exhibit unique features (singularities) which correspond to the orientation of the threefold symmetry axis of the radical along directions parallel and perpendicular to the applied magnetic field. However, only the parallel component of the spectrum is clearly identifiable.

Upon warming of the matrix, the spectra began to change. The thermal stability of the observed ESR signals strongly depended upon the Lewis acid used. As $\text{AsF}_6^-$, the ESR signal became more intense about 130 K and appeared to be more isotropic. At 180 K, the signal started to lose intensity, and it decayed rapidly at 230 K. This loss of signal intensity can be attributed to the disappearance of the condensed $\text{AsF}_6^-$ phase. However, a relatively weak residual signal remained about 240 K which can be attributed to the $^{15}\text{Ne}^+$ trapped in the solid $\text{N}_2\text{H}_4\cdot \text{AsF}_6^-$ formed during the UV photolysis. For the more volatile $\text{BF}_4^-$, the change from the anisotropic low-temperature spectrum to the more isotropic higher temperature one occurred at about 117 K. At 140 K, the...
sharp line on either side of the similar spectra after signed to systems exhibited broad lines. It became evident that spectra observed for the plot to second order under conditions of Stick plot to second order of the line positions of the radical irradiated at (a) unable to resolve that dipolar interactions occurred between sample tetrafluorotetrate. Reducing kilightli, main resonance, that the lines exhibited a shoulder to N attributable to between several samples exhibited different spectra at high have been due to the anion; was not investigated if the anion, was not investigated. The origin of these signals, which may have been due to the anion, was not investigated. The annealed samples exhibited spectra at high and low temperatures. The low-temperature spectrum, observed between 10 and 140 K, was similar to that previously attributed to 1 and is shown in Figure 1 for irradiated NaAsF4 at 26 K. Other salts gave similar spectra, except that the lines exhibited a shoulder to the high field side of the main resonance. The line width of the spectrum increased slightly with longer irradiation times but was independent of temperature. Reducing the amount of Na, by warming the sample resulted in a narrower line. These observations suggest that dipolar interactions occurred between nearby defect sites. There is one difference between our spectra and that observed by Mishra et al., even in the more dilute solutions, we were unable to resolve some of the features which were attributed to the alignment of the C4 axis of the radical perpendicular to the magnetic field. We did, however, observe shoulders at these positions.

As the temperature of the arsenate and antimonate salts is increased to the range 140 and 235 K, the low-temperature spectrum collapses and then forms a sharper one with a narrower span. This spectrum is independent of temperature between 240 and 340 K, where decomposition begins, and is shown in Figure 3 for irradiated NaFAsF4 at 240 K. The lifetime of the species at room temperature is about 2 weeks but decreases to about 10 min at 340 K. Similar spectra were observed for the irradiated borate salts between about 270 and 320 K.

In order to be certain that the spectra reported here are due to NaF4+, isotopically pure 14NaFAsF4 and 15NaF4BF4 were prepared. The signal observed for the irradiated salts exhibited the same temperature dependence as those obtained for 19F+ salts. However, since only ca. 15 mg of 19F+ salts was prepared, longer irradiation times had to be used resulting in slightly broadened lines. The low-temperature spectrum of 19F4+ in 15NaFAsF4 is shown in Figure 2, where the 19F triplets are replaced by 14N doublets. The high-temperature 19F4+ spectrum is shown in Figure 4 and is analogous to the high-temperature 15F4+ spectrum.

**Discussion**

**Low-Temperature Spectra of 19F4+**. Several unusual features become apparent upon close inspection of the 19F4+ spectra at low temperatures. Most significantly, the distinct, intense features of the spectra must be assigned to the radical with its threefold symmetry (C3) axis aligned parallel to the applied magnetic field. Generally, however, the most intense features of the spectra of axially symmetric radicals in powders are assigned to the orientation in which the symmetry axis is perpendicular to the applied field. Since no such features are observed here, it is clear that this spectrum cannot be treated in the conventional manner used for axial or nearly axial symmetry.

A second feature is that the positions of the lines in the spectrum that correspond to the |1 orientation do not fall into the positions calculated from the hyperfine splittings (hfs...
Table 1. Hyperfine Splittings of $^{14}$NF, and $^{15}$NF, at High and Low Temperatures

<table>
<thead>
<tr>
<th></th>
<th>26 K</th>
<th>240 K</th>
<th>24 K</th>
<th>240 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ (i)</td>
<td>30.8 $^c$</td>
<td>2.00 $^c$</td>
<td>30.9 $^c$</td>
<td>2.40 $^c$</td>
</tr>
<tr>
<td>$\alpha$ (j)</td>
<td>13.3 $^c$</td>
<td>12.48 $^c$</td>
<td>13.8 $^c$</td>
<td>12.90 $^c$</td>
</tr>
<tr>
<td>$\delta$ (i)</td>
<td>11.49 $^c$</td>
<td>7.86 $^c$</td>
<td>16.08 $^c$</td>
<td>13.03 $^c$</td>
</tr>
<tr>
<td>$\delta$ (j)</td>
<td>8.1 $^c$</td>
<td>9.14 $^c$</td>
<td>8.78 $^c$</td>
<td>12.75 $^c$</td>
</tr>
<tr>
<td>$\gamma$ (i)</td>
<td>9.0 $^c$</td>
<td>9.0 $^c$</td>
<td>7.7 $^c$</td>
<td>12.4 $^c$</td>
</tr>
<tr>
<td>$\gamma$ (j)</td>
<td>2.003 $^c$</td>
<td>2.007 $^c$</td>
<td>2.003 $^c$</td>
<td>2.007 $^c$</td>
</tr>
</tbody>
</table>

$^a$ Hyperfine splittings are in mT ($1$ mT $= 10^3$). $^b$ The sign of the $^{14}$N hfs is assumed to be positive; thus $^{15}$N hfs are negative by virtue of their nuclear moments. $^c$ These are effective values based on supposed axial symmetry for individual tensors: $\alpha_{(i)} = 30.8$ mT and $\alpha_{(j)} = 13.3$ mT (see text).

Figure 3. (a) ESR spectra of $^{14}$NF, at 242 K in NaAlCl₃ irradiated at 77 K. (b) Computer simulation of spectrum assuming axial symmetry and the parameters given in Table 1.

which are given in Table 1. These values are calculated from the expression above. For a system which exhibits a large hfs with axial symmetry, the field positions in which the unique axis is parallel to the magnetic field, $H_{||}$, are given by eq 1 to second order, where $g(\parallel)$, $g(\perp)$, and $g(\perp)$ are the parallel and perpendicular g factors and hfs, respectively. $H_{||}$ is given by $h/2\mu_B I$, $I$ is the total nuclear spin, and $M_I$ is the component of spin parallel to the magnetic field. The analogous equation for $H_{\perp}$ is given by eq 2.

$$H_{||} \approx \frac{1}{2} g(\parallel) M_I$$

$$H_{\perp} \approx \frac{1}{2} g(\perp) M_I$$

are the parallel and perpendicular g factors and hfs, respectively. $H_{||}$ is given by $h/2\mu_B I$, $I$ is the total nuclear spin, and $M_I$ is the component of spin parallel to the magnetic field. The analogous equation for $H_{\perp}$ is given by eq 2.

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$$H_{||} \approx \frac{1}{2} g(\parallel) M_I$$

$$H_{\perp} \approx \frac{1}{2} g(\perp) M_I$$

where $H_{||}$ is given by $h/2\mu_B I$. Field positions are plotted on the same scale, too, under the spectrum in Figure 4b, for the molecule oriented || and \perp to the field. Second-order shifts are only significant for $^{14}$NF, when the field is \perp to the $C_2$ axis of the radical. Note that for the || orientation, while the lines corresponding to $M(F) = \pm 1$ and $\pm 3$ are shifted away from the center of the spectrum.

A final complication in the interpretation of this spectrum is that there are several extra lines present which cannot be explained in the conventional analysis assuming axial symmetry. Similar features were observed in spectra of $^{14}$NF which were explained by the fact that, while the hyperfine tensors of each of the fluorine atoms are equivalent, they are not mutually parallel. This causes the axial component of the tensor to be at an angle of $180^\circ$ with respect to the $C_2$ axis. As a result, singularities in the spectrum appear which correspond to orientations of the radical with respect to the applied field which are other than parallel or perpendicular.

In the spectrum of $^{15}$NF, there are sets of lines which correspond to either the parallel or the perpendicular orientation. However, these do not occur in the positions expected from the values of the hfs. Because $\alpha_{(i)} > \alpha_{(j)}$, the lines $M(F) = \pm 1$, which correspond to parallel alignment, are shifted closer to the center of the spectrum, while those of...
The spectrum of \( \text{NF}_3^+ \) is more complicated because of the added anisotropy of the \( \text{N}^+ \) hfs. Here the nitrogen hyperfine tensor will determine the positions of the singularity of the spectrum. As a result, the treatment given by Maruani et al. for \( \text{CF}_3^+ \) needs to be modified. We report here, effective values for the hyperfine tensor, determined from the extrema of the spectra. In units of \( gT \), \( a_\| = 30.8, a_\perp = 3.8, a_\perp = 11.49 \) and \( a_\perp = 7.8 \). In contrast, Mishra et al. report \( a_\| = 30.0, a_\perp = 10.0, a_\perp = 11.3 \) and \( a_\perp = 9.0 \). The stick plot representing this analysis is shown in Figure 1b,c for the parallel and perpendicular orientations, respectively. The analysis of the parallel orientation is in agreement with the previous assignment; however, there is substantial difference between our analysis of the perpendicular orientation and the previous one, shown in Figure 1d. The analysis of the perpendicular components depends upon which features are selected. Since these features are buried within the spectrum and since extra lines appear, this assignment is indeed difficult. However, because of the large value of \( a_\perp \), there are downshifted fields of \( 1.5 \) mT due to second-order effects. Therefore, the features corresponding to the perpendicular orientation are those which are asymmetric with respect to the center of the spectrum, after allowing for the second-order splittings of the \( M_\| = 1/2 \) lines. Furthermore, the features that we have selected are consistent with the analyses of high-temperature spectra as well as those derived from the \( \text{NF}_3^+ \) spectra.

Low-Temperature Spectra of \( \text{NF}_3^+ \). In order to confirm the analysis of the \( \text{NF}_3^+ \) spectra, samples of isotopically pure \( \text{NF}_3^+ \) salts were prepared. Since only 15 mg of sample was available, long irradiation times were used to get the spectra. In units of \( gT \), the effective values moments of inertia between 235 and 340 K include \( K = 9.36 \), \( a_\perp = 8.70 \) and \( a_\perp = 12.48 \), and \( a_\perp = 200 \). These values are independent of temperature between 235 and 340 K.

High-Temperature Spectra of \( \text{NF}_3^+ \). In order to confirm the assignment of the \( \text{NF}_3^+ \) spectra, spectra of a \( \gamma \)-irradiated sample of \( \text{NF}_3^+ \), were obtained (Figure 4). These spectra can be analyzed in terms of one \( \text{N}^+ \) atom \( (l = 1/2) \) and the equivalent \( \text{F}^- \) atoms \( (l = 1/2) \). The hyperfine splittings are given in Table I. The \( \text{NF}_3^+ \)-containing samples exhibited the same thermal stability as the \( \text{NF}_3^+ \)-containing samples described above.

Comparison of High- and Low-Temperature Spectra. The g factors and hyperfine splittings of the different \( \text{NF}_3^+ \) ESR spectra are given in Table I. They are all due to \( \text{NF}_3^+ \). is established by the following observations: spectra of the irradiated \( \text{N} \) and \( \text{N}^+ \) salts contain nuclei of the correct spins and numbers; fluorine atom hfs of \( \text{NF}_3^+ \) and \( \text{NF}_3^+ \) are equal at high and low temperatures, respectively, while the respective \( \text{N} \) atom hfs are in the correct ratio of their nuclear moments; high-temperature spectra reversely change into the low-temperature spectra, which are less intense; computed values of the isotopic hfs are the same in high- and low-temperature spectra; provided that the sign of \( a_\perp \) at low temperature is taken as negative.

The reason for the difference between the high-temperature and the low-temperature spectra is probably due to temperature-dependent rotation of \( \text{NF}_3^+ \) about a single axis. Spectra of \( \text{CF}_3^+ \) in a 1:30 CF:KBr matrix change from a characteristic of a stationary radical to one characteristic of a freely rotating radical, as the temperature is increased from 4.2 to 35 K. Examples in which similar changes occur between 77 and 300 K include \( \text{NH}_3^+ \) and \( \text{ND}_3^+ \), in their respective ammonium perchlorates and \( \text{PF}_6^- \), in \( \text{KPF}_6 \). The average \( \text{hfs} \) and axes for \( \text{NH}_3^+ \) and \( \text{ND}_3^+ \) as \( \text{PF}_6^- \) were attributed to rotations of these radical ions.

As the temperature of the \( \text{NF}_3^+ \)-containing samples is increased, the spectra change between two different anisotropies. At low temperatures, the spectra are indicative of motionless \( \text{NF}_3^+ \), while at high temperatures, the spectra are indicative of uniaxial rotation. Most likely, this rotation occurs about an axis close to that of its minimum moment of inertia and is probably accompanied by some librational X-ray studies on \( \text{NF}_3^+ \) and Lewis acid condensed phases are similar to those in the nitrogen hfs. As the temperature is increased, the average \( \text{hfs} \) and axes for the \( \text{NH}_3^+ \) and \( \text{ND}_3^+ \) as \( \text{PF}_6^- \) were attributed to rotations of these radical ions. Inversion of the radical about the nitrogen would be expected to result in more nearly complete averaging.

Supporting evidence for rotation of \( \text{NF}_3^+ \) is provided by the fact that the \( a_\perp \) values observed for \( \text{NF}_3^+ \) and \( \text{NF}_3^+ \) are not identical. Since \( \text{NF}_3^+ \) has a pyramidal structure (see below), the moments of inertia of \( \text{NF}_3^+ \) and \( \text{NF}_3^+ \) must be different. This causes their rotational axes to be different, resulting in different \( a_\perp \) values.

UV-photolyzed mixtures of \( \text{NF}_3 \), \( \text{BF}_3 \), and Lewis acid at low temperatures exhibited spectra which were similar to that of Figure 1, except that the lines were broader. The line width increased slightly with longer photolysis, while the intensity increased. The higher temperature spectra (see for example Figure 1) can be interpreted in terms of the high symmetry parameters of the \( \text{NF}_3^+ \) spectrum observed for the \( \gamma \)-irradiated salts (see Figure 3), although the line widths are quite different. For the photolyzed samples, the transition between the low and higher temperature spectra occurred at much lower temperatures than the \( \gamma \)-irradiated salts and the thermal stability of the radical depended upon the volatility of the Lewis acid used (see Results section). This suggests that these radicals are associated with solid \( \text{AsF}_3 \), or \( \text{BF}_3 \). The weaker residual signals observed after complete evaporation of the \( \text{NF}_3 \) Lewis acid condensed phases are similar to those in the \( \gamma \)-irradiated \( \text{NF}_3 \) salts. This suggests that they are due to \( \text{NF}_3^+ \) trapped in small amounts of \( \text{NF}_3 \) salts formed during the photolysis.
cannot be accurately determined. The value of $\rho^0/\rho^s$ for $\text{CF}_2$ is 2.9, while that of $\text{NF}_2$ is 4.1. This suggests that the free electron in $\text{NF}_2$ has more p character than that in $\text{CF}_2$. This in turn suggests that the hybridization of the XF bonds in $\text{CF}_2$ is nearly sp$^3$ but that in $\text{NF}_2$ is between sp$^3$ and sp$^2$. This in turn indicates that $\text{NF}_2^*$ is more planar than $\text{CF}_2$, in contrast to the conclusion of Mishra et al. This is further supported by the fact that the observed anisotropy in the fluorine hfs is greater for $\text{NF}_2^*$ than for $\text{CF}_2$. Recent theoretical calculations based on the isotropic hfs of $\text{BF}_2^*$, $\text{CF}_2^*$, and $\text{NF}_2^*$ also indicate that the planarity increases from $\text{BF}_2^*$ toward $\text{NF}_2^*$. The same conclusions are reached if the values of $\alpha_0^0$ and $\beta_0^0$ reported by Hurst and Coodin are used. These values are approximately 15% larger than those used here, so that smaller spin densities are computed. Although these absolute values appear more realistic, they leave the ratios of $\rho^0/\rho^s$ unchanged.

The spin densities of $\text{NF}_2^*$ and $\text{CF}_2^*$ are also compared in Table III. The spin density distribution for $\text{NF}_2^*$ is calculated from the ESR data of Kasat and Whipple and the data from the isotropic hfs of Farmer et al. Values in mT$^2$ are $\alpha_0(\parallel) = 4.9$, $\alpha_0(\perp) = 0.4$, $\alpha_0(\perp) = 2.1$, and $\alpha_0(\perp) = 16.9$. In $\text{Ni}^+$, the unpaired electron is primarily in a p orbital so that there is no delocalization of the unpaired electron into the orbital of the lone pair on nitrogen. Thus, the structure of this radical is surprisingly different from that of $\text{Ni}^2^*$. Work is underway to analyze, in detail, the hyperfine splittings of the $\text{Ni}^2^*$ radical and determine the angle between the nitrogen and fluorine hyperfine tensors. In the $\text{CF}_2^*$ radical, a $\chi$ was found to be 17.9(3) Efdul et al. reported that the direction of the hfs was not perpendicular to the C1 bond, but at an angle of 54$^\circ$ to it. A precise analysis of the low-temperature spectrum of $\text{Ni}^2^*$ may substantiate the above conclusions. Since the $\text{Ni}^2^*$ radical is slightly more planar, $\alpha$ for $\text{Ni}^2^*$ may be different from that of $\text{CF}_2^*$.

