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# SYNTHESES OF $NF_4^+$ SALTS DERIVED FROM THE LEWIS ACIDS $AlF_3$ AND $BeF_2$

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## SUMMARY

The new salts $NF_4Be_2F_5$ and $NF_4AlF_4$ were prepared from concentrated $NF_4HF_2$ solutions and $BeF_2$ and $AlF_3$ respectively.

## INTRODUCTION

Salts containing the $NF_4^+$ cation are of significant practical interest for high detonation pressure explosives [1] or solid-propellant $NF_3$-$F_2$ gas generators for chemical lasers [2]. For these applications, it is desirable to maximize the usable fluorine content, expressed as weight percent of fluorine available as $F_2$ or $NF_3$ upon thermal decomposition of the salt. Optimization of the usable fluorine content is best achieved by the selection of an anion which is as light as possible, is multiply charged and, if possible, is itself an oxidizer capable of fluorine evolution. Of the presently known $NF_4^+$ salts, $(NF_4)_2NiF_6$ (64.6%), $(NF_4)_2MnF_6$ (59.9%), $(NF_4)_2SiF_6$ (59.0%), $(NF_4)_2TiF_6$ (55.6%) and $NF_4BF_4$ (53.7%) have the highest usable fluorine contents. Theoretically, a further increase in the usable fluorine content of $NF_4^+$ salts should be possible by the use of the very light and multiply charged anions, $BeF_4^{2-}$ and $AlF_6^{3-}$. Their $NF_4^+$ salts would have a usable fluorine content of 71.7 and 69.3 percent, respectively. In this paper, we report on the syntheses of $NF_4^+$ salts containing anions derived from $BeF_2$ and $AlF_3$.

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## EXPERIMENTAL

Apparatus Volatile materials used in this work were handled in a stainless steel-Teflon FEP vacuum line. The line and other hardware used were well passivated with $ClF_3$ and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter [3].

Infrared spectra were recorded in the range 4000-200 $cm^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Company). Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar-ion laser and Claassen filter [4] for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Elemental analyses were carried out as previously described [5].

Materials Literature methods were used for the syntheses of $NF_4SbF_6$ [6] and $NF_4HF_2$ solutions in HF [7]. Hydrogen fluoride (Matheson) was dried by storage over $BiF_5$ to remove the $H_2O$ [8]. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox. Beryllium difluoride was prepared by pyrolysis of $(NH_4)_2BeF_4$ at 270° to 360°C in a $N_2$ flow tube using Al boats as sample containers. The $(NH_4)_2BeF_4$ was prepared by combining solutions of beryllium metal in 12% aqueous HF and of $NH_4HF_2$ (15% excess) in 5% aqueous HF. Most of the solvent was evaporated at 120°C and the resulting slurry was filtered at 0°C, washed three times with an ice cold 20% ethanol solution, and dried at 110°C for 24 hours. The purity of $BeF_2$ and $(NH_4)_2BeF_4$ was checked by vibrational spectroscopy, and no impurities could be detected. Aluminum trifluoride was prepared by treating freshly sublimed $AlCl_3$ twice with a large excess of anhydrous HF at ambient temperature, followed by removal of HCl and the excess of HF in vacuo at elevated temperature.

Preparation of $NF_4Be_2F_5$ Dry CsF (30.34 mmol) and $NF_4SbF_6$ (30.47 mmol) were loaded in the drybox into one half of a prepassivated Teflon double-U metathesis apparatus. Dry HF (20 ml) was added on the vacuum line and the mixture was stirred with a Teflon coated magnetic stirring bar for 15 minutes at 25°C. After cooling the apparatus to -78°C, it was inverted, and the $NF_4HF_2$ solution was filtered into the other half of the apparatus which contained 12.14 mmol of $BeF_2$. The mixture was stirred for 65 hours at 25°C, followed by removal of most of the HF until the onset of $NF_4HF_2$ decomposition became noticeable. The concentrated mixture was stirred at 25°C for 14 hours and a clear, colorless solution resulted. All volatile materials were pumped off at 55°C for 15 hours, leaving behind a white solid (1.448g, 97% yield based on $BeF_2$) which, based on its elemental analysis, had the following composition (weight %): $NF_4BeF_3 \cdot 1.06BeF_2$, 84.06; $NF_4SbF_6$, 11.23; $CsSbF_6$ 4.71. Anal. Calcd: $NF_3$, 31.45; Be, 7.58; Cs, 1.70; Sb, 5.75. Found: $NF_3$, 31.43; Be, 7.58; Cs, 1.69; Sb, 5.74.

