Reaction of $LiAlH_4$ with the above solutions produced a white solid. The infrared spectrum of the solid was identical with $MgZnH_4$ formed in section (a). The x-ray powder diffraction pattern is listed in Table II. It is surprising to note that the lines do not correspond exactly with the lines observed for $MgZnH_4$ prepared in (a). However, the lines are quite different from the patterns obtained either for a physical mixture of MgH_2 and ZnH_2 or for $Mg(ZnH_3)_2$. It is of course possible that $MgZnH_4$ prepared by this method may have a different crystal structure than the product formed in (a). The vacuum DTA–TGA of this compound was identical with that of $MgZnH_4$ formed in (a) and the data are listed in Table III.

In conclusion, $MgZnH_4$ and $Mg(ZnH_3)_2$ were prepared by two different routes. The integrity of these complexes as a single compound rather than a physical mixture of MgH_2 and ZnH_2 has been established by their characteristic x-ray powder diffraction patterns.

Registry No. $Mg(ZnH_3)_2$, 60949-89-5; $MgZnH_4$, 60949-90-8; MgH_2, 7693-27-8; ZnH_2, 14018-82-7; $Zn(CH_3)_2$, 544-97-8; $LiCH_3$, 917-54-4; $LiAlH_4$, 16853-85-3; $Mg(CH_3)_2$, 2999-74-8; $MgBr_2$, 7789-48-2.

References and Notes

(1) E. C. Ashby and J. J. Watkins, *Inorg. Chem.*, **12**, 2493 (1973).

(2) E. C. Ashby, R. Kovar, and R. Arnott, *J. Am. Chem. Soc.*, **92**, 2182 (1970); E. C. Ashby, S. C. Srivastava, and R. Arnott, *Inorg. Chem.*, **14**, 2422 (1975).

(3) E. C. Ashby, T. F. Korenowski, and R. D. Schwartz, *J. Chem. Soc., Chem. Commun.*, 157 (1974).

(4) E. C. Ashby and H. S. Prasad, *Inorg. Chem.*, **14**, 2869 (1975).

(5) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p 92.

(6) D. H. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(7) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).

(8) E. C. Ashby, P. Claudy, J. Bousquet, and J. Etienne, *J. Chem. Educ.*, **52**, 618 (1975).

(9) C. R. Noller, *Org. Synth.*, **12**, 86 (1932).

(10) E. C. Ashby and R. Arnott, *J. Organomet. Chem.*, **14**, 1 (1968).

(11) R. G. Beach and E. C. Ashby, *Inorg. Chem.*, **10**, 1888 (1971).

(12) E. C. Ashby, R. D. Schwartz, and B. D. James, *Inorg. Chem.*, **9**, 325 (1970).

(13) The ether content was determined by difference in weight [100% – (% zinc + % magnesium + % hydrogen)] after the compound had been dried under vacuum at room temperature.

(14) E. C. Ashby and R. G. Beach, *Inorg. Chem.*, **9**, 2300 (1970).

(15) G. O. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzback, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 4585 (1951).

(16) D. F. Evans and I. Wharf, *J. Chem. Soc. A*, 783 (1968).

(17) R. West and W. Glaze, *J. Am. Chem. Soc.*, **83**, 3580 (1961).

(18) F. Hein, A. Schleede, and J. Kallmeyer, *Z. Anorg. Allg. Chem.*, **311**, 260 (1961).

(19) F. Kaufmann, A. Gerandelle, B. Kaempf, F. Schue, A. Deluzatche, and A. Maillard, *J. Organomet. Chem.*, **24**, 13 (1970).

(20) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4140 (1966).

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Synthesis and Characterization of $(NF_4)_2TiF_6$ and of Higher NF_4^+ and Cs^+ Poly(perfluorotitanate(IV)) Salts

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Metathesis between Cs_2TiF_6 and NF_4SbF_6 in HF solution was used to prepare the novel perfluoroammonium salt $(NF_4)_2TiF_6$. The compound is a white crystalline solid, stable to about 200 °C. It was characterized by elemental analysis and infrared, Raman, and ^{19}F NMR spectroscopy. X-ray powder data show that the compound (tetragonal, $a = 10.715$ Å, $c = 11.114$ Å) is isotypic with $(NF_4)_2GeF_6$ and $(NF_4)_2SnF_6$. Thermal or HF solution displacement reactions between NF_4BF_4 and TiF_4 produced the polyperfluorotitanate(IV) salts $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$. Heating of NF_3, F_2, and TiF_4 to 190 °C at an autogenous pressure of 160 atm produced a salt of the approximate composition $NF_4Ti_6F_{25}$. For comparison, TiF_4 and the salts Cs_2TiF_6, $Cs_2Ti_2F_{10}$, and $CsTi_2F_9$ were synthesized and characterized by vibrational spectroscopy.