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Registry No. $^{14}\text{NF}_2^*$, 13106-70-4; $^{15}\text{NF}_2^*$, 67724-5-8.

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(18) N. D. Chasten, personal communication.
(26) D. Lind, personal communication.
APPENDIX E

FORMATION AND DECOMPOSITION MECHANISM OF NF₄⁺ SALTS

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KARL O. CHRISTE, RICHARD D. WILSON, and IRA B. GOLDBERG

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The thermal decompositions of NF₄BF₄ and NF₄AsF₆ were studied in a sapphire reactor at different temperatures by total-pressure measurements. It was found that the rates, previously reported by Solomon and co-workers for NF₄AsF₆, significantly differ from those of the present investigation, although both studies result in a 1/2 reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies: $E_{NF₄BF₄} = 36.6 \pm 0.8 \text{ kcal mol}^{-1}$ and $E_{NF₄AsF₆} = 44.7 \pm 4.2 \text{ kcal mol}^{-1}$. The suppression of the decomposition rates by NF₃, F₂, and BF₃ or AsF₅ was measured. A critical evaluation of all experimental data available on the NF₄⁺ salt formation and decomposition suggests the following reversible reaction mechanism:

$$\text{F}_2 + 2\text{F} + \text{NF}_3 \rightleftharpoons \text{NF}_4^+ + \text{F}_2$$

A Born Haber cycle calculated for NF₄BF₄ shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF₄SbF₆ at 250 °C was also studied.

Introduction

The formation and decomposition reactions of NF₄⁺ salts are of significant theoretical and practical interest. From a theoretical point of view, the question arises as to whether NF₄⁺ or NF₃ is produced as an unstable intermediate. This would be highly unusual because second-row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decomp-
Formation and Decomposition of \( \text{NF}_4^+ \) Salts

is necessary in order to improve on existing synthetic methods. Several mechanisms have previously been postulated for the formation of \( \text{NF}_4^+ \) salts. In 1966, Christie and co-workers suggested in their original reports on the synthesis of \( \text{NF}_4\text{AsF}_6 \) by low-temperature glow discharge that either \( \text{NF}_4^+ \) or \( \text{F}^+ \) (or \( \text{F}_2^+ \)) is generated in the discharge. These radical cations could then react with either \( \text{F}_2 \) or \( \text{NF}_4 \) to yield \( \text{NF}_4^+ \). In 1972, Solomon and co-workers reported\(^1\) the results from a kinetic study of the thermal decomposition of \( \text{NF}_4\text{AsF}_6 \) in Monel. Based on total pressure measurements, their conclusion was that the decomposition involved the equilibrium dissociation step

\[
\text{NF}_4\text{AsF}_6 \rightarrow \text{NF}_4^+ + \text{AsF}_6^-. \]

followed by irreversible decomposition of the unstable \( \text{NF}_4^+ \).

\[
\text{NF}_4^+ \rightarrow \text{NF}_4 + \text{F}_2. \]

The latter step was taken to be a 1/2-order reaction. From the temperature dependence of the kinetic constants, a value of 41 kcal mol\(^{-1}\) was obtained for the sum of the overall heat of sublimation and the activation energy for the decomposition of \( \text{NF}_4\text{AsF}_6 \) in 1973. Christie and co-workers proposed\(^4\) an alternate mechanism for the formation of \( \text{NF}_4^+ \) salts. This mechanism accounted for the fact that \( \text{NF}_4^+ \) salts can be synthesized by UV photolysis. It involved the steps

\[
\text{F}_2 \rightarrow 2\text{F} \quad \text{F} + \text{AsF}_6 \rightarrow \text{AsF}_5 + \text{NF}_4 \quad \text{NF}_4^+ + \text{AsF}_5 \rightarrow \text{F}_2 + \text{F} \quad \text{AsF}_5 + \text{F}_2 \rightarrow \text{AsF}_6 + \text{NF}_4. \]

Part of this mechanism was later experimentally confirmed by ESR studies\(^5\) which showed that the \( \text{NF}_4^+ \) radical cation is indeed formed as an intermediate in both the low-temperature UV photolysis and the γ-irradiation-induced decomposition of \( \text{NF}_4^+ \) salts.

Since the observation of \( \text{NF}_4^+ \) as an intermediate\(^6\) is incompatible with the mechanism proposed\(^1\) by Solomon and since at elevated temperatures metal reactors rapidly absorb \( \text{F}_2 \), Lewis acid mixtures, a reinvestigation of the thermal decomposition of \( \text{NF}_4\text{AsF}_6 \), in an inert sapphire reactor was undertaken. In particular, a more detailed investigation of the suppression effects of \( \text{F}_2 \), \( \text{F}_4 \), and \( \text{AsF}_6 \) was expected to yield valuable information. Furthermore, no quantitative data had previously been available on the decomposition rates of \( \text{NF}_4\text{BF}_4 \) and the formation rates of \( \text{NF}_4\text{SBF}_4 \).

Experimental Section

Thermal Decomposition Studies. The samples of \( \text{NF}_4\text{BF}_4 \) and \( \text{NF}_4\text{AsF}_6 \) were prepared as previously described and showed no detectable impurities. All decomposition experiments were carried out in a sapphire reactor (Tecnova Co.). The reactor was connected by a Swagelok compression fitting, containing a Teflon front ferrule, to a stainless steel valve and a pressure transducer (Validyne). Model DP7. 0 1000 mm Hg, the output of which was recorded on a strip chart. The reactor had a volume of 38.7 ml and was heated by immersion into a constant-temperature (±0.05 °C) circulating oil bath. The reactor was passivated at 250 °C with \( \text{BF}_3 \) or \( \text{F}_2 \). AsF₆ mixtures until the pressure remained constant over a period of several days, and weighed amounts of \( \text{NF}_4^+ \) salts were added in the dry nitrogen atmosphere of a glovebox. After immersion of the reactor into the hot oil bath, the reactor was evacuated, and the pressure change was monitored as a function of time. Control experiments were carried out at the beginning and end of each series of measurements to ascertain that the rate did not significantly change during each series. The composition of the gaseous decomposition products was shown by chemical analysis, infrared spectroscopy, and gas chromatography to be \( \text{BF}_3 \), \( \text{F}_2 \), and the corresponding Lewis acid. For the curve fitting of the kinetic data the method of linear least squares was used with the listed uncertainties being 2σ of the calculated slope.

Formation of \( \text{NF}_4\text{SBF}_4 \). Because of the high corrosion of high-pressure \( \text{NF}_4 \), \( \text{F}_2 \), \( \text{SBF}_4 \) mixtures at elevated temperatures, the \( \text{NF}_4 \), \( \text{F}_2 \), \( \text{SBF}_4 \) reaction system could not be monitored directly with a pressure transducer or gauge. Consequently, more detailed investigations of the high-corrosion reaction were necessary. Monel cylinders were each loaded with 50 mmol of \( \text{SBF}_4 \), and a twofold excess of \( \text{NF}_4 \) and \( \text{F}_2 \) was added. The cylinders were simultaneously placed into an oven preheated to 250 °C and were removed separately from the oven after certain time intervals. After the cylinders were cooled, all material volatilized at 25 °C was pumped off, and the amount of \( \text{NF}_4^+ \) salt formed was determined by the observed weight increase and spectroscopic analyses.

Results and Discussion

Thermal Decomposition of \( \text{NF}_4\text{BF}_4 \) and \( \text{NF}_4\text{AsF}_6 \). The thermal decomposition of \( \text{NF}_4\text{BF}_4 \) and \( \text{NF}_4\text{AsF}_6 \) in a constant-volume reactor was studied by total-pressure measurements over a temperature range of about 35 °C for each compound. Since screening experiments had shown that even well-passivated nickel or Monel reactors rapidly reacted with gases, this latter step was taken to follow. However, the addition of \( \text{BF}_4 \) or \( \text{AsF}_6 \), a monochloride reactor was used. This reactor was found to be completely inert toward these gas mixtures over extended time periods. Furthermore, it was found that the decomposition rates increased with increasing sample size. The rates did not increase linearly with the sample size because the increased pressure enhances the suppression of the rates (see below). In order to minimize the effect of changes in the sample size during a given series of experiments, we used the largest feasible samples and the smallest available reactor volume. In this manner, only a small percentage of the sample was decomposed in a given series of experiments. The first and the last experiment of each series were carried out under identical conditions and showed that the change in rate due to the small, but inevitable, sample-size change was indeed negligible.

The results of our measurements on \( \text{NF}_4\text{BF}_4 \) and \( \text{NF}_4\text{AsF}_6 \) are summarized in Tables I and II. In agreement with the previous report\(^1\) on the thermal decomposition of \( \text{NF}_4\text{AsF}_6 \), smooth decomposition curves were obtained. The decomposition rates steadily decreased with increasing pressure in the reactor and the initial rates were restored upon evacuation of the reactor, indicating that the decomposition products suppress the decomposition rates. This was confirmed by studying the influence of different gases on the decomposition rates of \( \text{NF}_4\text{BF}_4 \) and \( \text{NF}_4\text{AsF}_6 \). The addition of \( \text{He} \) did not noticeably influence the rates, whereas \( \text{F}_2 \) and \( \text{NF}_4 \) resulted in a weak suppression. However, the addition of \( \text{BF}_4 \) to \( \text{NF}_4\text{BF}_4 \) or of \( \text{AsF}_6 \) to \( \text{NF}_4\text{AsF}_6 \) resulted in strong rate suppressions (see Tables I and II).

For all decomposition experiments, plots of \( \text{P}^1 \) vs. time resulted in straight lines (see Figures 1 and 2) indicating a 1/2 reaction order. The resulting global kinetic constants are given in Table III. Arrhenius plots of these constants resulted in straight lines (see Figure 3) and in the global decomposition activation energies \( E_{\text{act}} = 36.6 \pm 0.8 \text{ kcal mol}^{-1} \) and \( E_{\text{act}} = 44.7 \pm 4.2 \text{ kcal mol}^{-1} \), the latter value being in good agreement with that of 41 kcal mol\(^{-1}\) previously reported.\(^1\)

The fact that the small mole fraction ranges of sample decomposition studied in these experiments were truly representative for the overall decomposition rates was established by following the decomposition of small samples at somewhat higher temperatures over almost the entire mole fraction (α) range. A typical decomposition curve obtained for \( \text{NF}_4\text{BF}_4 \) at 253 °C (see Figure 4) does not exhibit any sigmoid character, and the \( \text{P}^1 \) vs. time plot is linear for about the first 25% of α.

Although the results previously reported\(^1\) for the decomposition of \( \text{NF}_4\text{AsF}_6 \), in Monel resulted in a linear \( \text{P}^1 \) vs. time plot, the reported rates were higher than ours by a factor of

RI/RD80-157

E-2
Table 1. Thermal Decomposition of NF₄BF₄ in a Sapphire Reactor

<table>
<thead>
<tr>
<th>Time, h</th>
<th>He (500°C)</th>
<th>E₂ (500°C)</th>
<th>NF₄⁺ (500°C)</th>
<th>BJ₄⁺ (500°C)</th>
<th>197°C</th>
<th>204°C</th>
<th>213°C</th>
<th>215°C</th>
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<td>300</td>
<td>277</td>
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</tbody>
</table>

$a$ Sample size 2.65 g. $b$ Reactor volume 38.3 mL. $c$ The values given in parentheses indicate the pressure in mmHg of the added gas at the beginning of each experiment.

...about 7. Unfortunately the sample size and the exact reactor volume used in ref 3 were not given. However, the estimated reactor volume (100 cm³ Monel cylinder + Wallace-Tierman...
Formation and Decomposition of NF_2* Salts

**Table II. Thermal Decomposition of Ni₂,AsF₅ in a Sapphire Reactor**

<table>
<thead>
<tr>
<th>time, h</th>
<th>200°C</th>
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<td>23.6</td>
<td>136.2</td>
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</tr>
</tbody>
</table>

*Sample rate 1.86 g. * Reactor volume 38.7 mL. * The values given in parentheses indicate the pressure (mmHg) of the added gas at the beginning of each experiment.

**Table III. Global Kinetic Constants** for the Thermal Decomposition of Ni₂,BrF₅ and Ni₂,AsF₅

<table>
<thead>
<tr>
<th>temp., °C</th>
<th>Ni₂,BrF₅</th>
<th>Ni₂,AsF₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>182.2</td>
<td>0.96 ± 0.01</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>188.9</td>
<td>1.74 ± 0.02</td>
<td>0.33 ± 0.01</td>
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<tr>
<td>190.8</td>
<td>2.11 ± 0.02</td>
<td>0.33 ± 0.01</td>
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<td>197.4</td>
<td>3.39 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>204</td>
<td>6.08 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>213.3</td>
<td>12.79 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>275</td>
<td>14.68 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>190.8 (He)</td>
<td>2.29 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>190.8 (NF₃)</td>
<td>1.86 ± 0.04</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>190.8 (N₂)</td>
<td>1.92 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>190.8 (BF₃)</td>
<td>0.314 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
</tbody>
</table>

* Units mol⁻¹ L · mol⁻¹ s⁻¹ ±error limits 2σ

smaller than those of our experiments. This should have resulted in rates lower than ours. The only possible explanations for the previously reported higher rates are absorption of the suppressing AsF₅ by Monel and/or inaccurate temperature control (heating of the cylinder in a tube furnace).

A large discrepancy of ~ 10° exists between the previously reported results and our kinetic constants (see Table III). Most of this discrepancy (~ 10°) appears to be computational.

Furthermore, the previously reported data for the suppression by AsF₅ are inconsistent. Whereas the experimental data in Tables 6 and 7 of ref 3 show strong rate suppression by AsF₅, the kinetic constants given in Table 8 of ref 3 imply only mild suppression by AsF₅. The previously reported strong rate suppression by Ni₁ could not be confirmed by the present study. Our data (see Table III) show that Ni₂F₅ is only a weak suppressor, comparable to L₃, and that AsF₅ or BF₃ is the only strong suppressor. This is an important observation, because the alleged strong suppression by Ni₂F₅ had caused us to propose in a previous publication a mechanism for the formation of Ni₂,AsF₅ involving the incorrect (see below) steps F + AsF₅ → Ni₂,AsF₅ and AsF₅ + Ni₂ → Ni₂,AsF₅ + NF₃.

**Thermal Synthesis of NF₂·BrF₅**. Whereas the thermal synthesis of NF₂·AsF₅ proceeds at too slow a rate for practical kinetic measurements, the rate of formation of NF₂·BrF₅ is sufficiently fast. However, BrF₅ tends to form poly-

**Figure 5. Formation rate of Ni₂,Sbf₅ from NF₂, F₂, and Sbf₅ at 250°C**

**Table IV. Conversion of Ni₂, BrF₅ to Ni₂, Sbf₅ at 250°C**

<table>
<thead>
<tr>
<th>prod compn.</th>
<th>conv of Ni₂, Sbf₅, to Ni₂, Sbf₅,</th>
<th>react. time, h</th>
</tr>
</thead>
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<td>1</td>
<td>1.00 ± 0.00</td>
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<td>0.89 ± 0.00</td>
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<td>4</td>
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<td>62.9</td>
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<td>5</td>
<td>0.59 ± 0.00</td>
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<tr>
<td>7</td>
<td>0.31 ± 0.00</td>
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<tr>
<td>8</td>
<td>0.10 ± 0.00</td>
<td>90.4</td>
</tr>
<tr>
<td>9</td>
<td>0.06 ± 0.00</td>
<td>95.0</td>
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</table>

* Mole ratio of starting materials Ni₂, BrF₅, and Sbf₅. Starting pressure 110 atm. residual pressure calculated for 100% conversion to Ni₂, Sbf₅, 44 atm. The Monel cylinders (95-mL volume) were placed horizontally in the oven, preheated to 250°C. One hour was required until the cylinders reached 250°C. This point was taken as zero reaction time.
about 110 atm to determine its formation rate. The results are summarized in Table IV and Figure 5 and show that at this temperature the initial formation rate of NEF₂⁺ salts is surprisingly rapid. The subsequent slow-down of the reaction is probably caused by a lowering of the SBF₃ partial pressure in the system due to the formation of polyantimonate anions. Their thermal dissociation equilibria to SBF₃ and SBF₄ will then control the SBF₃ pressure in the system and become the rate-limiting step.

**Reaction Mechanism.** As pointed out in the Introduction, the formation and decomposition mechanism of NEF₂⁺ salts is of great interest because it appears to involve an unusual hypervalent species such as NEF₂⁺, NEF₃⁺, AsF₅⁺, or BF₄⁻. The following experimental data are known, and the correct mechanism must be compatible with all of these conditions.

1. Certain NEF₂⁺ salts, such as NEF₂SBF₃ and NEF₂AsF₅⁺, can, depending upon the system pressure, be either formed or decomposed at the same temperature. This implies pressure-dependent equilibria and reversibility of the formation and decomposition reactions.

2. ESR measurements have shown that the NEF₂⁺ radical cation is a crucial intermediate in both the low-temperature UV photolytic synthesis and γ-irradiation-induced decomposition of NEF₂⁺ salts. Furthermore, the fluorination of NEF₂⁺ to NEF₄⁺ appears to require F atoms.

3. In the thermal decomposition of either NEF₂BF₄ or NEF₂AsF₅⁺, BF₄⁻ or AsF₅⁺ acts as a strong rate suppressor, whereas both NEF₄⁺ and F⁻ suppress the decomposition rates only mildly (see above results).

4. Filtered UV radiation or heating to 120 °C supplies sufficient activation energy for the formation of NEF₂⁺ salts. This is a strong indication that the first step in the synthesis must be the dissociation of F⁻ into two fluoride atoms (IP(F⁻) = 36.8 kcal mol⁻¹).