Preparation of $NF_4AlF_4$ Freshly prepared $AlF_3$ (0.469g, 5.58 mmol) was combined with $NF_4HF_2$ (generated as described above from 33.8 mmol of $NF_4SbF_6$) in 35 ml of HF. The mixture was stirred at 25°C for 1 hour, then most of the HF solvent was pumped off until incipient decomposition of $NF_4HF_2$ became noticeable. After stirring for 2 hours at 25°C, this concentrated mixture turned into a clear solution. The remaining HF solvent and the excess of $NF_4HF_2$ were removed at 55°C for 40 hours in a dynamic vacuum. The weight (1.257g) of the solid white residue agreed with that expected for 5.58 mmol of $NF_4AlF_4$ (1.077g) containing, as in the case of the analagous $NF_4Be_2F_5$ preparation, about 17 weight % of $NF_4SbF_6$ and $CsSbF_6$. The presence of these ions was confirmed by vibrational spectroscopy which also demonstrated the absence of any unreacted $NF_4HF_2$.

## RESULTS AND DISCUSSION

The syntheses of $(NF_4)_2BeF_4$ and $(NF_4)_3AlF_6$ by direct methods involving $NF_3$, $F_2$ and the corresponding Lewis acid in the presence of an activation energy source [9] is not possible because $BeF_2$ and $AlF_3$ are nonvolatile polymeric solids. Simple metatheses

$$M_3AlF_6 + 3NF_4SbF_6 \xrightarrow{\text{solvent}} 3MSbF_6\downarrow + (NF_4)_3AlF_6$$

were also investigated where M was either Cs or Na and the solvents were either $BrF_5$ at 25°C, HF at -78°C or molten $NF_4SbF_6$ at 275°C under 1000 psi

$NF_3$ and $F_2$ pressure. In all cases, no evidence for $(NF_4)_3AlF_6$ was obtained, probably because the $AlF_6^{3-}$ and $BeF_4^{2-}$ anions are very strong Lewis bases which undergo rapid solvolysis, such as

$$AlF_6^{3-} + 2HF \rightarrow 2HF_2^- + AlF_4^-$$

This metathetical approach was further complicated by the fact that the $AlF_4^-$ salts appear to be quite insoluble and therefore cannot be separated from the highly insoluble alkali metal $SbF_6^-$ salts. Since previous studies in our laboratory had demonstrated that these solubility and separation problems can be overcome by digesting a polymeric insoluble Lewis acid, such as $UOF_4$ [10] or $WOF_4$ [11], in a large excess of a highly concentrated $NF_4HF_2$ solution, this approach was also applied to $AlF_3$ and $BeF_2$.

The concentrated solutions of $NF_4HF_2$ in HF were prepared according to

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

followed by its addition to either $AlF_3$ or $BeF_2$. After digesting these mixtures at 25°C until clear solutions were obtained, the excess of unreacted $NF_4HF_2$, which in the absence of a solvent is unstable at 25°C, was decomposed at 55°C

$$NF_4HF_2 \rightarrow NF_3 + F_2 + HF$$

and pumped off. Based on the observed material balances and spectroscopic and elemental analyses, the solid residues consisted of mainly $NF_4Be_2F_5$ and $NF_4AlF_4$ with some $NF_4SbF_6$ and $CsSbF_6$ as the expected impurities. Attempts to purify $NF_4AlF_4$ by recrystallization or extraction with HF were unsuccessful due to the low solubilities of the salts involved and due to solvolysis. It appears that the presence of a high $HF_2^-$ ion concentration is required to diminish the acidity of the HF solvent and to suppress the solvolyses of the strong Lewis bases $AlF_6^{3-}$, $AlF_4^-$ or $BeF_4^{2-}$. The fact that at the end of the digestion periods of $AlF_3$ or $BeF_2$ in HF solutions of $NF_4HF_2$ clear solutions were obtained, while $NF_4AlF_4$ and $NF_4Be_2F_5$ appear to possess only limited solubilities in HF, suggests the possibility that, in the presence of a large excess of $HF_2^-$, either $AlF_6^{3-}$ or $BeF_4^{2-}$ might exist in these solutions. Obviously, an excess of $HF_2^-$ should suppress the following solvolysis reactions

$$AlF_6^{3-} + 2HF \rightarrow AlF_4^- + 2HF_2^-$$

$$AlF_4^- + HF \longrightarrow AlF_3 + HF_2^-$$

Unfortunately the nature of the complex fluoro anions in these solutions could not be established because these anions are inherently poor Raman scatterers. Nor do they result in separate $^{19}F$ NMR signals due to rapid exchange with the HF solvent.