Introduction

Although the nonexistence of an NF_5 parent molecule and the high ionization potentials of NF_3 and fluorine made the original synthesis of NF_4^+ salts difficult,[1] their surprisingly high thermal stability permits the syntheses of salts of relatively weak Lewis acids. Thus, the preparation of stable NF_4^+ salts[2,3] containing GeF_5^-, GeF_6^{2-}, SnF_5^-, and SnF_6^{2-} anions has been recently reported. Since NF_4^+ salts are of significant interest for solid propellant NF_3–F_2 gas generators[4] for chemical HF–DF lasers, the synthesis of novel higher performing NF_4^+ salts is desirable. In this paper, we report on the syntheses and properties of NF_4^+ salts derived from TiF_4.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those previously described.[2-4] The CsF was fused in a platinum crucible and powdered in the drybox. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[5] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. Pure NF_4BF_4 was prepared from NF_3, F_2, and BF_3 by uv photolysis[2] at −196 °C and the NF_4SbF_6 was synthesized as previously described.[4] A 10 year old sample of commercial TiF_4 (Allied) had undergone partial hydrolysis but was converted back to pure TiF_4 by fluorinating it in a Monel cylinder for 2 days at 250 °C with F_2 at 70 atm. Both, treated and untreated, samples of TiF_4 were used in the displacement reactions with NF_4BF_4. In some cases the course of the reactions was influenced by the choice of the TiF_4.

Synthesis of Cs_2TiF_6. Dry CsF (40.3 mmol) and TiF_4 (20.15 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (3 ml of liquid) was added at −78 °C. The mixture was warmed to 24 °C and stirred for 1 h until all solid material had dissolved. The volatile materials were pumped off at 70 °C for 2 h. The white solid residue (8.621 g; weight calcd for 20.15 mmol of Cs_2TiF_6 8.619 g) was shown by infrared and Raman spectroscopy to be Cs_2TiF_6 of excellent purity. The products obtained from both untreated and prefluorinated TiF_4 were undistinguishable. The solubility of Cs_2TiF_6 in anhydrous HF at 24 °C was found to be about 4 g/g of HF.

Synthesis of $Cs_2Ti_2F_{10}$. This salt was synthesized from equimolar amounts of Cs_2TiF_6 and prefluorinated TiF_4 either by heating in a Monel cylinder to 180 °C for 7 days or by stirring the mixture in liquid anhydrous HF for 4 days at 25 °C and pumping off the volatile material at 50 °C for 3 h. The observed weights closely corresponded to those expected for $Cs_2Ti_2F_{10}$. Vibrational spectroscopy showed only small amounts of TiF_6^{2-} and $Ti_2F_9^-$ for the product of the thermal reaction and of TiF_4, $Ti_2F_9^-$, TiF_6^{2-}, and a higher polyanion (Raman band at 778 cm^{-1}) for the HF reaction.

Synthesis of $CsTi_2F_9$. This salt was prepared as described above for $Cs_2Ti_2F_{10}$, except for using Cs_2TiF_6 and TiF_4 in a 1:3 mole ratio. Vibrational spectroscopy showed that the product from the HF reaction contained mainly $Ti_2F_9^-$ with traces of TiF_4 and $Ti_2F_{10}^{2-}$ being present. The product from the thermal reaction was a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.

Table I. Results from the Displacement Reactions between NF_4BF_4 and TiF_4

Reactants (mol)	Reaction conditions	Products (mol)
NF_4BF_4 (6), untreated TiF_4 (6)	HF, 24 °C, 18 h	$NF_4Ti_2F_9$ (4), NF_4BF_4 (4)
NF_4BF_4 (6), untreated TiF_4 (12)	HF, 24 °C, 72 h	$NF_4Ti_2F_9$ (6)
NF_4BF_4 (6), prefluor TiF_4 (6)	HF, 24 °C, 138 h	$NF_4Ti_3F_{13}$ (~2), NF_4BF_4 (~4), small amt of $NF_4Ti_2F_9$
NF_4BF_4 (6), prefluor TiF_4 (12)	HF, 24 °C, 96 h	$NF_4Ti_3F_{13}$ (4), NF_4BF_4 (2)
NF_4BF_4 (6), untreated TiF_4 (6)	190 °C, 18 h	$NF_4Ti_2F_9$ (~3), NF_3 (~3), BF_3 (~6), small amt of NF_4BF_4 and $NF_4Ti_3F_{13}$
NF_4BF_4 (6), untreated TiF_4 (6)	160 °C, 60 h	$NF_4Ti_3F_{13}$ (2), NF_4BF_4 (1.4), NF_3 (2.6), BF_3 (4.6)
NF_4BF_4 (6), prefluor TiF_4 (6)	170 °C, 20 h	$NF_4Ti_2F_9$ (3), NF_4BF_4 (3), BF_3 (3)
NF_4BF_4 (6), prefluor TiF_4 (12)	170 °C, 20 h	$NF_4Ti_2F_9$ (3.6), $NF_4Ti_3F_{13}$ (1.6), BF_3 (5.4), NF_4BF_4 (0.6)
NF_4BF_4 (6), prefluor TiF_4 (12)	170 °C, 192 h	$NF_4Ti_2F_9$ (6), BF_3 (6)

The synthesis of higher polyperfluorotitanate(IV) anions was attempted by heating a 1:5 mole ratio mixture of Cs_2TiF_6 and TiF_4 to 180 °C for 7 days. Vibrational spectroscopy, however, showed the presence of only $Ti_2F_{10}^{2-}$, $Ti_2F_9^-$, and unreacted TiF_4.