5. The tendency for NEF₂⁺ salts by thermal activation strongly decreases with decreasing Lewis acid strength, i.e., SBF₃ > AsF₅⁺ > PF₅ > BF₄⁻. Since the corresponding NEF₂⁺ salts all possess sufficient thermal stability, a mechanism involving the initial formation of NEF₂⁺ followed by its reaction with the corresponding Lewis acid, cannot explain the lack of thermal formation of salts such as NEF₂PF₅ or NEF₂BF₄. It can be explained, however, by the formation of intermediates of lower thermal stability such as NEF₂⁺ salts. For SBF₃ or AsF₅⁺, these NEF₂⁺ salts were shown to still possess the lifetime required for their efficient conversion to NEF₂⁺ salts, whereas NEF₂⁺BF₄⁻ was found to be of considerably lower thermal stability.

6. ESR flow tube experiments gave no indication of interaction between F atoms and NEF₂⁺ as expected for the reaction step AsF₅⁺ + F⁻ → AsF₆⁺.

7. Infrared matrix isolation studies of the thermolysis products from either NEF₂AsF₅⁺ or (NEF₂⁺)NEF₂⁺ gave no evidence for the formation of NEF₂⁺.

8. Lewis acids such as BF₅, PF₅, AsF₅⁺, or SBF₃ do not form stable adducts with NEF₂⁺, even at low temperatures.

Since NEF₂⁺, P, and I have ionization potentials of 13.0 eV, 15.6 eV, and 17.4 eV, respectively, any mechanism involving the initial formation of either NEF₂⁺, P, or I can be ruled out, based on condition 4. This leaves us with Schemes I–IV as possibilities.

**Scheme I**

\[ \text{NEF}_2 + \text{AsF}_5^+ \rightarrow \text{NEF}_2\text{AsF}_5^+ \]

**Scheme II**

\[ \text{NEF}_2^+ + \text{AsF}_5 \rightarrow \text{NEF}_2\text{AsF}_5^+ \]

**Scheme III**

\[ \text{NEF}_2^+ + \text{AsF}_5 \rightarrow \text{NEF}_2\text{AsF}_5^+ \]

**Scheme IV**

\[ \text{NEF}_2^+ + \text{AsF}_5 \rightarrow \text{NEF}_2\text{AsF}_5^+ \]

Scheme I can be ruled out because it does not comply with conditions 8 and 3. In Scheme I, NEF₂⁺ would be expected to suppress as strongly as AsF₅⁺. Scheme II can be eliminated because of the fact that it violates condition 3 (i.e., NEF₂⁺ should be a stronger suppressor than AsF₅⁺). This implies that condition 6. Scheme III is unacceptable because it does not comply with conditions 2 and 5. Scheme IV is the only mechanism which agrees with all experimental data and therefore is our preferred mechanism. This mechanism differs from all the mechanisms previously proposed. It appears to be generally applicable to NEF₂⁺ salts, except for certain decomposition reactions in which NEF₂⁺ oxidatively fluorinates the anion.

In view of the rather complex mechanism of Scheme IV and the observed fractional reaction order for the decomposition process, a mathematical analysis of the kinetic data was too complex and beyond the scope of the present study.

**Borb Haber Cycle for NEF₂BF₄.** It was of interest to examine the thermodynamic soundness of Scheme IV. NEF₂BF₄ was chosen for this purpose because it is the only NEF₂⁺ salt for which the heat of formation has experimentally been determined. The Borb Haber cycle is shown in Scheme V, where all heats of formation or reaction are given in kcal mol⁻¹ from the known heats of reaction of NEF₂⁺BF₄⁻ and NEF₂BF₄. The heat of reaction 5 is known to be 34.8 kcal mol⁻¹. Furthermore, the heat of dissociation of F⁻ reaction 1, is known to be 36.8 kcal mol⁻¹. A reasonably close estimate for step 3, the heat of formation of solid NEF₂⁺BF₄ from NEF₂⁺ and BF₄⁻, can be made from the known heat of dissociation of NEF₂⁺BF₄. Since NEF₂⁺ and BF₄⁻ are expected to be quite similar (see below), it is reasonable to assume that step 3 has a heat of reaction similar to that of NEF₂⁺ + BF₄⁻ = NEF₂⁺BF₄⁻. Consequently, the sum of steps 2 and 4 should be about 53 kcal mol⁻¹. Whereas the heat of reaction of step 2 is difficult to estimate, the heat of

**Scheme V**

\[ \text{NEF}_2^+ + \text{AsF}_5 \rightarrow \text{NEF}_2\text{AsF}_5^+ \]

(See above)
Formation and Decomposition of NF₄⁺ Salts

reaction of (4) is easier to estimate because it represents the dissociation energy of the fourth N-F bond in NF₄⁺. In NF₄⁺, the heat of dissociation of the third N-F bond is 58 kcal mol⁻¹.²²⁻²⁷ and it seems reasonable to assume that the dissociation energy of the fourth N-F bond in NF₄⁺ is similar to or slightly less than this value. Consequently, step 2 should be approximately thermochemically neutral.

The proposition that steps 2 and 4 should so markedly differ in their heats of reaction, although both involve the formation of one additional N-F bond, is not unreasonable. In step 2 a hypervalent NF₄⁺ radical is formed which would possess nine valence electrons on the central nitrogen atom. By analogy with the known NF₃O molecule,²⁸ this energetically unfavorable structure can be circumvented by assuming strong contributions from resonance structures such as

\[
\begin{align*}
N & \equiv F \\
& \equiv F
\end{align*}
\]

These resonance structures result in a strong polarization, i.e., weakening of all N-F bonds, when compared to those in NF₃. This is demonstrated by the bond lengths of 1.371 and 1.43 Å observed for NF₂ and NF₃O,²⁸ respectively. Thus the energy gained by the formation of a fourth N-F bond in the NF₄⁺ radical is largely compensated by a significant weakening of the remaining N-F bonds. In contrast, the reaction of the NF₄⁺ radical cation with a fluorine atom, i.e.,

\[
\begin{align*}
N & \equiv F \\
& \equiv F
\end{align*}
\]

does not significantly change the nature of the existing N-F bonds and, therefore, is expected to result in a heat of reaction close to the energy of this bond.

An alternate, attractively simple, and preferable explanation for the above bond weakening effect in NF₄⁺ can be offered if one assumes that, due to the large energy difference between the 2p and 3s nitrogen orbitals, the ninth nitrogen valence electron occupies an antibonding orbital. Experimental evidence for such a model has recently been reported²⁹ by Nishikida and Williams for the NF₄O radical anion which is isoelectronic with NF₃. On the basis of the observed FSR data, NF₂O possesses a spin density of 0.27 in the nitrogen 2s orbital suggesting that the unpaired electron indeed occupies an antibonding orbital.

A third possible, although less likely, explanation would be the assumption of a trigonal-bipyramidal structure for NF₄⁺, in which two axial fluorines and nitrogen form a semibonnet three-center, four-electron bond while the three equatorial positions are occupied by two fluorine ligands and the unpaired electron. Although all three models are basically a formalism describing the same net result, i.e., an increase of the bond length and ionicity of the NF bonds, model III should result in significantly different bond angles and therefore be experimentally distinguishable from models I and II.

It should be pointed out that the global activation energy (38.6 kcal mol⁻¹) of the decomposition of NF₄H₂ to NF₃ + F + H₂, and the heat of formation of NF₄H₂ from NF₃ + F + H₂ (44.6 kcal mol⁻¹) are the same within experimental error. It is difficult to say whether this is coincidental or if it implies that the corresponding forward reactions, i.e., steps 2-4 of the Born-Haber cycle, occur without activation energy. Examples of the latter case are known for the endothermic dissociation of solids such as carbonates.³⁰ If for NF₄⁺ salts the global decomposition activation energies should indeed be identical with the heats of formation from NF₃, F, and the corresponding Lewis acid, a value of about 372 kcal mol⁻¹ can be predicted for ΔH°₂₅K,NF₄⁺ on the basis of ΔH°₂₅K,F = 45 kcal mol⁻¹ and ΔH°₂₅K,NF₃ = 29.55 kcal mol⁻¹.

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Registry No. NF₄BF₄, 15640-93-4; NF₄AsF₆, 16871-75-3; NF₄SbF₆, 16871-76-4; NF₄, 7783-54-2; F₂, 7782-41-4; SbF₆, 7783-70-2.

References and Notes

(15) J. B. Goldberg, unpublished results.
(16) K. O. Christe, unpublished results.
(21) G. C. Sinkey, unpublished results.
APPENDIX F

SIMPLIFIED SYNTHESIS OF NF₄SBF₆

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SHORT COMMUNICATION

Simplified Synthesis of NF₄SBF₆

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In NH₄ chemistry, the NF₄SBF₆ salt plays a key role. It is most
amenable to large scale production and serves as a starting material for the
metathetical synthesis of numerous other NH₄ salts [1-4]. The most
convenient previously reported [5] method involved the reaction of SBF₆
with an excess of NH₄ and F₂ at elevated temperature and pressure according
to:

\[ \text{NH}_4^+\text{F}_2\text{SBF}_6 \xrightarrow{250^\circ C/20-100 \text{ atm}} \text{NF}_4^+\text{SBF}_6 \]

In view of its appreciable cost and its detrimental physical and
chemical properties, it was desirable to replace SBF₆ by a starting material
which is cheaper, more readily available and easier to handle. Since it is
well known [6] that, under conditions similar to those of the above NH₄SBF₆
synthesis, SBF₄ can be liberated by F₂ to SBF₃:

\[ \text{SBF}_4 \xrightarrow{F_2} \text{SBF}_3 \]

a direct synthesis of NF₄SBF₆ from SBF₃, F₂ and NH₄ was logical. The possible
combination of the two steps was experimentally verified, as shown by the following
equation:

\[ \text{NH}_4^+\text{F}_2\text{SBF}_3 \xrightarrow{250^\circ C/60 \text{ atm}} \text{NF}_4^+\text{SBF}_6 \]

Although no efforts were made to maximize all the reaction parameters, the
high yield and purity of the thus obtained NF₄SBF₆ demonstrates the feasibility
of this simplified synthesis.

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EXPERIMENTAL

A prepassivated (with CIF₃) 95 ml monel cylinder was loaded in the dry nitrogen atmosphere of a glove box with SbF₅ (51 mmol). The cylinder was connected to a metal vacuum system, evacuated, and charged at -196°C with NF₃ (65 mmol) and F₂ (98 mmol). The cylinder was heated for five days to 250°C. The excess of unreacted NF₃ and F₂ was pumped off at ambient temperature, leaving behind a white crystalline residue (10 g, weight expected for 31 mmol of NF₄SbF₆ = 10.1 g). Based on its infrared and Raman spectra and its chemical analysis, this solid consisted of high purity NF₄SbF₆. It did not contain any detectable amounts of polyantimonate salts.

ACKNOWLEDGEMENTS

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REFERENCES

APPENDIX G

SYNTHESIS AND PROPERTIES OF $\text{NF}_4^+\text{ClO}_4^-$ AND $\text{NF}_4^+\text{HF}^-\cdot\text{nHF}$
AND SOME REACTION CHEMISTRY OF $\text{NF}_4^+$ SALTS

Contribution from Rocketdyne, a Division of Rockwell International Corporation, Canoga Park, California 91304

SYNTHESIS AND PROPERTIES OF
$\text{NF}_4^+\text{ClO}_4^-$ AND $\text{NF}_4^+\text{HF}_2^-\cdot\text{nHF}$ AND SOME REACTION CHEMISTRY OF $\text{NF}_4^+$ SALTS

Karl O. Christe,* William W. Wilson and Richard D. Wilson

Received • • • •

Abstract

The possibility of synthesizing $\text{NF}_4^+\text{XO}_4^-$ ($X = \text{Cl}, \text{Br}, \text{i}$) salts by metathesis between $\text{NF}_4\text{SbF}_6$ and $\text{CsXO}_4$ in anhydrous HF solution at $-78^\circ$ was studied. Of these $\text{NF}_4\text{XO}_4^-$ salts, $\text{NF}_4\text{ClO}_4^-$ was isolated and characterized by vibrational and $^{19}\text{F}$ NMR spectroscopy. It is an unstable white solid decomposing at $25^\circ$ to give $\text{NF}_3$ and $\text{FOClO}_3$ in high yield. The $\text{NF}_4\text{BrO}_4^-$ salt is of marginal stability in HF solution and decomposes to $\text{NF}_3^-$, $\text{O}_2^-$ and $\text{BrFO}_2^-$. Attempts to isolate $\text{NF}_4\text{BrO}_4^-$ as a solid resulted in explosions. The $\text{NF}_4\text{IO}_4^-$ salt could not be prepared due to the facile fluorination of $\text{IO}_4^-$ to $\text{IF}_4O_2^-$ by either HF or $\text{BrF}_5$. Attempts to prepare $\text{NF}_4\text{XF}_4^0^- (X = \text{Cl}, \text{Br})$ salts by metathesis between $\text{NF}_4\text{SbI}$ and $\text{CsXF}_4$ in $\text{BrF}_5$ solution at $25^\circ$ were unsuccessful; with $\text{BrF}_4O_2^-$, fluoride abstraction occurred resulting in the formation of $\text{NF}_3^-$, $\text{F}_2^-$ and $\text{BrF}_3^0$, whereas $\text{CsClF}_4$ underwent a displacement reaction with $\text{BrF}_5$ to give $\text{CsBrF}_6$ and $\text{ClF}_3^0$. The metathetical synthesis of $\text{NF}_4\text{NO}_3^-$ could not be studied in HF due to the reaction of $\text{NO}_3^-$ with HF to give $\text{NO}_2^+$, $\text{H}_2O$, and $\text{HF}^-$. The metathesis between $\text{NF}_4\text{SbF}_6$ and CsF in HF at $-78^\circ$ did not produce $\text{NF}_4^+$, but an unstable white solid of the composition $\text{NF}_4^+\text{HF}_2^-\cdot\text{nHF}$. The composition, thermal stability, spectroscopic properties and decomposition products of this solid were studied.

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G-1
The $\text{NF}_4^+\text{HF}_2^-$ salt is stable in HF solution at 25°C and the synthetic usefulness of these solutions for the synthesis of other $\text{NF}_4^+$ salts is briefly discussed. Attempts to prepare $\text{NCI}_4^+$ and $\text{NCl}_2\text{O}_4^+$ salts by F-Cl exchange between $\text{BCl}_3^+$ and $\text{NF}_4^+$ and $\text{NF}_2\text{O}_4^+$ were unsuccessful.

**Introduction**

The first reports on the successful syntheses of $\text{NF}_4^+$ salts were published in 1966. Since then, numerous $\text{NF}_4^+$ salts have been prepared and characterized which contain as counterions $\text{BF}_3^-$, $\text{XF}_5^-$ ($X = \text{Ge, Ti, Sn}$), $\text{XF}_6^-$ ($X = \text{As}$, $\text{Sb}$, $\text{Bi}$), or $\text{XF}_6^-$ ($X = \text{Ge}$, $\text{Sn}$, $\text{Ti}$, $\text{Ni}$). 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, $\text{F}^-$, or oxygen containing anions. Although in 1968 Tolberg and coworkers found evidence for the existence of unstable $\text{NF}_4^+$ salts probably containing the $\text{HF}_2^-$ or the $\text{ClO}_4^-$ anion, these salts were not well characterized and no data were published. In this paper, we describe the synthesis and characterization of $\text{NF}_4^+\text{HF}_2^-\text{nHF}$ and $\text{NF}_4^+\text{ClO}_4^-$ and the attempted syntheses of $\text{NF}_4^+\text{BrO}_4^-$, $\text{NF}_4^+\text{BrF}_4^-$, $\text{NF}_4^+\text{ClF}_4^-$, and $\text{NF}_4^+\text{NO}_3^-$. Since the existence of a stable $\text{NOCI}_2\text{SbCl}_6^-$ salt has recently been reported, it appeared interesting to study the possibility of exchanging fluorine for chlorine in either $\text{NF}_4^+$ or $\text{NF}_2\text{O}_4^+$ salts using $\text{BCl}_3$.

**Experimental**

**Materials.** Literature methods were used for the syntheses of $\text{NF}_4\text{SbF}_6$, $\text{NF}_2\text{OSbF}_6$, $\text{CsClF}_4\text{O}$, and $\text{CsBrF}_4\text{O}$. The $\text{BrF}_5^-$ (Matheson) was treated with 35 atm of $\text{F}_2$ at 200°C for 24 hours and then purified by fractional condensation through traps kept at -64°C 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 \( \text{BiF}_5 \) to remove the last traces of \( \text{H}_2\text{O} \). The \( \text{CsF} \) (American Potash) was fused in a platinum crucible and ground in the dry box. The \( \text{CsClO}_4 \) (ROC/RIC) was used as received. The \( \text{CsNO}_3 \) was prepared from aqueous \( \text{Cs}_2\text{CO}_3 \) and \( \text{HNO}_3 \) using a pH-electrode for endpoint detection. It was purified by recrystallization from \( \text{H}_2\text{O} \) and dried in an oven at 100\(^\circ\)C for 24 hours. The \( \text{BCl}_3 \) (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 \( \text{ClF}_3 \) and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Metathetical reactions were carried out either in HF or \( \text{BrF}_5 \) solution 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 4mm Teflon FEP or thin-walled Kel-F tube.

Infrared spectra were recorded in the range 4000-200cm\(^{-1}\) on a Perkin-Elmer Model 283 spectrophotometer. Room temperature spectra of solids were obtained 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 \( \text{N}_2 \) cooled sample holder of a low-temperature infrared cell\(^{24}\) with external CsI windows. Spectra of gases were obtained using a Teflon cell of 5cm pathlength equipped with AgCl windows.
The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-A exciting line and a Claassen filter \(^{25}\) for the elimination of plasma lines. Sealed quartz, Teflon FEP or Kel-F Tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded 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 CFCI\(_3\).