Although the above described experiments did not permit the isolation of either $(NF_4)_3AlF_6$ or $(NF_4)_2BeF_4$, they resulted in the syntheses of the new salts $NF_4Be_2F_5$ and $NF_4AlF_4$. The existence of the $Be_2F_5^-$ anion is well known, and the infrared spectrum observed for $NF_4Be_2F_5$ (see Figure 1) confirms the presence of $Be_2F_5^-$ [12]. Due to the poor scattering by the anion, the Raman spectrum of $NF_4Be_2F_5$ (see Figure 1) is dominated by the $NF_4^+$ lines. These lines are in excellent agreement with a tetrahedral $NF_4^+$ cation exhibiting splittings into the degenerate components of each mode due to site symmetry lowering or slight distortion of the cation. The assignments for $NF_4^+$ agree well with our previous observations [13] and are summarized in Table 1.

The results of this study demonstrates that, in principle, the synthesis of $NF_4^+$ salts containing complex fluoro anions derived from either $AlF_3$

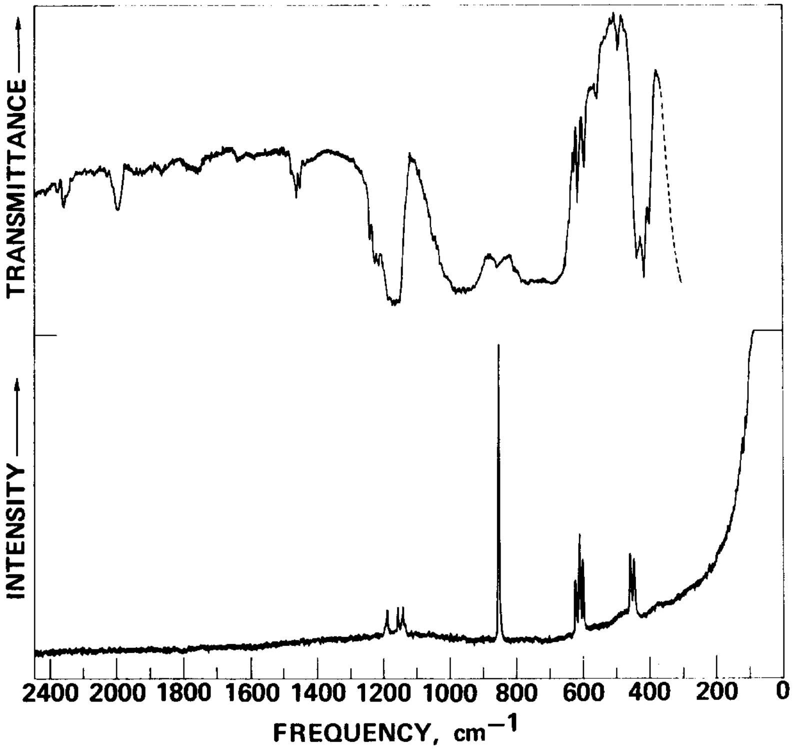

Fig. 1. Infrared and Raman Spectrum of Solid $NF_4Be_2F_5$

or $BeF_2$ is possible. However, the isolation of $NF_4^+$ salts containing the strongly basic $AlF_6^{3-}$ or $BeF_4^{2-}$ anions remains a challenge for the synthetic fluorine chemist.

TABLE 1

Vibrational Spectra of $NF_4Be_2F_5$

| Obsd freq, $cm^{-1}$ and rel. intens. | | Assignment for $NF_4^+$ in point group $T_d$ |
|---|---|---|
| IR | Ra | |
| 2310vw | | $2\nu_3(A_1 + E + F_2)$ |
| 1995 w | | $\nu_1 + \nu_3\ (F_2)$ |
| 1455 w | | $\nu_1 + \nu_4\ (F_2)$ |
| 1444 | | |
| 1234 mw | | $2\nu_4\ (A_1 + E + F_2)$ |
| 1220 | | |
| 1210 | | |
| 1185 sh | 1189 (1.0) | $\nu_3\ (F_2)$ |
| 1160 vs | 1158 (1.0) | |
| 1145 sh | 1141 (1.0) | |
| 955 s,br | | $Be_2F_5^-$ |
| | 851 (10) | $\nu_1\ (A_1)$ |
| 765 ms, br | | $Be_2F_5^-$ |
| 690 ms, br | | |
| 623 mw | 621 (1.9) | $\nu_4(F_2)$ |
| 611 m | 610 (3.3) | |
| 597 mw | 599 (2.4) | |
| 558 vw | | |
| 498 vw | | |
| | 458 (2.2) | $\nu_2(E)$ |
| | 447 (2.1) | |
| 436 m | | $Be_2F_5^-$ |
| 416 ms | | |
| 400 mw | | |

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