Synthesis of $(NF_4)_2TiF_6$. The metathetical synthesis of $(NF_4)_2TiF_6$ from saturated HF solutions of NF_4SbF_6 (10.00 mmol) and Cs_2TiF_6 (5.00 mmol) was carried out in the apparatus previously described[3] for the synthesis of $(NF_4)_2SnF_6$. After combination of the solutions of the two starting materials at room temperature and formation of a $CsSbF_6$ precipitate, the mixture was cooled to −78 °C and filtered. The volatile materials were pumped off at 50 °C for 1 hr. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly $CsSbF_6$ containing, due to the hold up of some mother liquid, a small amount of $(NF_4)_2TiF_6$. The filtrate residue (1.55 g; weight calcd for 5 mmol of $(NF_4)_2TiF_6$ 1.71 g) had the following composition (mol %): $(NF_4)_2TiF_6$, 88.5; $CsSbF_6$, 11.5. Found: NF_3, 36.3; Ti, 12.21; Sb, 4.11; Cs, 4.4. Calcd for a mixture of 88.5% $(NF_4)_2TiF_6$ and 11.5% $CsSbF_6$: NF_3, 36.43; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 90% $(NF_4)_2TiF_6$ and 10% $CsSbF_6$, in good agreement with the above elemental analysis.

Displacement Reactions between NF_4BF_4 and TiF_4. These displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder. For the HF solution reactions, the solid starting materials (6 mmol of NF_4BF_4 in each experiment) were placed in a passivated Teflon FEP ampule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon-coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50 °C for 3 h and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90-ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by *PVT*, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table I.

Direct Synthesis of NF_4^+ Poly(perfluorotitanates(IV)). Prefluorinated TiF_4 (11.3 mmol), NF_3 (200 mmol), and F_2 (200 mmol) were heated in a passivated 90-ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200 °C for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted TiF_4 in addition to a small amount of NF_4^+ and a poly(perfluorotitanate(IV)) anion (probably $Ti_6F_{25}^-$; see below) having its strongest Raman line at 784 cm^{-1}. During the next two heating cycles (190–195 °C for 14 days and 180 °C for 35 days) the solid gained 149 and 41 mg, respectively. The vibrational spectra did not show any evidence of unreacted TiF_4, and the relative intensities of the bands due to NF_4^+ had significantly increased. Furthermore, the 784-cm^{-1} Raman line had become by far the most intense Raman line. Additional heating to 230 °C for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. On the basis of the observed weight increase and the lack of spectroscopic evidence for the presence of lower poly(perfluorotitanate(IV)) anions, the solid product appears to have the approximate composition $NF_4Ti_6F_{25}$ (calcd weight increase 205 mg; obsd weight increase 198 mg).

Results and Discussion

Syntheses of NF_4^+ Salts. Perfluoroammonium salts of TiF_4 were prepared by the following methods.

(1) Metathesis:

$$Cs_2TiF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF soln}} 2CsSbF_6\downarrow + (NF_4)_2TiF_6$$

The yield of $(NF_4)_2TiF_6$ in this reaction is practically quantitative, except for material losses caused by the retention of a certain amount of mother liquor by the filter cake. The purity of the material obtained in this manner was approximately 88.5 mol %, the remainder being $CsSbF_6$.

(2) Direct Synthesis from NF_3, F_2, and TiF_4:

$$NF_3 + F_2 + 6TiF_4 \xrightarrow[160\ \text{atm}]{190\ °\text{C}} NF_4Ti_6F_{25}$$

Heating of TiF_4 with a large excess of NF_3 and F_2 to 180–195 °C for 50 days under an autogenous pressure of about 160 atm produced a solid of the approximate composition $NF_4Ti_6F_{25}$. Significant increases or decreases of the reaction temperature resulted in lower conversions of NF_3 to NF_4^+.

(3) Displacement Reactions:

$$NF_4BF_4 + nTiF_4 \rightarrow NF_4TiF_5{\cdot}(n-1)TiF_4 + BF_3$$

These reactions were carried out either in anhydrous HF solution at room temperature or by heating the solid starting materials in a Monel cylinder to 160–190 °C. The composition of the products was influenced by both the reaction conditions and the choice of the TiF_4 starting material (see Table I). For the HF solution displacement reactions, the use of prefluorinated TiF_4 (see below) resulted in the following approximate stoichiometry, independent of the mole ratio of the starting materials

$$NF_4BF_4 + 3TiF_4 \xrightarrow{\text{HF, 24 °C}} NF_4Ti_3F_{13} + BF_3$$

When untreated TiF_4 was used, the reaction stoichiometry changed from 1:3 to 1:2, again independent of the mole ratio of the starting materials

$$NF_4BF_4 + 2TiF_4 \xrightarrow{\text{HF, 24 °C}} NF_4Ti_2F_9 + BF_3$$

In the thermal displacement reactions, the use of prefluorinated TiF_4 at 170 °C resulted in a clean 1:2 reaction between NF_4BF_4 and TiF_4 according to

$$NF_4BF_4 + 2TiF_4 \xrightarrow{170\ °\text{C}} NF_4Ti_2F_9 + BF_3$$

When an excess of NF_4BF_4 was used, the reaction was complete in 20 h, producing a mixture of $NF_4Ti_2F_9$ and unreacted NF_4BF_4. When we used a 1:2 mole ratio of NF_4BF_4 and TiF_4, however, longer heating periods were required to avoid the formation of some $NF_4Ti_3F_{13}$ as a by-product.