Preparation and Properties of \(\text{NF}_4\text{ClO}_4\). 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 \(\text{NF}_4\text{ClO}_4\cdot \text{NF}_4\text{SbF}_6\) (10.03 mmol) and CsClO\(_4\) (10.02 mmol) were placed into the 3/4" o.d. Teflon FEP bottom U-trap of the metathesis apparatus. Anhydrous HF (8.56 g) was added at \(-196^\circ\). The mixture was kept at \(-78^\circ\) for 15 hours and then for 2 hours at \(-45^\circ\) with agitation. The entire metathesis apparatus was cooled to \(-78^\circ\) and inverted to separate the CsSbF\(_6\) precipitate from the \(\text{NF}_4\text{ClO}_4\) solution. Dry N\(_2\) (2 atm) was used to pressurize the solution during this filtration step. The HF solvent was pumped off at \(-78^\circ\) and \(-45^\circ\) 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 \(-112^\circ\), \(-186^\circ\) and \(-210^\circ\). The \(-210^\circ\) trap contained 8.0 mmol of NF\(_3\) and the \(-186^\circ\) trap had 8.0 mmol of FOCIO\(_3\) which were identified by infrared, Raman and \(^{19}\)F NMR spectroscopy. \(^{27}\) The filter cake (3.60 g, weight calc'd 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 $\text{NF}_4\text{ClO}_4$ which, based on its vibrational spectra, consisted of a mixture of $\text{NF}_4\text{SbF}_6$ and $\text{CsSbF}_6$. The 20% of $\text{NF}_4\text{ClO}_4$ unaccounted for by the above material balance corresponds to the amount of product in the mother liquor typically retained by the $\text{CsSbF}_6$ 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. Based on the above material balance, the $\text{NF}_4\text{ClO}_4$ prepared in this manner had a purity of 95 weight percent.

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

The thermal stability of solid $\text{NF}_4^+\text{ClO}_4^-$ was studied by pumping on a sample at a given temperature for one hour and measuring the amount of $\text{NF}_3$ and $\text{FOClO}_3$ evolved. Whereas at -13°C $\text{NF}_4\text{ClO}_4$ 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 $\text{NF}_4\text{ClO}_4$ yields the very shock-sensitive $\text{FOClO}_3$ in high yield, appropriate safety precautions should be taken when working with this compound.

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G-5
Reaction of $\text{NF}_4\text{SbF}_6$ with CsBrO$_4$. The compatibility of CsBrO$_4$ with HF was established in the same manner as described above for CsIu$_4$. The solubility of CsBrO$_4$ in HF at 25$^\circ$C was in excess of 1 g per g of HF. For the metathetical reaction, $\text{NF}_4\text{SbF}_6$ and CsBrO$_4$ (1.0 mmol each) in HF (2 ml) were stirred at 20$^\circ$C for 1.5 hours, then half of the solvent was pumped off and the mixture was cooled to -78$^\circ$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 $\text{NF}_4^+$, BrO$_4^-$ $^{31}$ and FBrO$_2$ $^{32}$ with the intensity of the FBrO$_2$ bands growing with time at the expense of those of $\text{NF}_4^+$ and BrO$_4^-$. The $^{19}$F NMR spectrum showed resonances characteristic of $\text{NF}_4^+$ (sharp triplet of equal intensity at $\phi$ -217 with $J_{\text{NF}}$ = 227 Hz) and $\text{NF}_3$ (broad triplet of equal intensity at $\phi$ -143 with $J_{\text{NF}}$ = 150 Hz) and a broad line at $\phi$ 186 attributed to HF ($\phi$ 196) undergoing rapid exchange with FBrO$_2$ ($\phi$ -205). $^{33}$

Caution! Explosions occurred when attempts were made to isolate solid $\text{NF}_4\text{BrO}_4$ from an HF solution which had never been warmed above -78$^\circ$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 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 $\text{NF}_4\text{SbF}_6$ with CsBrF$_4$ in BrF$_5$. A mixture of $\text{NF}_4\text{SbF}_6$ (0.536 mmol) and CsBrF$_4$ (0.449 mmol) was placed in the drybox into a $\frac{3}{4}$" o.d. Teflon FEP ampule and BrF$_5$ (4 ml liquid) was added at -196$^\circ$C using the vacuum line. The contents of the ampule were warmed to 20$^\circ$C and stirred with a magnetic stirring bar for 2.5 hours. The ampule was cooled to -196$^\circ$C and the noncondensable material (0.42 mmol of F$_2$) was distilled off. The material volatile at -95$^\circ$C was distilled off and consisted of 0.48 mmol of $\text{NF}_3$. The material volatile at 20$^\circ$C was separated by fractional condensation through a series of traps kept at -64$^\circ$C, -78$^\circ$C and -196$^\circ$C. The -64$^\circ$C trap contained BrF$_3$ (0.43 mmol),
In addition to some BrF₅. The two colder traps contained the bulk of the BrF₅. The solid nonvolatile reaction product (205 mg, weight calc'd for 0.449 mmol CsSbF₆ and 0.087 mmol NF₄SbF₆ = 194 mg) was shown by vibrational spectroscopy to consist mainly of CsSbF₆ containing some NF₄SbF₆.

Reaction of CsClF₄O with BrF₅. In a sapphire reactor, CsClF₄O (1.234 mmol) and BrF₅ (15 mmol) were combined at -196°C. The mixture was kept at 20°C for 12 hours. The volatile products were distilled off and consisted of BrF₅ and ClF₃O(1.2 mmol). The solid residue (405 mg, weight calc'd for 1.234 mmol of CsBrF₆ = 403 mg) was shown by vibrational spectroscopy to consist of CsBrF₆.

Preparation and Properties of NF₄HF₃-nHF. In a typical experiment, NF₄SbF₆ 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 hours, then cooled to -78°C and filtered. Most of the HF solvent was removed by pumping at -78°C for 36 hours, -64°C for 12 hours, -57°C for 6 hours and -45°C for 6 hours. 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°C and -210°C. The amounts and mole ratios of HF (-126°C trap) and NF₃ (-210°C trap) were periodically measured while cooling the sample back to -45°C. Several hours of warming to ambient temperature and to 40°C were required to achieve complete decomposition of the salt. A total of 8.32 mmol of NF₃ and 19.63 mmol of HF were collected with the HF:NF₃ mole ratio ranging from 10.1 at the start to 1.54 towards 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 NF₄SbF₆ and some CsSbF₆. The filter cake (3.5 g, weight calc'd for 10.0 mmol of CsSbF₆ = 3.687 g) consisted of CsSbF₆. The 15% of NF₄⁺ value unaccounted for by the above material balance is in line with the amount of material in the mother liquor generally retained by the CsSbF₆ filter cake in similar reactions (see NF₄ClO₄ preparation.)
Based on the above material balance, the purity of $\text{NF}_4\text{HF}_2\cdot n\text{HF}$ obtained in this manner is about 97 mol% with the CsSbF$_6$ and NF$_4$SbF$_6$ 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 $\text{NF}_4\text{HF}_2\cdot n\text{HF}$, the originally liquid sample first turned milky and pasty, then after recooling it to -45$^\circ$C had the appearance of a white dry solid which melted very slowly when warmed again to 20$^\circ$. 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 one mmol scale. The $^{19}\text{F}$ NMR spectrum of the compound in HF solution showed the signal (triplet of equal intensity at $\phi$ -216.2 with $J_{\text{NF}} = 230$ Hz and a line width of less than 3 Hz) characteristic of $\text{NF}_4^+$ and a broad line at $\phi$ 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 $\text{NF}_4^+$ 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$^\circ$ the solvent band had disappeared. When this sample was frozen at -110$^\circ$, 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$^\circ$ showed again only bands due to $\text{NF}_4^+$.

Reactions of $\text{NF}_4\text{SbF}_6$ and $\text{NF}_2\text{OSbF}_6$ with $\text{BCl}_3$. A sample of $\text{NF}_4\text{SbF}_6$ (1.85 mmol) was treated in a Teofion FEP ampule with a tenfold excess of $\text{BCl}_3$ for three hours at 20$^\circ$. The volatile products were separated by fractional condensation and shown to consist of NF$_3$ and mixed BF$_x$Cl$_{13-x}$ type compounds. A small amount of solid residue (60 mg) was identified by vibrational spectroscopy as NO$^+$SbCl$_6$.
A sample of NF$_2$OSbF$_6$ was similarly treated with BCl$_3$. The volatile products consisted again of mixed BF$_{3-x}$Cl$_x$ type compounds, but NO$^+$/SbF$_6^{3-x}$ was formed in almost quantitative yield as a nonvolatile residue.

Results and Discussion

The general usefulness of the metathetical reaction

$$\text{NF}^+$/SbF$^-$/ + Cs$^+$/X$^-$/ \rightarrow \text{Cs}^+$/SbF$^-$/ + NF$^+_x$/X$^-$/

for the syntheses of otherwise inaccessible NF$^+_x$/X$^-$/ salts has previously been demonstrated 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$_4$/CIO$_4$. The CIO$_4^-$ anion was found to be stable in HF solution. Therefore, NF$_4$/CIO$_4$ was prepared according to

$$\text{NF}_4$/SbF$^-$/ + CsCIO$_4$/ \rightarrow \text{CsSbF}_6 + NF_4$/CIO$_4$$

The reaction must be carried out at low temperature since, even in HF solution, NF$_4$/CIO$_4$ undergoes decomposition at room temperature. The NF$_4$/CIO$_4$ salt can be isolated as a white solid, stable up to about $-13^\circ$. At $0^\circ$ slow decomposition and at $25^\circ$ rapid decomposition of the solid was observed according to

$$\text{NF}_4$/CIO$_4$$ \rightarrow \text{NF}_3 + \text{FOCIO}_3$$

In HF solution the rate of decomposition is slower, but follows the same path. The essentially quantitative formation of FOCIO$_3$ is noteworthy and represents a new and convenient synthesis of FOCIO$_3$.  

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(1-4)
Based on the observed material balance, the yield of NF₄ClO₄ is high and the only significant loss of material is due to the amount of mother liquor retained by the CsSbF₆ filter cake. The purity of the NF₄ClO₄ product is also high and the impurities present are CsSbF₆, 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 NF₄ClO₄, both in HF solution and the solid state, was established by vibrational and ¹⁹F NMR spectroscopy. The ¹⁹F NMR spectrum of NF₄⁺ClO₄⁻ in HF solution showed the signal characteristic for tetrahedral NF₄⁺. The Raman spectra of this solution confirmed the presence of tetrahedral NF₄⁺ (1170 w, br, 855 vs, p, 612 m, 448 mw), and ClO₄⁻ (940 s, p, 620 w, 460 w). The infrared and Raman spectra of solid NF₄ClO₄ are given in Figure 1, together with the observed frequencies and their assignments in point group Tₐ. As expected for a solid, splittings of some bands into their degenerate components and crystal splittings are observed. In addition v₁(A₁) and v₂(E) which ideally are infrared inactive were observed in the infrared spectrum as extremely weak bands. The pronounced Christiansen effect 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 NF₄ClO₄ is considerably less sensitive than its decomposition product FOClO₃.

Reaction of NF₄SbF₆ with CsBrO₄. The BrO₄⁻ anion was found to be stable in HF solution, thus allowing the metathetical reaction

\[
\text{NF}_4\text{SbF}_6 + \text{CsBrO}_4 + 78^\circ \rightarrow \text{CsSbF}_6 + \text{NF}_4\text{BrO}_4
\]

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

$$\text{NF}_4\text{BrO}_4 \rightarrow \text{NF}_3 + [\text{FOBrO}_3]$$

$$[\text{FOBrO}_3] \rightarrow \text{FBrO}_2 + \text{O}_2$$

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

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

$$10^- + 4\text{HF} \rightarrow 1\text{F}_4\text{O}_2^- \text{(cis and trans isomer)} + 2\text{H}_2\text{O}$$

$$1\text{F}_4\text{O}_2^- + 2\text{HF} \rightarrow \text{HF}_2^- + \text{HOF}_4\text{O}$$

$$10^- + 2\text{BrF}_5 \rightarrow 1\text{F}_4\text{O}_2^- \text{(trans isomer mainly)} + 2\text{BrF}_3\text{O}$$

The metathesis between $\text{CsF}_4\text{O}_2$ and $\text{NF}_4\text{SbF}_6$ in HF, followed by the thermal decomposition of the metathesis product, produces the novel compounds, cis- and trans- $\text{OIF}_4\text{OF}$, and will be reported in a separate paper.

Reaction of $\text{NF}_4\text{SbF}_6$ with $\text{CsBrF}_4$. Although $\text{CsBrF}_4$ reacts with HF $39$ according to

$$\text{CsBrF}_4 + \text{HF} \rightarrow \text{CsHF}_2 + \text{BrF}_3\text{O}$$
BrF₅ does not interact with CsBrF₄⁺ and therefore is a suitable solvent for studying the reaction of NF₄⁻SbF₆ with CsBrF₄⁺. The following reaction was observed

\[
\text{BrF}_5 + \text{CsBrF}_4^+ \rightarrow \text{CsSbF}_6 + \text{BrF}_3^0 + F_2 + \text{NF}_3
\]

The formation of these products indicates that the salt NF₄⁺BrF₄⁻ is not stable under these conditions and that, contrary to the NF₄⁻ClO₄⁻ and NF₄⁺IF₄⁻₂ reactions, fluoride abstraction from BrF₄⁻ is preferred over the fluorination of BrF₄⁻ to either BrF₄OF or BrF₅⁻. A similar fluoride abstraction has previously been observed for BrF₅⁻:

\[
\text{NF}_4\text{SbF}_6 + \text{CsBrF}_4^+ \rightarrow \text{CsSbF}_6 + \text{NF}_3 + F_2 + \text{BrF}_5
\]

but not for BrF₄⁻ which was fluorinated to BrF₅⁻:

\[
\text{NF}_4\text{SbF}_6 + \text{KBrF}_4 \rightarrow \text{KSF}_6 + \text{NF}_3 + \text{BrF}_5
\]

The corresponding metathesis between CsClF₄⁻ and NF₄⁺SbF₆ was not studied because it was found that CsClF₄⁻ reacts with BrF₅⁻ according to

\[
\text{CsClF}_4^- + \text{BrF}_5^- \rightarrow \text{CsBrF}_6 + \text{ClF}_3^- + \text{BrF}_5^- + \text{NF}_3 + F_2
\]

The formed CsBrF₆ would be capable of undergoing with NF₄⁺SbF₆ the above given fluoride abstraction reaction.

Reaction of CsNO₃ with HF. The compatibility of CsNO₃ with HF was studied in order to explore the feasibility of synthesizing NF₄⁻NO₃⁻. Although CsNO₃ is quite soluble in HF and can be recovered as such from HF solutions, Raman spectra of these solutions showed the absence of NO₃⁻ and the presence of NO₂⁻ as the only nitrogen oxygen containing species.

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These results imply an equilibrium, such as

\[ \text{NO}_3^- + 4\text{HF} \xrightleftharpoons{\text{HF}} \text{NO}_2^+ + \text{H}_2\text{O} + 2\text{HF}_2 \]

which has previously been postulated for these solutions. In view of the absence of \( \text{NO}_3^- \) in HF solution, no metathetical reactions between \( \text{CsNO}_3 \) and \( \text{NF}_4\text{SbF}_6 \) were attempted.

Preparation and Properties of \( \text{NF}_4\text{HF}_2 \cdot n\text{HF} \). The \( \text{NF}_4^+\text{F}^- \) salt, which has an active fluorine content in excess of 90 weight percent, would be of extreme interest. However, previous attempts to prepare this salt from \( \text{NF}_3 \) and \( \text{F}_2 \) at -196°C by either bremsstrahlung or uv-photolysis were unsuccessful indicating that the salt is unstable with regard to its decomposition to \( \text{NF}_3 \) and \( \text{F}_2 \). The instability of \( \text{NF}_4^+\text{F}^- \) can be explained by the small size of the \( \text{F}^- \) anion resulting in an insufficient lattice energy to stabilize the salt. However, the anion size and thereby the lattice energy can be sufficiently increased by the addition of \( \text{F}^- \) to a Lewis acid, such as \( \text{BF}_3 \) or \( \text{MF}_5 \) (\( \text{M} = \text{P}, \text{As}, \text{Sb}, \text{or Bi} \)). Since most of the metathetical reactions for the production of \( \text{NF}_4^+ \) salts are carried out in anhydrous HF, which is an acid, it was of interest to define the nature and stability of a possible \( \text{NF}_4^+\text{HF}_2^- \) salt. A previous unpublished study of the \( \text{LiF} - \text{NF}_4\text{SbF}_6 \) system in HF at ambient temperature had provided evidence that after removal of the precipitated \( \text{LiSbF}_6 \) a stable solution was obtained containing the \( \text{NF}_4^+ \) cation. All attempts to isolate a salt at temperatures of -44°C and above from this solution resulted in decomposition to \( \text{NF}_3, \text{F}_2 \) and HF. Removal of the solvent at -78°C resulted in a wet solid which was not characterized.

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

\[ \text{NF}_4\text{SbF}_6 + \text{CsHF}_2 \xrightarrow{-78^\circ\text{C}} \text{CsSbF}_6 + \text{NF}_4\text{HF}_2 \]
Based on the observed material balance, the soluble product consisted of about 97 mole% $\text{NF}_4\text{HF}_2$ with the remainder being $\text{CsSbF}_6$ and excess of either starting material. In agreement with the previous observation, $\text{NF}_4\text{HF}_2$ is stable in HF solution at ambient temperature and shows in the $^{19}\text{F}$ NMR spectrum the characteristic $\text{NF}_4^+$ signal. The presence of the $\text{NF}_4^+$ cation and the virtual absence of anions other than those due to solvated $\text{F}^-$ 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 of tetrahedral $\text{NF}_4^+$. The difficulty in observing bands due to solvated $\text{HF}_2^-$ is not surprising in view of HF being a weak scatterer and the expected broadness of the lines of $\text{HF}_2^-$ undergoing rapid exchange with the solvent HF.

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

$$\text{NF}_4\text{HF}_2 \cdot n\text{HF} \rightarrow \text{NF}_3 + \text{F}_2 + (n+1)\text{HF}$$

It was found that the mole ratio of $\text{NF}_3: \text{HF}$ was about 10.1 at the beginning and 1.54 towards the end of this decomposition. These results demonstrate that complete removal of solvated HF from $\text{NF}_4\text{HF}_2$ is extremely difficult and is accompanied by decomposition of most of the $\text{NF}_4^+$ salt itself. The presence of a solvated $\text{HF}_2^-$ and the virtual absence of anions other than those due to solvated $\text{F}^-$ 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 of $\text{HF}_2^-$. Upon removal of most of the solvated HF, these bands lost intensity, resulting in a spectrum consisting exclusively of the $\text{NF}_4^+$ bands (see trace C of Figure 2).
It is also noteworthy that with decreasing HF content, the melting point of NF$_4$HF$_2$·nHF increases and approaches room temperature for n approaching zero. The decomposition of NF$_4$HF$_2$·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$_4$. A careful analysis of such systems is therefore necessary to avoid the interpretation of such (NF$_4$HF$_2$)$_n$MF $\approx$ (NF$_4$)$_n$MF$^+ _x$ salts.

The possibility of preparing stable HF solutions of NF$_4$HF$_2$ 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$_4$HF$_2$ can be converted into other NF$_4^+$ salts. This was first demonstrated by reacting NF$_4$HF$_2$ solutions with BF$_3$ to form NF$_4$BF$_4^+$ and has recently been extended to the formation of other salts, which due to the low solubility of their cesium salts are not amenable to direct metathetical reactions.

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References

Diagram Captions

Figure 1. Low-temperature vibrational spectra of solid NF\textsubscript{4}\textsuperscript{+}CIO\textsubscript{4}\textsuperscript{-}. The infrared spectrum was recorded as a dry powder between AgCl disks. The broken line indicates absorption due to the AgCl window material. The Raman spectrum was recorded with a spectral slit width of 6 cm\textsuperscript{-1}. The given assignments are for ideal tetrahedral NF\textsubscript{4}\textsuperscript{+} cations (N) and CIO\textsubscript{4}\textsuperscript{-} anions (C) ignoring site symmetry and solid state effects.

Figure 2. Raman spectra of liquid and solid NF\textsubscript{4}\textsuperscript{+}HF\textsubscript{2}•nHF in a Kel-F capillary. Trace A, spectrum of a concentrated HF solution at -75\textdegree. The given assignments are for tetrahedral NF\textsubscript{4}\textsuperscript{+}. Trace B, sample of trace A cooled to -110\textdegree. In addition to the NF\textsubscript{4}\textsuperscript{+} bands, the spectrum shows bands attributed to HF\textsubscript{2}•nHF. Trace C, spectrum of the solid at -110\textdegree 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\textdegree. All spectra were recorded with a spectral slit width of 8 cm\textsuperscript{-1}.
The graph shows the infrared spectra of \( \text{NF}_4^+ \text{HF}_2^- \cdot n\text{HF} \) in different states:

- **A** (liquid, \(-75^\circ\))
  - \( \nu_3 (F_2) \) at 1170 cm\(^{-1}\)

- **B** (solid, \(-110^\circ\))
  - \( \nu_3 (F_2) \) at 1170 cm\(^{-1}\)
  - \( \nu_1 (A_1) \) at 854 cm\(^{-1}\)

- **C** (solid, \(-110^\circ\))
  - \( \nu_4 (F_2) \) at 612 cm\(^{-1}\)
  - \( \nu_2 (E) \) at 448 cm\(^{-1}\)

The frequencies (in cm\(^{-1}\)) are key markers for identifying the vibrational modes of the molecule in various states.
APPENDIX H

SYNTHESIS AND PROPERTIES OF NF\textsuperscript{4}SO\textsubscript{3}F\textsuperscript{-}

Contribution from Rocketdyne, A Division of
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Abstract

The novel salt NF\textsuperscript{4}SO\textsubscript{3}F\textsuperscript{-} was prepared by metathesis between NF\textsubscript{4}SbF\textsubscript{6} and CsSO\textsubscript{3}F in anhydrous HF solution at -78\degree. In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid which is stable at 0\degree, but slowly decomposes at +10\degree to produce FOSO\textsubscript{2}F and NF\textsubscript{3} in high yield. The ionic nature of the compound, both in the solid state and in HF solution, was established by Raman and \textsuperscript{19}F NMR spectroscopy. Cesium sulfate was found to react with anhydrous HF producing CsSO\textsubscript{3}F as the major product. Similarly, CsPO\textsubscript{2}F\textsubscript{2}, the Raman spectrum of which is reported, was found to react with HF to give CsPF\textsubscript{6} in quantitative yield.

Introduction

Among oxidizers, the NF\textsuperscript{4} cation is unique. In spite of being one of the most powerful oxidizers known, it possesses high kinetic stability,\textsuperscript{1} thereby permitting its combination with a surprisingly large number of anions to form stable or metastable salts. Anions capable of NF\textsuperscript{4} salt formation include BF\textsubscript{4}\textsuperscript{-2-9}, XF\textsubscript{5} (X=Ge,Ti,Sn)\textsuperscript{9-11}, XF\textsubscript{4} (X=P,As,SB,Bi)\textsuperscript{6,7,9,12-19}, XF\textsubscript{6} (X=Ge,Sn,Ti, Ni,Mn)\textsuperscript{9-11,20,21}, ClO\textsubscript{4}\textsuperscript{-22}, \textsuperscript{22}HF\textsubscript{2}, \textsuperscript{22}CIO\textsubscript{4}, \textsuperscript{22}ClO\textsubscript{2}, \textsuperscript{22}ClO\textsubscript{3}, \textsuperscript{22}ClO\textsubscript{4}, \textsuperscript{22}ClO\textsubscript{5}, \textsuperscript{22}ClO\textsubscript{6}, \textsuperscript{22}ClO\textsubscript{7}, \textsuperscript{22}ClO\textsubscript{8}, and several perfluoro polyanions.\textsuperscript{6,10,11,19} Recent studies have shown that NF\textsuperscript{4} salts of oxygen containing anions are of particular interest because hypofluorites, such as OIF\textsubscript{4}O\textsubscript{4/3} or FOClO\textsubscript{5}, can be formed during their thermal decomposition.

In this paper we would like to report results on the possible synthesis of salts derived from sulfur or phosphorus oxyfluorides. We are aware of only

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one unpublished study\textsuperscript{3} in this area, in which the evolution of some FOSO\textsubscript{2}F from either an NF\textsubscript{4}SbF\textsubscript{6}-HOSO\textsubscript{2}F solution at -78\degree C or a supposedly dry mixture of NF\textsubscript{4}SbF\textsubscript{6} and LiSO\textsubscript{3}F at room temperature was interpreted\textsuperscript{3} as evidence that NF\textsubscript{4}SO\textsubscript{3}F, if it exists, is unstable even at -78\degree C. In view of the relative stability of NF\textsubscript{4}ClO\textsubscript{4}\textsuperscript{22} and the similarity between ClO\textsuperscript{4-} and isoelectronic SO\textsubscript{3}F\textsuperscript{-} and PO\textsubscript{3}F\textsuperscript{2-} the isolation of NF\textsubscript{4}SO\textsubscript{3}F and NF\textsubscript{4}PO\textsubscript{3}F\textsubscript{2} seemed possible.

Experimental

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.\textsuperscript{22} Literature methods were used for the synthesis of NF\textsubscript{4}SbF\textsubscript{6},\textsuperscript{6} ClOSO\textsubscript{2}F\textsuperscript{24} and HOPO\textsubscript{2}F\textsubscript{2}.\textsuperscript{25} The CsPO\textsubscript{2}F\textsubscript{2} was prepared by the addition of Cs\textsubscript{2}CO\textsubscript{3} to a 10\% excess of HOPO\textsubscript{2}F\textsubscript{2} frozen at -196\degree C. The mixture was allowed to react at room temperature with agitation, and the volatile products and excess HOPO\textsubscript{2}F\textsubscript{2} were pumped off at 40\degree C for 12. hours. Based on the observed material balance and vibrational spectra, the solid residue consisted of CsPO\textsubscript{2}F\textsubscript{2} of high purity. The Cs\textsubscript{2}SO\textsubscript{4} was obtained from aqueous Cs\textsubscript{2}CO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} using a pH-electrode for endpoint (pH of 3.86) detection. The solution was taken to dryness and dried in an oven at 100\degree C for 24 hours. The CsSO\textsubscript{3}F was prepared by allowing CsCl(10.3 mmol) and ClOSO\textsubscript{2}F (15.5 mmol) to react in a 10 ml stainless steel cylinder at ambient temperature for several days. All volatile material was removed from the cylinder, and the solid product was pumped on overnight. The weight of the solid (2.43 g vs. 2.40 g theoretical) together with its infrared and Raman spectra confirmed the completeness of the reaction and the identity of the product.

Preparation and Properties of NF\textsubscript{4}SO\textsubscript{3}F\textsuperscript{-}. The compatibility of the SO\textsubscript{3}F\textsuperscript{-} anion with HF was established by dissolving CsSO\textsubscript{3}F in dry HF and recording the Raman spectra of the starting material, the HF solution, and of the solid residue recovered after removal of the solvent. All spectra showed the bands characteristic\textsuperscript{26} for SO\textsubscript{3}F\textsuperscript{-}. The \textsuperscript{19}F NMR spectrum of the HF solution was also recorded and consisted of a singlet at \( \delta = 33.8 \) (downfield from external CFCI\textsubscript{3}) for SO\textsubscript{3}F\textsuperscript{-} and a relatively narrow HF solvent peak at \( \delta = 191 \).
In a typical preparation of \( \text{NF}_4\text{SO}_3\text{F} \), \( \text{NF}_4\text{SbF}_6 \) (3.145 mmol) and \( \text{CsSO}_3\text{F} \) (3.146 mmol) were combined in a previously described Teflon metathesis apparatus. Dry HF\(^{22} \) (3 ml liquid) was added and the resulting mixture was stirred at ambient temperature for 3 hours with a magnetic stirring bar, followed by cooling to \(-78^0\) and filtration at this temperature. The HF solvent was pumped off from the filtrate at \(-30^0\) for 3 hours leaving behind a white solid residue. The thermal stability of this residue was established by incremental warm up of the solid in a dynamic vacuum and by trapping, measuring (PVT) and identifying (infrared spectroscopy) the volatile decomposition products.

Up to \(0^0\), only HF and small amounts of \( \text{NF}_3 \) were collected indicating the possible presence of small amounts of unstable \( \text{NF}_4\text{HF}_2\cdot\text{nHF}^{22} \) in the product. At temperatures of \(9^0\) or higher, significant decomposition of the solid was observed, producing equimolar amounts of \( \text{NF}_3 \) and \( \text{FOSO}_2\text{F} \). Allowing for about 20% of the product solution being retained, as generally seems to be the case with similar metathetical reactions,\(^{22}\) by the filter cake and being lost during solvent pump-off, the yield of \( \text{NF}_3 \) and \( \text{FOSO}_2\text{F} \) was essentially quantitative. The filtercake (1.0 g, weight celled for 3.15 mmol of \( \text{CsSbF}_6 = 1.10 \) g) was shown by vibrational spectroscopy to be \( \text{CsSbF}_6 \)\(^{28}\) and did not show any detectable impurities.

Caution! \( \text{FOSO}_2\text{F} \) has been reported\(^{29,30}\) to have explosive properties. The compound should therefore be handled with appropriate safety precautions.

For the spectroscopic identification of \( \text{NF}_4\text{SO}_3\text{F} \), reactions were carried out on a 1 mmol scale in a previously described manner. The \(^{19}\)F NMR spectrum of a solution of \( \text{NF}_4\text{SO}_3\text{F} \) in HF at \(-50^0\) showed the signals characteristic for \( \text{NF}_4^+ \) (triplet of equal intensity at \( \vartheta = 215 \) with \( J_{\text{NF}} = 226 \) Hz and a linewidth of less than 3 Hz), \( \text{SO}_3\text{F}^- \) (singlet at \( \vartheta = -53.5 \)), and HF (broad singlet at \( \vartheta = 193 \)). No evidence for the presence of \( \text{FOSO}_2\text{F}^{27} \) was observed. The Raman spectra of the HF solution at \(25^0\) and of solid \( \text{NF}_4\text{SO}_3\text{F} \) at \(-100^0\) were also recorded and are shown in Figure 1. The spectra showed the presence of only small amounts of \( \text{CsSbF}_6 \)\(^{28}\) indicating a purity of \( \text{NF}_4\text{SO}_3\text{F} \) in excess of 90 weight percent, in agreement with the observed material balance. Raman and \(^{19}\)F NMR spectra of HF solutions of \( \text{NF}_4\text{SO}_3\text{F} \), which were kept at \(25^0\) for several days, showed no evidence of \( \text{FOSO}_2\text{F} \) formation.

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Reaction of Cs$_2$SO$_4$ with HF. The Cs$_2$SO$_4$ salt was found to be highly soluble in HF. Raman spectra of these solutions and of the solid residue obtained after the solvent removal, showed the complete absence of the SO$_4^{2-}$ anion$^{28}$ and the presence of the SO$_3^{2-}$ anion$^{20}$. The presence of the SO$_3^{2-}$ anion in the HF solution was confirmed by $^{19}$F NMR spectroscopy which showed a strong singlet at $\delta$ -33.8, characteristic for SO$_3^{2-}$.

Reaction of CsPO$_4$F with HF: A sample of CsPO$_4$F$_2$ (2.1 mmol) was treated with anhydrous HF (5 ml liquid) for 12 hours at 25$^\circ$C. The white solid residue, left behind after removal of the solvent, was identified by its infrared and Raman spectrum as CsPO$_4$F$_2$ (2.1 mmol) and did not contain detectable amounts of PO$_2$F$_2$.$^{31-33}$

Results and Discussion

The novel salt NF$_4$SO$_3$F$^-$ was prepared from NF$_4$SbF$_6$ and CsSO$_4$F by low-temperature metathesis in anhydrous HF solution according to:

$$\text{NF}_4\text{SbF}_6 + \text{CsSO}_4\text{F} \rightarrow \text{CsSbF}_6 + \text{NF}_4\text{SO}_3\text{F}$$

The NF$_4$SO$_3$F salt can be isolated as a white solid which is stable at 0$^\circ$C, but slowly decomposes at +10$^\circ$C to produce NF$_4$SO$_3$F and FOSO$_2$F in high yield according to:

$$\text{NF}_4\text{SO}_3\text{F} \rightarrow \text{NF}_4 + \text{FOSO}_2\text{F}$$

Its HF solution appears to be stable at ambient temperature. The thermal stability of NF$_4$SO$_3$F$^-$ is very similar to that$^{22}$ of NF$_4$ClO$_4$. This is not surprising since SO$_3^{2-}$ and ClO$_4$ are isoelectronic and chemically very similar. This chemical similarity is also demonstrated by their decomposition modes, which in both cases produce the corresponding hypofluorites in high yield.

The decomposition of NF$_4$SO$_3$F$^-$ represents a new, high yield, convenient synthesis of FOSO$_2$F. The previously reported methods for the preparation of FOSO$_2$F involved either the fluorination of SO$_3^{2-}$,F$^{35}$ or S,OF$_2$.$^{36}$ NF$_4$SO$_3$F$^-$ is the third known example of an NF$_4$ salt of an oxy-anion producing on thermal decomposition the corresponding hypofluorite. The other two known examples are NF$_4$ClO$_4$$^{17}$ and

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This indicates that the thermal decomposition of unstable NF₄⁺ salts of oxy-anions may be a general method for the synthesis of hypofluorites.

The ionic nature of NF₄SO₃F, both in the solid state and in HF solution, was verified by Raman and ¹⁹F NMR spectroscopy. The Raman spectra are shown in Figure 1 and demonstrate the presence of the bands characteristic for NF₄⁺ and SO₃F⁻. The observed frequencies and their assignments are summarized in Table I. The SO₃F⁻ bands in NF₄SO₃F are very similar to those observed for CsSO₃F (see Figure 1). The minor frequency shift observed for the SF stretching mode is not surprising in view of a previous infrared study of the alkali metal salts which showed that the frequency of this fundamental strongly depends on the nature of the cation and varied from 812 cm⁻¹ in LiSO₃F to 715 cm⁻¹ in CsSO₃F. The observed splitting of some of the modes of both the NF₄⁺ cation and the SO₃F⁻ anion into their degenerate components is easily explained by solid state effects and has also been observed for NF₄⁺IO₄⁻.

The ¹⁹F NMR spectrum of NF₄⁺SO₃F⁻ in HF solution showed a triplet of equal intensity at ß=215 with JNF = 226 Hz and a linewidth of less than 3MHz, characteristic for NF₄⁺, a singlet at ß=33.5, characteristic for SO₃F⁻, and the characteristic HF signal at ß=193. The assignment of the ß=33 signal to SO₃F⁻ was verified by recording the spectrum of CsSO₃F in HF under the same conditions.