With untreated TiF_4, some of the NF_4^+ salt was used up for the fluorination of the partially hydrolyzed TiF_4; however, the main product formed at 190 °C was again $NF_4Ti_2F_9$. When the reaction temperature was lowered to 160 °C, the main product was $NF_4Ti_3F_{13}$.

The above results are not surprising in view of our present understanding of NF_4^+ chemistry. It appears that the nature of the Lewis acid determines the possible synthetic routes toward their NF_4^+ salts. If a sufficiently strong Lewis acid is monomeric at the reaction temperature, a direct synthesis from NF_3, F_2, and the Lewis acid is possible. The initial step in this direct synthesis is the generation of F atoms[1] from F_2 by either discharge,[6,7] radiation,[1,2,8] or heating.[4,9] These F atoms then react with the monomeric Lewis acid to form a Lewis acid–F· radical,[10] a species which might be capable[1,11] of supplying the energy (ionization potential of NF_3 minus the energy released by the formation of the ion pair) required for the oxidation of NF_3 to NF_3^+. The latter cation can then be readily fluorinated by either F· or F_2 to NF_4^+. A typical example for this scheme is the low-temperature UV photolysis of the NF_3–F_2–BF_3 system[1,2,10]

$$F_2 \xrightarrow{h\nu} 2F\cdot$$

$$F\cdot + BF_3 \rightarrow BF_4\cdot$$

$$BF_4\cdot + NF_3 \rightarrow NF_3^+BF_4^-$$

$$NF_3^+BF_4^- + F\cdot \rightarrow NF_4^+BF_4^-$$

On the other hand, if the Lewis acid is polymeric at temperatures above the thermal decomposition point of its NF_4^+ salt, indirect synthetic methods must be used. A typical example is SnF_4 (sublimation point 704 °C), where metathesis

$$Cs_2SnF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF soln}} 2CsSbF_6\downarrow + (NF_4)_2SnF_6$$

and the displacement reaction

$$2NF_4BF_4 + 2SnF_4 \xrightarrow{\text{HF soln}} (NF_4)_2Sn_2F_{10} + 2BF_3$$

have successfully been applied[3] to the syntheses of its NF_4^+ salts.

The physical properties of TiF_4 (polymeric solid at room temperature with a vapor pressure of 1 atm at 284 °C) are intermediate between those of BF_3 (bp −101 °C) or GeF_4 (1 atm vapor pressure at −36 °C) and SnF_4 (bp 705 °C). Consequently, the successful, although slow, direct thermal synthesis of an NF_4^+ salt of TiF_4 and the pronounced tendency of TiF_4 to form polyanions are not unexpected. However, the actual composition of the polyanions was surprising. Whereas both GeF_4 and SnF_4 in their displacement reactions[2,3] with NF_4BF_4 form exclusively the $Ge_2F_{10}^{2-}$ and $Sn_2F_{10}^{2-}$ anions, respectively, no evidence was obtained for the formation of $Ti_2F_{10}^{2-}$ in the corresponding reactions of TiF_4. Instead, only the polymeric anions $Ti_2F_9^-$ and $Ti_3F_{13}^-$ were observed. Since TiF_6^{2-} is known[12] to associate with TiF_5^- or TiF_4 to form $Ti_2F_{11}^{3-}$ and $Ti_2F_{10}^{2-}$, respectively, the failure to observe the two latter anions in the NF_4BF_4–TiF_4 displacement reactions suggests that TiF_6^{2-} is not formed as an intermediate in appreciable quantities. Furthermore, the absence of observable amounts of $Ti_2F_{10}^{2-}$ indicates either that TiF_5^- preferentially associates with TiF_4 rather than with itself or that the smallest TiF_4 units present which will accept a fluoride ion are dimers. Unfortunately, the structures both of solid TiF_4 and of the species present in its HF solutions are unknown. Consequently, it is at present inappropriate to rationalize the different behavior of TiF_4 and of the two main-group tetrafluorides.

The fact that the displacement reaction in HF solution resulted for untreated TiF_4 in a lower polyanion ($Ti_2F_9^-$) than for prefluorinated TiF_4, is consistent with previous reports[13] on the solubility of TiF_4 in HF. Thus TiF_4 is only sparingly soluble in anhydrous HF, but its solubility is significantly increased by the addition of a Lewis base, such as an alkali metal fluoride or water. Apparently, the base, i.e., F^- ions, helps to depolymerize the TiF_4. Since the untreated TiF_4 was partially hydrolyzed, it probably generated upon addition to the HF solution some H_2O, which in the presence of HF and TiF_4 would be protonated to yield OH_3^+ and a polytitanate anion. No chemical interaction between OH_3^+ and NF_4^+ is expected, since it has previously been demonstrated that $OH_3^+SbF_6^-$ and $NF_4^+SbF_6^-$ can coexist in HF solution.[14]

A previous study[13] on the relative strength of fluoro acids in HF solution had placed BF_3, SnF_4, and TiF_4 in categories 2, 3, and 5, respectively, where the acid strength decreased with increasing category number. The results from our studies, i.e., the fact that both SnF_4 and TiF_4 are capable of quantitatively displacing BF_4^- from NF_4BF_4 in HF solution, indicate that this acid classification is not generally valid.

Syntheses of Cs Salts. For the characterization of the poly(perfluorotitanate(IV)) anions in their NF_4^+ salts, a better knowledge of these anions was required. Very little information on poly(perfluorotitanate(IV)) has previously been published. Except for a recent DSC study on $NOTiF_5$, which was shown to decompose at 225 °C to $NOTi_2F_9$ and FNO,[15] the only detailed study on poly(perfluorotitanates) was carried out by Dean.[12] Studying the TiF_4–$(Pr_2NH_2)_2TiF_6$ system in SO_2 solution by ^{19}F NMR spectroscopy, he established the presence of the $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{2-}$, and $Ti_2F_9^-$ anions, in addition to other unidentified polymeric anions.

Our study in anhydrous HF as a solvent showed that pure Cs_2TiF_6 is formed from stoichiometric amounts of CsF and either untreated or prefluorinated TiF_4

$$2CsF + TiF_4 \xrightarrow{\text{HF}} Cs_2TiF_6$$

The compound $Cs_2Ti_2F_{10}$ can be produced from an equimolar mixture of Cs_2TiF_6 and TiF_4 by either HF treatment at room temperature or heating of the solids to 180 °C

$$Cs_2TiF_6 + TiF_4 \xrightarrow[\text{HF, 25 °C}]{\text{180 °C or}} Cs_2Ti_2F_{10}$$

Vibrational spectroscopy showed only traces of TiF_4, TiF_6^{2-}, and $Ti_2F_9^-$, indicating that under these conditions $Ti_2F_{10}^{2-}$ is clearly the favored species.

When the mole ratio of Cs_2TiF_6 to TiF_4 was changed to 1:3, the reaction in HF solution produced almost exclusively $Ti_2F_9^-$ according to

$$Cs_2TiF_6 + 3TiF_4 \xrightarrow{\text{HF, 25 °C}} 2CsTi_2F_9$$

Only traces of TiF_4 and $Ti_2F_{10}^{2-}$ were present. The thermal reaction, however, produced a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.

A further increase of the TiF_4 ratio in the thermal reactions did not produce any evidence for the formation of polyanions higher than $Ti_2F_9^-$ but resulted in unreacted TiF_4. The HF solution study was not extended beyond the 1:3 Cs_2TiF_6:TiF_4 mole ratio.

Properties. The most interesting one of the novel salts prepared during this study is $(NF_4)_2TiF_6$, since it has the highest usable fluorine content of any presently known NF_4^+ salt. All the NF_4^+ perfluorotitanates(IV) are white crystalline solids. Based on observations of their thermal decompositions in sealed glass capillaries and on the results of the direct thermal synthesis and of the thermal displacement reactions, these NF_4^+ salts are stable to at least 200°. By analogy with the other known NF_4^+ salts, it is difficult to obtain meaningful decomposition temperatures from either melting point determinations or DSC data.[2,3] All salts are hygroscopic and hydrolyze in water with quantitative NF_3 and less than quantitative O_2 evolution, in agreement with previous findings.[2] The hydrolysate shows the yellow color characteristic for titanyl salts. The $(NF_4)_2TiF_6$ salt is highly soluble in HF and moderately soluble in BrF_5. For the polyanion salts, the

Table II. X-Ray Powder Data for $(NF_4)_2TiF_6$[a]

d_{obsd}	d_{calcd}	Intens	hkl
6.23	6.26	vw	111
5.57	5.56	vs	002
4.93	4.93	w	102
3.49	3.50	s	103
3.39	3.39	s	310
2.94	2.93	ms	213
2.782	2.778	m	004
2.465	2.463	w	331
2.315	2.318	mw	323
2.201	2.200	s	422
2.100	2.101	w	510
1.990	1.990	vw	520 502
1.892	1.894	m	440
1.789	1.789	mw	600 442
1.663	1.664	mw	226
1.641	1.644	mw	306

[a] Tetragonal; $a = 10.715$ Å, $c = 11.114$ Å; Cu Kα radiation; Ni filter.