In view of the above mentioned usefulness of NF₄⁺ salts of oxy-anions for the preparation of novel hypofluorites, it appeared interesting to attempt the syntheses of (NF₄)₂SO₄ and NF₄PO₂F₂. The thermal decomposition of these two hypothehtical salts would offer an opportunity to prepare the yet unknown hypofluorites, SO₄(OF)₂ and PO₄F₂(OF). However, both the SO₄⁻ and PO₄F₂⁻ anion were found to interact with anhydrous HF according to:

\[ \text{SO}_4^{2-} + 3\text{HF} \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O} + \text{HF}^- \]

and

\[ \text{PO}_4^{2-} + 4\text{HF} \rightarrow \text{PF}_6^- + 2\text{H}_2\text{O} \]

Attempts to prepare PO₄F₂(OF) by fluorination of HOPOF₂ with atomic fluorine, generated by the controlled decomposition of NF₄HF₂·H₂O, were also unsuccessful. The main products were NF₄PH₆³⁻ and an unidentified nonvolatile phosphorus oxyfluoride.
Although vibrational spectra have been reported \textsuperscript{31-33} for the $\text{PO}_2\text{F}_2^-$ anion, the previous assignment of several fundamentals is open to question. Figure 2 and Table 2 summarize the vibrational spectra of CsPO$_2$F$_2$, obtained in our study. The given assignment was made by analogy with that of isoelectronic $\text{SO}_2\text{F}_2$ which is well established. \textsuperscript{37-39} Whereas, the splitting of $\nu_8(B_2)$ can easily be explained by Fermi resonance with $\nu_4 + \nu_9(B_2)$, the reason for the observed splitting of $\nu_4$ is less obvious. The possibility of one of the components assigned to $\nu_4$ actually being due to the $\nu_5(A_2)$ torsional mode cannot be ruled out, but is unlikely due to the facts that this mode should be infrared inactive under $C_{2v}$ selection rules and usually is of such low intensity in the Raman spectra that it is very difficult to observe.

In summary, the present study shows that within the isoelectronic series, ClO$_4^-$, SO$_3$F$^-$, PO$_2$F$_2^-$, SO$_4^{2-}$, the first two anions are capable of forming NF$_4^+$ salts of moderate stability which can decompose to NF$_3$ and the corresponding hypofluorites. The syntheses of NF$_4$PO$_2$F$_2$ and (NF$_4$)$_2$SO$_4$ by metathesis in HE was prevented by the reaction of PO$_2$F$_2^-$ and SO$_4^{2-}$ with the solvent to yield PF$_6^-$ and SO$_3$F$^-$, respectively.

Acknowledgement. The authors thank Drs. L. R. Grant and W. W. Wilson for helpful discussions and to the Office of Naval Research, Power Branch, and the Army Research Office for financial support of this work.
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H-8
Table 1. Raman Spectra of NF$_4$SO$_3$F and CsSO$_3$F

<table>
<thead>
<tr>
<th>Obsd freq, cm$^{-1}$, and rel intensity$^a$</th>
<th>NF$_4$SO$_3$F</th>
<th>CsSO$_3$F</th>
<th>Assignment (point group)</th>
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</thead>
<tbody>
<tr>
<td>HF solution solid</td>
<td>1277 (0.7)</td>
<td>1278 (0.7)</td>
<td>$v_4$ (E)</td>
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<tr>
<td></td>
<td>1267 (0.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1165 (0.4)</td>
<td>1166 (1.3)</td>
<td>$v_3$ (F$_2$)</td>
</tr>
<tr>
<td></td>
<td>1152 (1.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1087 (6.7)$p$</td>
<td>1083 (10)</td>
<td>1076 (10)</td>
<td>$v_1$ (A$_1$)</td>
</tr>
<tr>
<td>853 (10)$p$</td>
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<td>749 (1.1)</td>
<td>$v_1$ (A$_1$)</td>
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<td>738 (0.8)</td>
<td>719 (1.2)</td>
<td>$v_2$ (A$_1$)</td>
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<tr>
<td>612 (3)</td>
<td>612 (6)</td>
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<td>$v_4$ (F$_2$)</td>
</tr>
<tr>
<td>575 (1.2)</td>
<td>584 (1.7)</td>
<td>582 (2)</td>
<td>$v_5$ (E)</td>
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<tr>
<td></td>
<td>563 (2.5)</td>
<td>560 (2.2)</td>
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<tr>
<td>446 (2.8)</td>
<td>450 (4)</td>
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<td>400 (1)</td>
<td>415 (2.5)</td>
<td>406 (3.8)</td>
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<tr>
<td></td>
<td>404 (2.3)</td>
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(a) uncorrected Raman intensities
<table>
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<tr>
<th>Obsc freq, cm(^{-1}) and rel intens</th>
<th>Assignment (point group C(_{2v}))</th>
<th>Approximate description of mode</th>
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<tr>
<td>CsPO(_4)F(_2)</td>
<td>SO(_2)F(_2)</td>
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<td>Raman</td>
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<td>1142 vs</td>
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<td>1270 vs</td>
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<td>313 (31.7)</td>
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<tr>
<td>516 (6.0)</td>
<td>520 sh</td>
<td>552 m</td>
</tr>
<tr>
<td>370 sh</td>
<td></td>
<td>391 m</td>
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<tr>
<td>553 (5.7)</td>
<td>351 m</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>1513 (0.4)</td>
<td>1523 vs</td>
<td>1504 w</td>
</tr>
<tr>
<td>501 (2)</td>
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<td>539 m</td>
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<tr>
<td>850 (0.7)</td>
<td>850 sh</td>
<td>888 w</td>
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<tr>
<td>830 (1.2)</td>
<td>825 vs</td>
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<tr>
<td>501 (2)</td>
<td>503 s</td>
<td>544 m</td>
</tr>
</tbody>
</table>

\(^a\) Data from this study; uncorrected Raman intensities; since \(\nu_7\) and \(\nu_9\) have very similar frequencies and intensities, their assignments are tentative.

\(^b\) Data from ref. 36-38

\(^c\) From microwave data, ref. 37

\(^d\) In Fermi resonance with \(\nu_{A1} F_2 = 598 \text{ cm}^{-1}\)
Diagram Captions

Figure 1. Raman spectra of $\text{NF}_4\text{SO}_3\text{F}^-$. Upper trace, HF solution at $25^\circ\text{C}$, middle trace, neat solid at $-100^\circ\text{C}$. Weak bands due to the sample tubes and small amounts of CsSbF$_6$ were subtracted from the spectra. Bottom trace, solid CsSO$_3$F at $25^\circ\text{C}$. The spectra were recorded with spectral slitwidths of 8, 6 and 4 cm$^{-1}$, respectively.

Figure 2. Raman spectrum of solid CsPO$_2$F$_2$ recorded at $25^\circ\text{C}$ with a spectral slit width of 5 cm$^{-1}$. 
APPENDIX I

SYNTHESIS AND PROPERTIES OF NF₄⁺UF₅O⁻

William W. Wilson, Richard D. Wilson and Karl O. Christe*

Received . . . .

Abstract

A new method for the synthesis of NF₄⁺ salts is reported. It permits the synthesis of otherwise inaccessible salts derived from nonvolatile Lewis acids which do not possess HF-soluble cesium salts. The method was successfully applied to the synthesis of the novel salt NF₄⁺UF₅O⁻. This compound is a yellow solid, stable at room temperature. It was characterized by analysis and vibrational spectroscopy.

Introduction

Most NF₄⁺ salts, derived from volatile strong Lewis acids, can be prepared directly from NF₃, F₂ and the Lewis acid in the presence of a suitable activation energy source [1,2]:

\[
\text{NF}_3 + F_2 + X F_n \xrightleftharpoons{\Delta E} NF_4^+ X F_{n+1}^-
\]

If the Lewis acid is polymeric and nonvolatile, its NF₄⁺ salt can usually be prepared by an indirect metathetical process [3,4], provided a compatible solvent is available in which the starting materials are soluble and one of the products is insoluble. This metathetical approach has been demonstrated for several NF₄⁺ salts [3 - 7]. A typical example is the synthesis of \((\text{NF}_4)_2\text{NiF}_6\) in anhydrous HF solution [7] using the cesium salts. The latter salts are preferred because they exhibit the most favorable solubility products for a metathesis in HF[4]:

\[
\text{Cs}_2\text{NIF}_6 + 2\text{NF}_4\text{SbF}_6 \rightarrow 2\text{CsSbF}_6^+ + (\text{NF}_4)_2\text{NiF}_6
\]

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However, in cases where the corresponding cesium salt starting material or both products are insoluble in the solvent and the Lewis acid is nonvolatile, neither one of the above approaches can be used. In this paper a method which circumvents these problems is described and is applied to the synthesis of the novel salt $\text{NF}_4\text{UF}_5^-$. 

**Experimental**

**Materials and Apparatus.** The equipment, handling techniques, and spectrometers used in this study have previously been described [8]. Literature methods were used for the syntheses of $\text{UF}_4$[9], $\text{KUF}_5$[10], and $\text{NF}_4\text{SbF}_6$[3]. The CsF (American Potash) was fused in a platinum crucible and ground in the dry box. The IF (Matheson) was dried by treatment with $\text{F}_2$, followed by storage over $\text{BiF}_5$ to remove last traces of water [4].

**Preparation and Properties of $\text{NF}_4\text{UF}_5^-$.** In a typical experiment, a solution of $\text{NF}_4\text{IF}_2$ (12.5 mmol) in anhydrous HF (12.5g) was prepared from $\text{NF}_4\text{SbF}_6$ and CsF at -78°, as previously described [8], and added to $\text{UOF}_4$ (6.18 mmol). The resulting mixture was kept at -78° for 40 hours, then warmed to -31° for 6 hours with stirring, followed by removal of all volatile products in vacuo by slowly raising the temperature from -31° to 20°. A yellow solid residue (2.70 g, weight calcd for 6.18 mmol of $\text{NF}_4\text{UF}_5$=2.71 g) was obtained. This compound was stable at ambient temperature and of low solubility in HF. It was identified by elemental analysis and vibrational spectroscopy as $\text{NF}_4\text{UF}_5^-$. For the elemental analysis, a weighed amount of sample was hydrolyzed in $\text{H}_2\text{O}$ and the NF$_3$ evolution was measured [12]. The hydrolysate was analyzed for Cs and Sb by atomic absorption spectroscopy, and for U gravimetrically as U$_3$O$_8$. Based on this analysis, the composition (weight %) of the yellow solid was: $\text{NF}_4\text{UF}_5$, 96.8; $\text{NF}_4\text{SbF}_6$, 1.7; CsSbF$_6$, 1.4.

The thermal decomposition of $\text{NF}_4\text{UF}_5^-$ was studied in a sapphire reactor, equipped with a pressure transducer. The onset and rate of decomposition was determined by total pressure measurements [13] in a closed system over the temperature range 40-60°. For the determination of the decomposition products,
a sample of NF$_4$UF$_5$O (2 mmol) was rapidly heated to 150°F in a dynamic vacuum, and the volatile products were collected in traps, cooled to -126°C and -210°C, and were identified by their infrared spectra. The -126°C trap contained 1.1 mmol of UF$_6$, and the contents of the -210°C trap consisted of 1.5 mmol of NF$_3$ and a small amount of OF$_2$. The infrared spectrum of the pale yellow solid residue (350 mg) showed strong bands characteristic for UF$_4$O$_3$ [9], UF$_2$F$_3$ [14], NF$_4$$^+$ [2-8], and two broad bands at 520 and 410 cm$^{-1}$, probably due to UF$_n$ vibrations. In addition, the spectrum indicated the presence of a small amount of UF$_5$O$^-$ [10,11].

Results and Discussion

Synthesis. The metathetical synthesis of NF$_4$UF$_5$O according to

\[ \text{HF} \quad \text{NF}_4\text{SbF}_6 + \text{MUF}_5 \rightarrow \text{M}_5\text{SbF}_6 \quad + \quad \text{NF}_4\text{UF}_5 \]

was not possible because both the MUF$_5$O (M = alkali metal) and NF$_4$UF$_5$O salts possess very low solubilities in anhydrous HF. Furthermore, in agreement with a previous report [10], we could not prepare a well defined CsUF$_5$O salt by the reaction of CsF with UF$_4$O in anhydrous HF solution. The product always contained a large amount of unreacted UF$_4$O. Attempts to obtain reasonably pure NF$_4$UF$_5$O by a metathetical reaction using stoichiometric amounts of UF$_4$O, CsF, and NF$_4$SbF$_6$ in HF as starting materials, were also unsuccessful due to the unfavorable solubilities. However, preparation of an HF solution of NF$_4$HF$_2$ [8] according to

\[ \text{HF} \quad \text{NF}_4\text{SbF}_6 + \text{CsHF}_2 \rightarrow -78^\circ \quad \text{NF}_4\text{HF}_2 \quad + \quad \text{CsSbF}_6 \]

followed by removal of the insoluble CsSbF$_6$ by filtration at -78°C and addition of this solution to UF$_4$O, resulted in NF$_4$UF$_5$O of about 97% purity.

\[ \text{HF} \quad \text{NF}_4\text{HF}_2 \quad + \quad \text{UF}_4 \rightarrow \quad \text{NF}_4\text{UF}_5 \quad + \quad \text{HF} \]

A twofold excess of NF$_4$HF$_2$ was used to ensure complete conversion of UF$_4$O to UF$_5$O$^-$. After solvent removal, the excess of unreacted NF$_4$HF$_2$ was decomposed [8] at 40°C to NF$_5$, F$_2$ and HF which were pumped off.
Properties. \( \text{NF}_4\text{UF}_5\text{O} \) is a yellow, crystallinic solid, stable up to about 50°C. Its composition was established by elemental analysis. The ionic nature of the salt was demonstrated by vibrational spectroscopy which showed the presence of the \( \text{NF}_4^+ \) cation and \( \text{UF}_5\text{O}^- \) anion. For comparison, a sample of \( \text{KUF}_5\text{O} \) was prepared from KF and \( \text{UF}_4\text{O} \) in HF, as previously reported [10] and its spectra were also recorded. The infrared spectra of \( \text{NF}_4\text{UF}_5\text{O} \) and \( \text{KUF}_5\text{O} \) are shown in Figure 1, and the observed infrared and Raman frequencies are summarized in Table 1. Whereas the infrared spectrum of \( \text{KUF}_5\text{O} \) is in good agreement with those [10,11] previously reported, the recording of a Raman spectrum with the available exciting line (4880 Å) was very difficult due to fluorescence, strong color and poor scattering. For \( \text{NF}_4\text{UF}_5\text{O} \), a similar, but not quite as severe, problem existed. Based on some of the Raman bands, observed for \( \text{UF}_5\text{O}^- \) in \( \text{NF}_4\text{UF}_5\text{O} \), and by comparison with the well defined infrared bands, it appears that some of the Raman bands previously reported [10] for \( \text{KUF}_5\text{O} \) are open to question.

The assignments of the bands due to \( \text{NF}_4^+ \) are well established [2-8] and require no further discussion. For the \( \text{UF}_5\text{O}^- \) anion, only the stretching vibrations can be assigned with some confidence. The band in the 810-835 cm\(^{-1} \) region occurs at too high a frequency for a U-F stretching mode and, therefore, is assigned to the UO stretch. The intensity and band width of the 580-600 cm\(^{-1} \) band in both the infrared and Raman spectra are comparable to those of the UO stretch and is therefore, assigned to the unique UF stretching mode. The broad intense infrared band at about 490 cm\(^{-1} \) should represent the antisymmetric UF\(_4^+ \) stretch, and the strong Raman band at about 490 cm\(^{-1} \) is assigned to the symmetric in-phase UF\(_4^+ \) stretching mode. The weak infrared band at about 430 cm\(^{-1} \) could be due to either the symmetric out-of-phase UF\(_4^+ \) stretching mode \( \nu_3(B_1) \), (assuming that for the solid the site symmetry of \( \text{UF}_5\text{O}^- \) is lower than \( C_{4v} \)), or the OUF\(_4 \) deformation mode \( \nu_9(E) \). However, for the latter assignment, the frequency appears somewhat high and is shifted in the wrong direction when going from \( \text{KUF}_5\text{O} \) to \( \text{NF}_4\text{UF}_5\text{O} \). Due to the stronger anion-cation interaction in \( \text{KUF}_5\text{O} \), the stretching modes are expected to be shifted to lower and the deformation modes to higher frequencies.

The thermal decomposition of \( \text{NF}_4\text{UF}_5\text{O} \) was studied in more detail since the decomposition of \( \text{NF}_4^+ \) salts containing oxyanions has been shown [8, 15, 16].
to be a useful synthetic route to hypofluorites. The $\text{NF}_4\text{UF}_5\text{O}$ salt is stable up to about 50°C, but started to decompose in a sapphire reactor at 60°C at an approximately linear rate, resulting in a pressure build-up of about 4.6 mm Hg per hour for a 2 mmol sample in a 38.7 cc volume. The nature of the decomposition products was established by rapid pyrolysis at 150°C in a dynamic vacuum. The main decomposition products, condensable at -210°C, were $\text{NF}_3$, $\text{UF}_6$, and a small amount of $\text{UF}_2$. The pale yellow solid residue contained $\text{UF}_4\text{O}$ and $\text{UO}_2\text{F}_2$ as the major products. The formation of $\text{UF}_4\text{O}$, $\text{UF}_6$, and $\text{UO}_2\text{F}_2$ as main decomposition products can be readily explained by assuming

$$\text{NF}_4\text{UF}_5\text{O} \rightarrow \text{NF}_3 + \text{F}_2 + \text{UF}_4\text{O}$$

as the primary decomposition step, followed by the well established [9, 17] decomposition of $\text{UF}_4\text{O}$

$$2\text{UF}_4\text{O} \rightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$$

The fact that the recovered amount of $\text{UF}_6$ exceeded that expected from this reaction sequence, can readily be explained by partial fluorination of $\text{UF}_4\text{O}$ or $\text{UF}_5\text{O}^{-}$ by the formed elemental fluorine.

Conclusion. The results of this study show that $\text{NF}_4^+$ salts which are derived from nonvolatile polymeric Lewis acids and are insoluble in HF, are accessible by treating the corresponding Lewis acid with an excess of $\text{NF}_4\text{HF}_2$ in HF solution. Although this approach has so far been demonstrated only for $\text{UF}_4\text{O}$, it might be of general use.