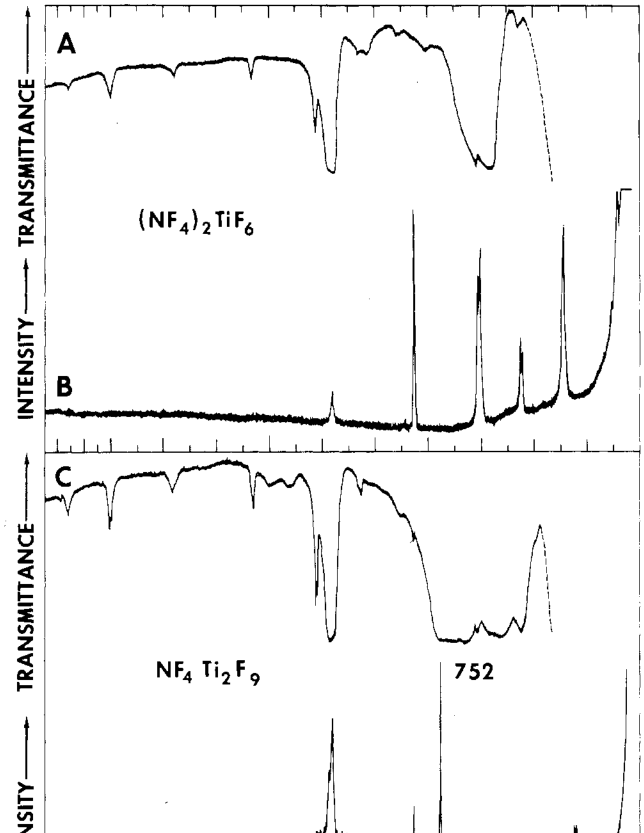


Figure 1. Vibrational spectra of solid $(NF_4)_2TiF_6$ and $NF_4Ti_2F_9$: traces A and B, infrared and Raman spectra of $(NF_4)_2TiF_6$, respectively; traces C and D, corresponding spectra of $NF_4Ti_2F_9$, prepared by the thermal (170 °C) displacement reaction between NF_4BF_4 and TiF_4 (1:2). The absorptions below 400 cm^{-1} in the infrared spectra (broken lines) are due to the AgCl windows. Weak bands, due to impurities, were deleted from the spectra. Raman spectra were recorded with a spectral slit width of 3 cm^{-1}. The insert was recorded at a higher recorder gain.

solubility decreases with increasing anion size.

The Cs^+ salts are also stable, white, crystallinic solids. The Cs_2TiF_6 salt is very soluble in HF (about 4 g/g of HF), but the solubility sharply decreases for the polyanion salts. The hydrolysis of the cesium poly(perfluorotitanates(IV)) was followed by Raman spectroscopy. The spectra obtained for the solid phase in equilibrium with the aqueous phase showed that the bands due to TiF_4 and the higher polyanion impurities disappeared first, accompanied by a simultaneous growth of the TiF_6^{2-} bands. The aqueous phase showed TiF_6^{2-} as the main constituent.

Table III. Crystallographic Data of $(NF_4)_2TiF_6$ Compared to Those of Other NF_4^+ Salts

	Tetragonal unit cell dimensions					
	a, Å	c, Å	V, Å^3	Z	Vol/F, Å^3	Calcd density, g/cm^3
NF_4PF_6[a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[b]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6[c]	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6[c]	8.006	5.821	373.10	2	18.66	3.68
NF_4BF_4[a]	9.944	5.229	517.04	4	16.16	2.27
$(NF_4)_2GeF_6$[a]	10.627	11.114	1255.14	$^{16}/_3$	16.81	2.59
$(NF_4)_2SnF_6$[d]	10.828	11.406	1337.35	$^{16}/_3$	17.91	2.73
$(NF_4)_2TiF_6$	10.715	11.114	1276.01	$^{16}/_3$	17.09	2.37

[a] Reference 2. [b] Reference 6. [c] Reference 4. [d] Reference 3.

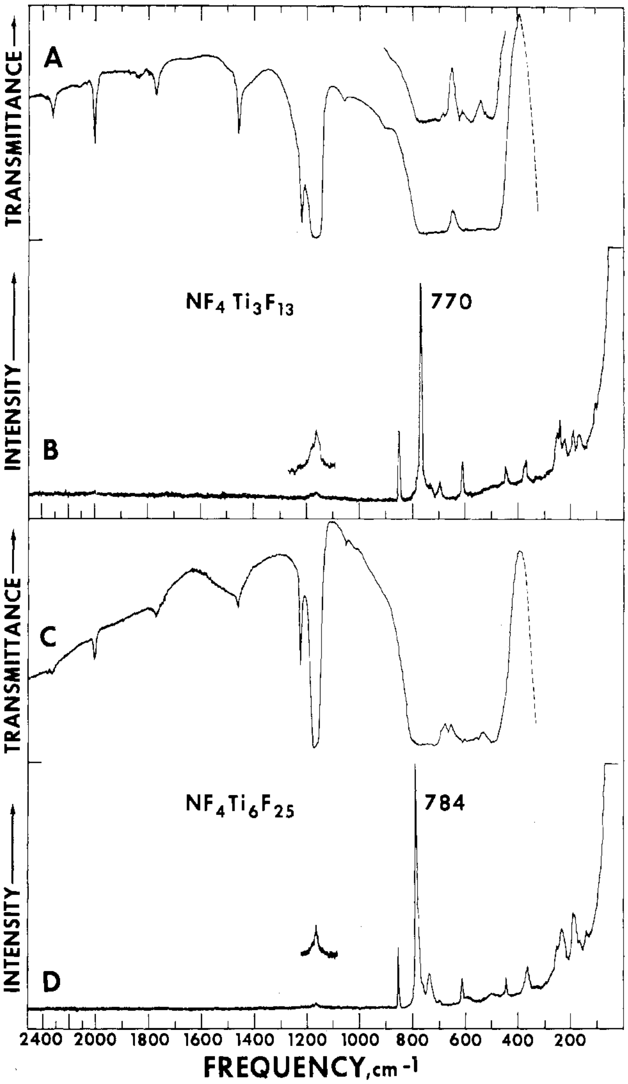


Figure 2. Vibrational spectra of solid $NF_4Ti_3F_{13}$ and $NF_4Ti_6F_{25}$, recorded under the same conditions as those of Figure 1. The samples of $NF_4Ti_3F_{13}$ and $NF_4Ti_6F_{25}$ were prepared by the displacement reaction between NF_4BF_4 and prefluorinated TiF_4 in HF and by direct synthesis from NF_3, F_2, and TiF_4 at 190 °C, respectively.

Table IV. Vibrational Spectra of Solid $(NF_4)_2TiF_6$ Compared to Those of Cs_2TiF_6

Obsd freq (cm^{-1}) and rel intens[a]				Assignments (point group)	
$(NF_4)_2TiF_6$		Cs_2TiF_6			
IR	Raman	IR	Raman	NF_4^+ (T_d)	TiF_6^{2-} (O_h)[b]
2340 sh				$2\nu_3$ ($A_1 + E + F_2$)	
2320 vw					
2003 w				$\nu_1 + \nu_3$ (F_2)	
1780 sh				$\nu_3 + \nu_4$ ($A_1 + E + F_2$)	
1760 vw					
1463 w				$\nu_1 + \nu_4$ (F_2)	
1219 mw				$2\nu_4$ ($A_1 + E + F_2$)	
1160 vs	1158 (1.4)			ν_3 (F_2)	
1132 sh, vw					
1060 vw				$\nu_2 + \nu_4$ ($F_1 + F_2$)	
1021 w					
910 vw					$\nu_1 + \nu_4$ (F_{1u})
	883 (0.1)			$2\nu_2$ ($A_1 + A_2 + E$)	
850 sh, vw	853 (10)			ν_1 (A_1)	
804 w					
611 mw	612 (5)			ν_4 (F_2)	
	607 sh				
	601 (8.0)		599 (10)		ν_1 (A_{1g})
563 vs		562 vs			ν_3 (F_{1u})
452 vw	450 (3.3)			ν_2 (E)	
	442 (2.6)				
	289 (8.2)		284 (9.8)		ν_5 (F_{2g})
	107 (0+)		84 (1.2)	Lattice vib	
	86 (2)		68 (3.2)		
			56 (1.7)		

[a] Uncorrected Raman intensities. [b] The site symmetry of TiF_6^{2-} in Cs_2TiF_6 is D_{3d}, but for simplicity and in view of the unknown site symmetry of TiF_6^{2-} in $(NF_4)_2TiF_6$, the assignments for TiF_6^{2-} were made for the point group (O_h) of the free ion.

Table V. Vibrational Spectra of Solid $CsTi_2F_9$, $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$

Obsd freq (cm^{-1}) and rel intens[a]								Assignments for NF_4^+ in point group T_d
$CsTi_2F_9$		$NF_4Ti_2F_9$		$NF_4Ti_3F_{13}$		$NF_4Ti_6F_{25}$		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
				2360 sh		2350 sh		$2\nu_3$ ($A_1 + E + F_2$)
		2320 vw		2320 vw		2320 vw		
		2004 w		2002 w		2002 w		$\nu_1 + \nu_3$ (F_2)
		1765 vw		1766 vw		1768 vw		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)
		1458 w		1458 w		1457 w		$\nu_1 + \nu_4$ (F_2)
		1400 vw						
		1322 vw						
		1223 vw		1220 mw		1220 mw		$2\nu_4$ ($A_1 + E + F_2$)
		1216 w						
		1164 vs	1169 (0.2)	1166 vs	1175 sh	1165 vw	1165 (0.1)	ν_3 (F_2)
			1158 (0.5)		1160 (0.2)			
		1054 vw		1055 vw		1051 vw		$\nu_2 + \nu_4$ ($F_1 + F_2$)
		904 vw		905 sh				
		853 vw	851 (3.8)		851 (3.2)		851 (2.4)	ν_1 (A_1)
725 vs, br	752 (10)	725 vs, br	752 (10)	760 vs, br	770 (10)	765 vs	784 (10)	
	701 (0.7)		702 (0.7)		731 (0.3)		735 (1.2)	
650 vs	670 (0.4)	650 vs	670 (0.5)	702 vs		712 vs		
	645 (0+)		645 (0+)		696 (0.8)		698 (0.1)	
				675 s		661 s		
		615 s	615 (0.5)	615 s	611 (1.6)	610 s	611 (0.9)	ν_4 (F_2)
		608 s	608 (1.6)					
530 vs, br		530 vs, br		578 vs		585 vs	588 (0+)	
446 vs		446 vs		502 vs		492 vs	500 (0+)	
			444 (0.5)		446 (0.9)		445 (0.7)	ν_2 (E)
			439 (1.1)					
390 sh	388 (0.9)	390 sh	389 (0.9)		371 (1.0)		363 (1.0)	
	327 (0.3)		326 (0.3)		252 (0.5)		251 sh	
	290 (0.8)		290 (0.9)		241 (2.0)		242 (1.5)	
	247 (2.4)		247 (2.4)		223 (0.5)		223 sh	
	238 (2.4)		237 (2.4)		190 (1.0)		188 (1.7)	
	225 sh		225 sh		168 (0.8)		165 sh	
	192 (0.5)		192 (0.5)				139 (0.4)	
	162 (0.4)		162 (0.4)					

[a] Uncorrected Raman intensities.