Acknowledgement. The authors are grateful to Drs. C. J. Schack and L. R. Grant for helpful discussions, to Mr. R. Rushworth for the elemental analyses, and to the Office of Naval Research, Power Branch, and the Army Research Office for financial support.
References

Figure 1. Infrared spectra of $\text{KI}_5\text{O}$ and $\text{NF}_3\text{UF}_5\text{O}$ recorded as dry powders pressed between AgCl disks. The broken lines represent absorption due to the AgCl window material.
APPENDIX J

SYNTHESIS AND CHARACTERIZATION OF (NF$_4$)$_2$MnF$_6$


Received . . .

Abstract

The synthesis of novel NF$_4^+$ salts containing doubly or triply charged third row transition metal fluoride anions, was studied. The new compound (NF$_4$)$_2$MnF$_6$ was prepared and characterized. The combination of good thermal stability and high active fluorine content makes (NF$_4$)$_2$MnF$_6$ an outstanding solid oxidizer.

Introduction

Due to the high energy content and high kinetic stability of the NF$_4^+$ cation,$^1$ NF$_4^+$ salts are important high-energy oxidizers, particularly for applications, such as solid propellant NF$_3$F$_2$ gas generators.$^2$-$^4$ In order to maximize the NF$_3$F$_2$ yields available from such salts, it is desirable to combine as many NF$_4^+$ cations as possible with a given anion. Furthermore, the anion should be as light as possible, contribute to the fluorine generation, and decompose to a nonvolatile fluoride, i.e. be "self-clinkerizing".$^4$ Of the presently known NF$_4^+$ salts,$^5$ (NF$_4$)$_2$NiF$_6$ has the highest active fluorine content and is self-clinkerizing. However, its marginal thermal stability limits its potential applications. Consequently, compounds of comparable fluorine content, but possessing better thermal stability, are highly desirable. This paper describes the results of a systematic study on the synthesis of NF$_4^+$ salts, derived from third row transition metal fluorides, and the successful synthesis of the novel (NF$_4$)$_2$MnF$_6$ salt.

Experimental

Materials and Apparatus. The equipment, handling techniques and spectrometers used in this study have previously been described.$^1$,$^5$ A literature method$^7$

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J-1
was used for the synthesis of \( \text{NF}_4 \text{SbF}_6 \). For the synthesis of \( \text{Cs}_2\text{MnF}_6 \), a previously reported method was slightly modified. Anhydrous \( \text{MnCl}_2 \) and dry \( \text{CsF} \), in a 1:2 mol ratio, were fluorinated in a Monel cylinder at \( 400^\circ\text{C} \) for 36 hours using a \( \text{MnCl}_2 : \text{F}_2 \) mol ratio of 1:10. Based on the observed material balance, elemental analysis, X-ray diffraction powder pattern, and vibrational spectra, the resulting yellow solid consisted of high purity \( \text{Cs}_2\text{MnF}_6 \).

The \( \text{Cs}_2\text{CuF}_6 \) salt was prepared by high pressure fluorination of a mixture of \( \text{CsF} \) and \( \text{CuCl}_2 \) in a 2:1 mol ratio. The conditions (\( 400^\circ\text{C}, 18 \text{ hours, 130 atm} \)) were similar to those previously reported. However, during unsuccessful attempts to prepare \( \text{Cs}_3\text{CuF}_6 \) in a similar manner, it was noticed that very mild fluorination conditions (flow reactor, \( 200^\circ\text{C} \)) sufficed to prepare \( \text{Cs}_2\text{CuF}_6 \). This brick-red compound was always formed as the major product, instead of the pale green \( \text{Cs}_3\text{CuF}_6 \). At the lower fluorination temperatures, the fluorination product also contained \( \text{CsClF}_4 \). The infrared spectrum of \( \text{Cs}_2\text{CuF}_6 \) showed major bands at 670, 570, 480 and 430 cm\(^{-1}\). The compatibility of \( \text{Cs}_2\text{CuF}_6 \) with different solvents was studied. In \( \text{BrF}_5 \), \( \text{Cs}_2\text{CuF}_6 \) is stable but highly insoluble, whereas in anhydrous HF, it is soluble but undergoes a reaction even at \( -78^\circ\text{C} \) resulting in the formation of a brown solid. When the \( \text{Cs}_2\text{CuF}_6 \)-HF solutions were warmed to room temperature, fluorine evolution was observed, in agreement with a previous report.

Preparation of \( (\text{NF}_4)_2\text{MnF}_6 \). Inside the \( \text{N}_2 \) atmosphere of a dry box a mixture of \( \text{NF}_4\text{SbF}_6 \) (37.29 mmol) and \( \text{Cs}_2\text{MnF}_6 \) (18.53 mmol) was placed into the bottom of a prepassivated (with \( \text{ClF}_3 \)) Teflon FEP double U-tube metathesis apparatus. Dry HF\(^{11} \) (20 ml liquid) was added at \( -78^\circ\text{C} \) on the vacuum line, and the mixture was warmed to \( 25^\circ\text{C} \) for 30 min with stirring. The mixture was cooled to \( -78^\circ\text{C} \) and pressure filtered at this temperature. The HF solvent was pumped off at \( 30^\circ\text{C} \) for 12 hours. The white filter-cake (14 g, weight calcd for 37.1 mmol of \( \text{CsSbF}_6 \)=13.7 g) was shown by Raman spectroscopy to consist mainly of \( \text{CsSbF}_6 \). The yellow filtrate residue (6.1 g, weight calcd for 18.5 mmol of \( (\text{NF}_4)_2\text{MnF}_6 \)=6.46 g) was shown by elemental analysis to have the following composition (weight %): \( (\text{NF}_4)_2\text{MnF}_6 \), 91.27; \( \text{NF}_4\text{SbF}_6 \), 4.27; \( \text{CsSbF}_6 \), 4.46. For the elemental analysis, a sample of \( (\text{NF}_4)_2\text{MnF}_6 \) was hydrolyzed in \( \text{H}_2\text{O} \), the \( \text{NF}_3 \) and \( \text{O}_2 \) evolution was measured by PVT and gas chromatography, and Cs, Sb, and Mn in the hydrolysate were determined by atomic absorption spectroscopy.

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Caution! The reaction of \((\text{NF}_4)_2\text{MnF}_6\) with \(\text{H}_2\text{O}\) is extremely violent, and proper safety precautions must be used.

The \(\text{CoF}_3\)–\(\text{NF}_4\text{HF}_2\) System. A suspension of \(\text{CoF}_3\) (231 mg = 2 mmol) in a freshly prepared concentrated \(\text{NF}_4\text{HF}_2-\text{HF}\) solution \(^5\) (15 mmol of \(\text{NF}_4\text{HF}_2\)) was stirred at \(-45^\circ\text{C}\) for 4 hours. The tan colored \(\text{CoF}_3\) did not appear to react, and no evidence for the formation of pale blue \(\text{CoF}_6^{3-}\) was observed. The HF solvent was pumped off while allowing the mixture to warm slowly towards ambient temperature. At this temperature, the \(\text{NF}_4\text{HF}_2-\text{HF}\) underwent decomposition and was also pumped off. To assure complete decomposition of \(\text{NF}_4\text{HF}_2\), the mixture was warmed to \(45^\circ\text{C}\) for 4 hours in a dynamic vacuum. The tan solid residue (250 mg) was shown by vibrational spectroscopy to be unreacted \(\text{CoF}_3\).

Results and Discussion

In view of the marginal thermal stability of \((\text{NF}_4)_2\text{NiF}_6\) it was interesting to investigate the possibility of synthesizing other \(\text{NF}_4\) salts containing multiply charged anions derived from higher oxidation state transition metal fluorides. It was hoped to obtain a salt which would be comparable to \((\text{NF}_4)_2\text{NiF}_6\) in its active fluorine content, but possess better thermal stability. The following anions were considered most promising: \(\text{CuF}_6^{3-}\), \(\text{NiF}_6^{3-}\), \(\text{CoF}_6^{3-}\), \(\text{MnF}_6^{3-}\), \(\text{CuF}_6^{2-}\), \(\text{CoF}_6^{2-}\), and \(\text{MnF}_6^{2-}\).

Attempted Syntheses of \((\text{NF}_4)_3\text{MF}_6\) Salts. In a previous study, \(^10\) it was shown that all these triply charged anions undergo solvolysis in HF. Furthermore, it was found that \(\text{CuF}_6^{3-}\) decomposed with \(\text{F}_2\) evolution, and \(\text{NiF}_6^{3-}\) disproportionated with \(\text{NiF}_6^{2-}\) formation, but that for \(\text{CoF}_6^{3-}\) the solvolysis to \(\text{CoF}_4^{+2}\text{HF}_2^{2-}\) could be suppressed by the addition of a 10 to 20 fold excess of fluoride ion to the solution. In view of these results, a simple metathetical reaction of an \(\text{MF}_6^{3-}\) salt in HF solution according to

\[
\text{HF} + \text{NF}_4\text{SbF}_6 + \text{CsSbF}_6 \rightarrow \text{CsSbF}_6 + (\text{NF}_4)_3\text{MF}_6
\]

is precluded by the unavoidable solvolysis of \(\text{NF}_4^{3-}\). However, the synthesis of a \(\text{NF}_4^{3-}\) salt might be possible in the presence of a large excess of fluoride.
ion, provided the excess of fluoride can be readily removed from the product. Such a method was recently discovered and successfully applied to the synthesis of $\text{NF}_4\text{UF}_5\text{O}$ according to

$$\text{NF}_4\text{HF}_2 + \text{UF}_4\text{O} \rightarrow \text{NF}_4\text{UF}_5\text{O} + \text{HF}$$

$\text{NF}_4\text{HF}_2$ is thermally unstable and decomposes at $30^\circ\text{C}$ to $\text{NF}_3\text{F}_2$ and $\text{HF}$, which are all gases. Therefore, the HF solvent can be pumped off first at low temperature, followed by decomposition and removal of the excess $\text{NF}_4\text{HF}_2$. Application of this method to the synthesis of $(\text{NF}_4)_2\text{CoF}_6$ according to

$$3\text{NF}_4\text{HF}_2 + \text{CoF}_3 \rightarrow (\text{NF}_4)_2\text{CoF}_6 + 3\text{HF}$$

was unsuccessful, and no evidence for the formation of a cobalt containing $\text{NF}_4^+$ salt was obtained. Only unreacted $\text{CoF}_3$ was recovered.

**Syntheses of $(\text{NF}_4)_2\text{MF}_6$ Salts.** Since the $\text{MF}_6^{2-}$ anions contain one negative charge less than the $\text{MF}_6^{3-}$ ones, they are less basic and, therefore, are less likely to undergo solvolysis in the strongly acidic solvent HF. The compatibility of $\text{TiF}_6^{2-}$ and $\text{NiF}_6^{2-}$ with HF has previously been demonstrated and led to the successful syntheses of $(\text{NF}_4)_2\text{TiF}_6^{13}$ and $(\text{NF}_4)_2\text{NiF}_6^{6}$. During this study the compatibility of $\text{Cs}_2\text{CuF}_6$ with HF was studied. It was found that $\text{Cs}_2\text{CuF}_6$ reacts, even at low temperature, with HF to form a dark brown solid. At room temperature, decomposition with fluorine evolution occurs. The compatibility of $\text{Cs}_2\text{CoF}_6$ with HF was not examined since Court had previously shown that this salt is unstable in HF solution.

In agreement with a previous report, $\text{MnF}_6^{2-}$ was found to be stable in HF solution. Consequently, the following metathetical reaction

$$2\text{NF}_4\text{SbF}_6 + \text{Cs}_2\text{MnF}_6 \rightarrow 2\text{CsSbF}_6 + (\text{NF}_4)_2\text{MnF}_6$$

was carried out which resulted in the isolation of the novel $(\text{NF}_4)_2\text{MnF}_6$ salt. This salt was obtained in high yield with a purity in excess of 90%. Since the by-products $\text{NF}_4\text{SbF}_6$ and $\text{CsSbF}_6$ are well characterized, no attempts were undertaken to purify the compound by well established recrystallization techniques.
Properties of (NF₄)₂MnF₆. The (NF₄)₂MnF₆ salt is a yellow, crystallinic solid which is highly soluble in anhydrous HF. At 24°C, its solubility exceeds 1.50 g per g HF. It is stable at room temperature and, in the absence of fuels, it is not shock sensitive. With water a violent reaction occurs, similar to that previously reported for (NF₄)₂NiF₆. By analogy with the other known NF₄ salts, the hydrolysis was found to result in quantitative NF₃ evolution and therefore, is a useful analytical method. The hydrolysis also produced oxygen in a NF₃:O₂ mole ratio of 8:5 in excellent agreement with the following equation:

\[ 4(NF₄)₂MnF₆ + 10H₂O \rightarrow 5NF₃ + 5O₂ + 20HF + 4MnF₅ \]

Thermal Decomposition. At 65°C, (NF₄)₂MnF₆ appears to be stable, but at about 100°C it starts to slowly decompose. Its decomposition rate in a sapphire reactor was monitored by total pressure measurements over the temperature range 100 to 130°C. Except for a slightly faster rate during the first 20 minutes, the decomposition pressures increased approximately linearly with time at 100°C. At 130°C the rates slightly accelerated with increasing time, however, this rate increase was quite small. At 100°C 0.17% of the sample decomposed in 17 hours, whereas, at 130°C 0.66% of the sample decomposed in the same time. The gaseous decomposition products consisted of NF₃ and F₂ in a mol ratio of about 1 to 1.2. For identification of the solid residue, a sample of (NF₄)₂MnF₆ was completely decomposed in a dynamic vacuum at 240°C. Based on its weight, X-ray powder diffraction pattern and mauve color, this residue was identified as MnF₃. Consequently, (NF₄)₂MnF₆ decomposes according to

\[ 2(NF₄)₂MnF₆ \rightarrow 4NF₃ + 5F₂ + 2MnF₃ \]

A comparison with the decomposition data previously published for (NF₄)₂NiF₆ shows that the thermal stability of (NF₄)₂MnF₆ is significantly higher than that of (NF₄)₂NiF₆ which in 6 hours at 100°C exhibited 9% decomposition.

Crystallographic Data. The X-ray powder diffraction pattern of (NF₄)₂MnF₆ is listed in Table 1. The pattern was indexed in the tetragonal system and
shows that the compound is isotypic with the other known (NF₄)₂MF₆ (M=Ti, Ni, Ge, Sn)⁶,⁸,¹³,¹⁵ salts (see Table 2). As expected, the size of the unit cell decreases from (NF₄)₂TiF₆ to (NF₄)₂NiF₆ owing to the transition metal contraction and then increases again when going from Ni to the main-group elements.

**NMR Spectrum.** The ionic nature of (NF₄)₂MnF₆ in HF solution was established by its ¹⁹F NMR spectrum which was recorded over the temperature range +20 to -75°C. It showed at all temperatures a broad resonance at δ -218 (downfield from external CFCl₃), characteristic of NF⁺. The lack of observable NF spin-spin coupling, generally seen for tetrahedral NF₄,¹⁶,¹⁷ is attributed to the influence of the paramagnetic MnF₆²⁻ anion which can provide rapid relaxation.

**Vibrational Spectra.** The ionic nature of (NF₄)₂MnF₆ in the solid state was established by its vibrational spectra which exhibit the bands characteristic for NF⁺¹⁵ and MnF₂⁻¹⁸. Figure 1 shows the infrared spectrum of (NF₄)₂MnF₆, compared to that of Cs₂MnF₆. Great difficulties were encountered in obtaining good quality Raman spectra with the blue 4880 Å exciting line of our spectrometer due to strong luminescence¹⁸ (ruby red light emission). However, the principal Raman lines of NF⁺¹⁵ and MnF₂⁻¹⁸ were observable even under these conditions. The observed vibrational frequencies and their assignments are summarized in Table 3. Since the assignments of NF⁺¹⁵ and MnF₂⁻¹⁸ are well established, no further discussion is required.

**Summary.** The present study shows that, in HF solution, solvolysis preempts the metathetical synthesis of NF⁺ salts containing triply charged MF₆⁻ anions derived from third row transition metal fluorides. On the other hand, three NF⁺ salts derived from doubly charged MF₆⁻ anions are accessible by this method. These salts are (NF₄)₂TiF₆,¹³ (NF₄)₂MnF₆, and (NF₄)₂NiF₆. All of them are stable at room temperature, with (NF₄)₂NiF₆ possessing the lowest thermal stability. The existence of stable NF⁺ salts of TiF₆²⁻, MnF₆²⁻ and NiF₆²⁻ can be explained by the favorable d⁰, d³ (high spin) and d⁶ (low spin) electron configurations, respectively, of these anions. The combination of good thermal stability with high active fluorine content (1.485 g per cm³) renders (NF₄)₂MnF₆ a very attractive candidate for solid propellant NF₃⁻F₂ gas generator compositions.
Acknowledgement. The authors are indebted to Drs. C. J. Schack, L. R. Grant, and M. Lustig for helpful discussion, to Mr. R. Rushworth for the elemental analyses, and to the U. S. Army Missile Command and the Army Research Office for financial support.
References

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Tetragonal, a = 10.60Å, c = 11.10Å, V = 1246.7Å³, \( Z = 16/3 \), \( \rho \text{ calc'd} = 2.48 \text{ g cm}^{-3} \), CuK\(\alpha\) radiation and Ni filter.
Table 2. Crystallographic Data of (NF$_4$)$_2$MnF$_6$ Compared to Those of Other (NF$_4$)$_2$MF$_6$ Salts$^a$

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<td></td>
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<td>c,Å</td>
<td>V,Å$^3$</td>
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<tr>
<td>(NF$_4$)$_2$TiF$_6$$^b$</td>
<td>10.715</td>
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<td>1276.0</td>
<td>17.09</td>
<td>2.37</td>
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<td>(NF$_4$)$_2$MnF$_6$</td>
<td>10.597</td>
<td>11.102</td>
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<td>(NF$_4$)$_2$NiF$_6$$^c$</td>
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<td>2.73</td>
</tr>
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</table>

---

$^a$ For all compounds Z = 16/3.

$^b$ Reference 13.

$^c$ Reference 6.

$^d$ Reference 15.

$^e$ Reference 8.
### Table 3. Vibrational Spectra of Solid \((\text{NF}_4)_2\text{MnF}_6\) and \(\text{Cs}_2\text{MnF}_6\)

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<td>(\text{Cs}_2\text{MnF}_6)</td>
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<td>IR</td>
<td>RA</td>
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<tr>
<td>2310vw</td>
<td>2000w</td>
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<tr>
<td>2(v_3(A + E + F_2))</td>
<td>(v_1 + v_3(F_2))</td>
</tr>
<tr>
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<td>1160vs</td>
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<td>450vw</td>
<td></td>
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<tr>
<td>338s</td>
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</table>

\(a\) uncorrected Raman intensities

\(b\) the actual site symmetries of \(\text{NF}_4^+\) and \(\text{MnF}_6^{-}\) in \((\text{NF}_4)_2\text{MnF}_6\) are probably lower than \(T_d\) and \(O_7\), respectively, as indicated by the large unit cell \((Z=16/3)\) and the observed slight deviations from the selection rules. However, since the actual site symmetries are unknown, the assignments are given for the idealized point groups.

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Diagram Caption

Figure 1. Infrared spectra of solid $\text{Cs}_2\text{MnF}_6$ and $(\text{NF}_4)_2\text{MnF}_6$ recorded at $25^\circ$ as dry powders pressed between AgCl disks. The broken lines indicate absorption due to the window material.
APPENDIX K

VIBRATIONAL SPECTRA OF \(^{15}NF_4^+AsF_6^-\) AND GENERAL VALENCE FORCE FIELD OF NF\(^+\)

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Canoga Park, California 91304

(Received . . .)

Abstract

Samples of \(^{14}NF_4\)AsF\(_6\) and \(^{15}NF_4\)AsF\(_6\) were prepared by low-temperature uv-photolysis and their vibrational spectra were recorded. The observed spectra are in agreement with space group P4/n for NF\(_4\)AsF\(_6\) and site symmetries of S\(_4\) and C\(_4\) for NF\(^+\) and AsF\(_6^-\), respectively. The observed \(^{14}N - ^{15}N\) isotopic shifts were used to compute a general valence force field for NF\(_4^+\).

Introduction

Since the first report [1,2] on the existence of NF\(_4^+\) salts numerous papers [3-25] dealing with NF\(_4^+\) chemistry have been published. The vibrational spectrum of NF\(_4^+\) is well known [5, 7-9, 13-15, 17-19], and its force field has been computed [5,7]. However, the earlier work permitted only computation of an approximate force field, since the F\(_2\) block has two fundamentals and three symmetry force constants. In view of the general interest in the NF\(_4^+\) cation, the computation of a general valence force field was highly desirable. In addition, it was hoped that the vibrational spectra might allow the determination of the space group of NF\(_4\)AsF\(_6\).

Experimental

The samples of \(^{14}NF_4\)AsF\(_6\) and \(^{15}NF_4\)AsF\(_6\) were prepared by low-temperature uv-photolysis of mixtures of F\(_2\), AsF\(_5\) and \(^{14}NF_3\) or \(^{15}NF_3\), respectively, in a quartz reactor, using a previously described method [15]. The \(^{15}NF_3\) starting material was prepared by glow-discharge of \(^{15}N_2\) (99% \(^{15}N\), Stohler Isotope Chemicals) and F\(_2\) (Rocketdyne), as previously described [26]. Volatile materials were handled in a stainless steel Teflon-FEP vacuum system and solids in the dry nitrogen atmosphere of a glove box.

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The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgCl disks in a Wilks mini press. The spectrometer was calibrated by comparison with standard gas calibration points [27,28]. The Raman spectra were recorded on Spex Ramalog and Cary Model 83 spectrophotometers using the 4880Å exciting line and quartz tubes as sample containers. The reported frequencies and isotopic shifts are believed to be accurate to ± 1 and ± 0.1 cm⁻¹, respectively.

Results and Discussion

The sample of $^{15}$NF₄AsF₆ was of high isotopic purity and its vibrational spectra did not exhibit any detectable bands due to the $^{14}$N isotope. To determine the $^{14}$N - $^{15}$N isotopic shifts, the corresponding $^{14}$N salt was prepared and studied by vibrational spectroscopy under identical conditions. Since the $^{15}$N salt spectra were identical to those previously published for the $^{14}$N salt [15], except for the isotopic shifts observed for $\nu_3$ and $\nu_4$ of NF⁺⁺, the actual spectra are not shown. The observed frequencies, $^{14}$N - $^{15}$N isotopic shifts and assignments are summarized in Table 1.

Although the assignments given in Table 1 were made for simplicity for tetrahedral NF⁺⁺ and octahedral AsF⁻⁻, the observed splittings of the degenerate modes and deviations from the $T_d$ and $O_h$ selection rules indicate that the actual site symmetries of the NF⁺⁺ and AsF⁻⁻ ions must be lower than $T_d$ and $O_h$, respectively. Unfortunately, the exact crystal structure of NF₄AsF₆ is unknown, however, based on its reported x-ray powder diffraction data [4], NF₄AsF₆ appears to be isotypic with PC1₄⁺PCl₆⁻ which belongs to space group P4/n (C₄h, Nr.85) [29,30]. In this space group, the NF⁺⁺ cation would occupy sites of symmetry $S_4$. As can be seen from comparison of Tables I and II, the observed NF⁺⁺ bands agree well with the predictions for $S_4$ site symmetry, but not with those for $D_2$ or $D_{2d}$. Similarly, the deviations from the $O_h$ selection rules, observed for AsF⁻⁻, are compatible with a site symmetry of $C_4$ (see Table III), but not with $D_{2d}$, $D_{2h}$, $D_2$ or $S_4$. Based on these results, alternate probable space groups, such as P4/nmm, P4₂/n, P4₂22, P4₂/mmc, P4/mnc, P4₂/mmm or P4/m, can be ruled out.
Since the A1 and E block of tetrahedral NF4+ contain only one fundamental vibration each, the values of the corresponding symmetry force constants are uniquely determined. For the F2 block which contains one stretching and one deformation mode, additional data, such as 14N - 15N isotopic shifts, are needed to allow the calculation of unique values for the three symmetry force constants.

In solid NF4AsF6 the F2 modes of NF4+ are split under S4 site symmetry into one B and one doubly degenerate E mode. Since the isotopic shifts of both modes are very similar (see Table II), weighting of the shifts can be neglected and a simple average was used. It should be pointed out however that in certain NF4+ salts, such as NF4BF4 [31], the 14N - 15N isotopic shifts of the v3(F2) components can differ by as much as 8 cm−1, thus requiring reliable mode assignments.

As expected from their G matrix elements, the 14N - 15N isotopic shifts of v1(A1) and v2(E) were found to be zero within experimental error. Those of v3(F2) and v4(F2) were measured to be 29.25± 0.25 and 1.8± 0.1 cm−1, respectively. These values were supported by preliminary measurements on 14NF4BF4 and 15NF4BF4 [31] which shows very similar averaged isotopic shifts for v3 and v4.

For the computation of the general valence force field of NF4+ the frequencies and isotopic shifts listed in Table 4 were used. For the F2 block, the possible ranges of the two diagonal symmetry force constants F33 and F44 and the 14N - 15N isotopic shifts of v3 and v4 were computed as a function of the interaction constant F34 by trial and error and by the use of the expressions previously reported [32] for the calculation of extremal force constant solutions. The results of these calculations are shown in Figure 1. The observed 14N - 15N isotopic shifts were used to graphically select the correct F2 block force field. The isotopic shift of v4 was preferred because, due to its smallness, anharmonicity corrections should be unimportant [33].

Since the slopes of the Δv3 and Δv4 versus F34 plots have opposite signs, the Δv4 range might be used as a rough estimate for the anharmonicity correction.
required for $\Delta v_3$. Figure 1 indicates an anharmonicity correction of about 1 cm$^{-1}$ for $\Delta v_3$, which is in line with previous estimates for similar molecules, such as NF$_3$ [34].

The general valence force field and the potential energy distribution (PED) of NF$_4^+$ are summarized in Table 4. The PED indicates significant mixing of $S_3$ and $S_4$, as expected [32, 36] for a strongly mass coupled system [32, 36]. The close agreement between the general valence force field of this study and the previously reported [5, 7] approximate force field is in line with Pfeiffer's analysis [37] which showed that for similar molecules the method of "step-wise coupling" gives the best agreement with the general valence force field values. A comparison of the NF stretching force constant of NF$_4^+$ (6.15 mdyn/Å) with those and the NF bond distances of FNO ($f_r = 2.15$ mdyn/Å, $r_{NF} = 1.512$ Å) and NF$_3$ ($f_r = 4.31$ mdyn/Å, $r_{NF} = 1.365$ Å) [35] suggests for NF$_4^+$ an unusually strong and short ($r \approx 1.24$ Å) NF bond.

Acknowledgement. The author is indebted to Drs. L. R. Grant, E. C. Curtis, C. J. Schack, and W. W. Wilson for useful discussions, to Mr. R. D. Wilson for experimental help, and to Dr. F. Purcell for the recording of some of the Raman spectra. This work was in part supported by the Office of Naval Research and the U. S. Army Research Office.
REFERENCES


Table 1. Vibrational Spectra of $^{14}$NF$_4$AsF$_6$ and $^{15}$NF$_4$AsF$_6$

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<th>AsF$_6^-$($O_h$)</th>
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(a) The site symmetry of NF$_4^-$ and AsF$_6^-$ in NF$_4$AsF$_6$ is $S_4$ and $C_4$, respectively (see text). However, since reliable assignments for the nearly degenerate vibrations cannot be made for $S_4$ and $C_4$, the observed spectra were assigned in point group $T_d$ and $O_h$, respectively.
Table II. Correlation Table for the Internal Vibrations of NF$_4^+$ in NF$_4$AsF$_6$

for Space Group P4/n and Z=2

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(a) Spectral activity
Table III. Correlation Table for the Internal Vibrations of AsF$_6^-$ in NF$_4$AsF$_6$ for Space Group P4/n and Z = 2

<table>
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<th>Site Group</th>
<th>Factor Group</th>
<th>Assignment</th>
</tr>
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<tr>
<td>$O_h$</td>
<td>$C_4$</td>
<td>$C_{4h}$</td>
<td>$\nu_{sym}$ AsF$_6^-$</td>
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<tr>
<td>$A_{1g}$</td>
<td>Ra</td>
<td>$A_g$, Ra</td>
<td>$A_g$, Ra</td>
</tr>
<tr>
<td></td>
<td>$A_{Ir}$, Ra</td>
<td>$A_u$, $I_{Ir}$, Ra</td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>Ra</td>
<td>$A_g$, Ra</td>
<td>$A_g$, Ra</td>
</tr>
<tr>
<td></td>
<td>$A_{Ir}$, Ra</td>
<td>$A_u$, $I_{Ir}$, Ra</td>
<td></td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>$I_r$, Ra</td>
<td>$E_g$, Ra</td>
<td>$E_g$, Ra</td>
</tr>
<tr>
<td></td>
<td>$E_{Ir}$, Ra</td>
<td>$E_u$, $I_{Ir}$, Ra</td>
<td></td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>$I_r$, Ra</td>
<td>$E_g$, Ra</td>
<td>$E_g$, Ra</td>
</tr>
<tr>
<td></td>
<td>$E_{Ir}$, Ra</td>
<td>$E_u$, $I_{Ir}$, Ra</td>
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</tr>
<tr>
<td>$F_{2g}$</td>
<td>Ra</td>
<td>$B_g$, Ra</td>
<td>$B_g$, Ra</td>
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<td></td>
<td>$E_{Ir}$, Ra</td>
<td>$E_u$, $I_{Ir}$, Ra</td>
<td></td>
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<tr>
<td>$F_{2u}$</td>
<td>$I_r$, Ra</td>
<td>$E_g$, Ra</td>
<td>$E_g$, Ra</td>
</tr>
<tr>
<td></td>
<td>$E_{Ir}$, Ra</td>
<td>$E_u$, $I_{Ir}$, Ra</td>
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</table>

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K-9
Table 4. Frequency Values, $^{14}_N - ^{15}_N$ Isotopic Shifts (cm$^{-1}$), General Valence Force Field$^a$ and Potential Energy Distribution for NF$_4^+$

<table>
<thead>
<tr>
<th></th>
<th>$\nu^{14}_{\text{NF}_4}$</th>
<th>$\nu^{15}_{\text{NF}_4}$</th>
<th>$\Delta \nu$</th>
<th>Symmetry Force Constants</th>
<th>PED</th>
</tr>
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<tbody>
<tr>
<td>A$_1$</td>
<td>$\nu_1$ 848.2</td>
<td>$\nu_1$ 848.2</td>
<td>0</td>
<td>$F_{11} = f_r + 3f_{rr} = 8.053$</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>$\nu_2$ 443.3</td>
<td>$\nu_2$ 443.3</td>
<td>0</td>
<td>$F_{22} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha} = 0.733$</td>
<td></td>
</tr>
<tr>
<td>F$_2$</td>
<td>$\nu_3$ 1158.95</td>
<td>1129.7 29.25$^{+0.25}$</td>
<td>$F_{33} = f_r - f_{rr} = 5.52^{+0.08}$</td>
<td>96F$<em>{33}$ + 43F$</em>{44}$ - 39F$_{34}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_4$ 611.15</td>
<td>609.35 1.8$^{+0.1}$</td>
<td>$F_{44} = f_\alpha - f_{\alpha\alpha} = 1.00^{+0.02}$</td>
<td>15F$<em>{33}$ + 67F$</em>{44}$ + 18F$_{34}$</td>
<td></td>
</tr>
</tbody>
</table>

$F_{34} = \sqrt{2} (f_{r\alpha} - f_{\alpha r}) = 0.73^{+0.03}$

$f_r = 6.153^{+0.1}$

$f_{rr} = 0.633^{+0.03}$

(a) Stretching, bending and stretch-bend interaction force constants have units of mdyn /Å, mdyn /Å radian$^2$ and mdyn /Å radian, respectively.
Figure 1. $F_2$ block force field (mdyn/Å) of NF$_4^+$. The diagonal symmetry force constants and $^{14}_N - ^{15}_N$ isotopic shifts are plotted as a function of the interaction constant $F_{34}$. The rectangles delineate the observed $^{14}_N - ^{15}_N$ isotopic shifts and their uncertainties. The broken vertical and solid horizontal lines indicate the resulting force constant ranges.
APPENDIX L

ASSAY OF NF₄⁺ SALTS OF COMPLEX FLUORO ANIONS

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ABSTRACT

The NF₄⁺ content of complex fluoro anion salts is reliably determined by quantitative measurement of the NF₃ evolved during hydrolysis using gasometric and chromatographic methods. The metal central atoms of the anions were determined by different techniques, including atomic absorption and x-ray fluorescence spectroscopy and gravimetry. The use of several semiquantitative methods and of qualitative methods for the detection of impurities or polyanions is briefly discussed.
APPENDIX M

Analysis of the Electron Paramagnetic Resonance Spectra of \( ^{14}\text{NF}_3^+ \) and \( ^{15}\text{NF}_3^+ \)

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ABSTRACT

Electron paramagnetic resonance spectra of \( ^{14}\text{NF}_3^+ \) and \( ^{15}\text{NF}_3^+ \) were analysed in detail using a computer simulation. The \(^{14}\text{N} \) or \(^{15}\text{N} \) hyperfine tensors were assumed to be axially symmetric, and parallel to the g-tensor. Three equivalent \(^{19}\text{F} \) hyperfine tensors were used in which the angle (\( \alpha \)) of the Z-component was allowed to vary with respect to the molecular symmetry axis. Values of the hyperfine couplings were in reasonable agreement with those derived from an approximate analysis of the spectra. The best value of \( \alpha \) was found to be \( 15 \pm 0.5^\circ \) indicating that the planarity of \( \text{XF}_3 \) radicals decreases in the sequence: \( \text{NF}_3^+ \), \( \text{CF}_3^- \), \( \text{BF}_3^- \). Some variation in the couplings in \( ^{14}\text{NF}_3^+ \) and \( ^{15}\text{NF}_3^+ \) was observed, and may be the result of slight molecular oscillations.
<table>
<thead>
<tr>
<th>Hyperfine Couplings of $\text{NF}_3^+$ (MHz)</th>
<th>$^{14}\text{NF}_3^+$</th>
<th>$^{15}\text{NF}_3^+$</th>
<th>$^{15}\text{NF}_3^+$</th>
<th>$\alpha(\text{N})/\text{MHz}$</th>
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<tbody>
<tr>
<td>$A_N(1)$</td>
<td>113.0</td>
<td>100.0</td>
<td>-135.0</td>
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<tr>
<td>$A_N(11)$</td>
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<td>317.0</td>
<td>-463.3</td>
<td>330.2</td>
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<tr>
<td>$A_N^{\text{iso}}$</td>
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<td>$A_F(x)$</td>
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<td>$A_F(y)$</td>
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<td>(-)80.0</td>
<td>(-)84.5</td>
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<td>$A_F^{\text{iso}}$</td>
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<td>$g(1)$</td>
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<tr>
<td>$g(11)$</td>
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<td>2.0060</td>
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<td>$g^{\text{iso}}$</td>
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<tr>
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<td>14.5°</td>
<td>14.5°</td>
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