X-Ray Powder Data. The powder pattern of $(NF_4)_2TiF_6$ is listed in Table II. After correction for weak lines due to $CsSbF_6$ and NF_4SbF_6, all observed lines could be indexed for a tetragonal unit cell. The resulting crystallographic parameters are compared in Table III to those of similar NF_4^+ salts. The similarity of the patterns of $(NF_4)_2TiF_6$, (N-

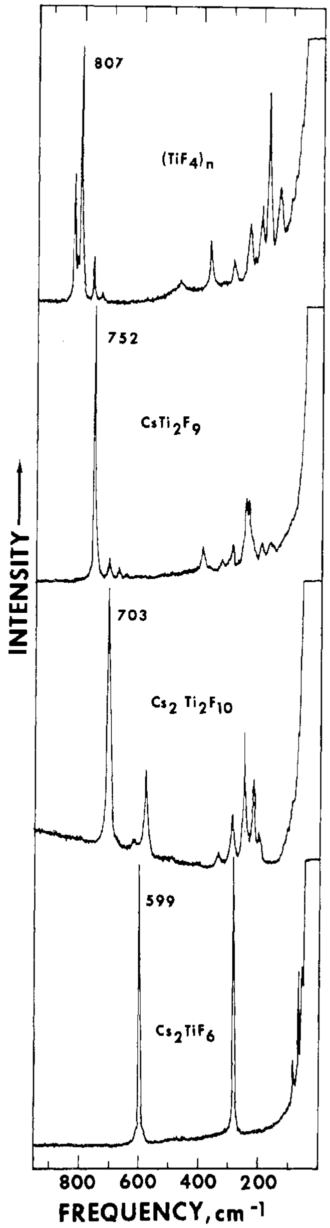


Figure 3. Raman spectra of solid Cs_2TiF_6, $Cs_2Ti_2F_{10}$, $CsTi_2F_9$, and prefluorinated TiF_4.

$F_4)_2SnF_6$,[3] and $(NF_4)_2GeF_6$[2] indicates that the three compounds are isotypic.

NMR Spectra. Since in HF solution rapid exchange between the solvent and the anion prevents observation of well-resolved anion spectra, the ^{19}F NMR spectrum of $(NF_4)_2TiF_6$ was recorded in BrF_5 solution. In addition to the solvent lines,[2] the spectrum showed the characteristic[9,16] triplet (ϕ −220.8, J_{NF} = 229 Hz) for NF_4^+ and the characteristic[12,17] TiF_6^{2-} signal at ϕ −81.7. The solubility of the NF_4^+ polytitanate salts in BrF_5 was too low to permit the observation of useful spectra. Since the ^{19}F NMR spectra of $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{2-}$, and $Ti_2F_9^-$ in SO_2 solution have previously been studied and assigned in detail by Dean,[12] no further work in this direction was undertaken.

Vibrational Spectra. The infrared and Raman spectrum of solid $(NF_4)_2TiF_6$ is shown in Figure 1. The observed frequencies are listed in Table IV. Comparison with the previously reported[2-4,8,16,18] spectra of other NF_4^+ salts demonstrates beyond doubt the presence of the NF_4^+ cation. The remaining bands are due to the anion and are in excellent agreement with those previously reported for TiF_6^{2-} in Cs_2TiF_6[17,19] and $(HgI)_2TiF_6$.[20] The observation of small splittings for some of the degenerate modes of NF_4^+ indicates that the site symmetry of NF_4^+ in the solid is lower than T_d. The same effect has previously been observed[3] for isotypic $(NF_4)_2SnF_6$.

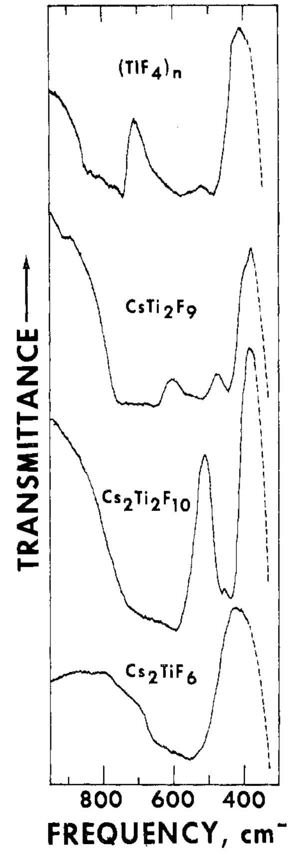
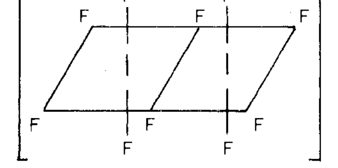


Figure 4. Infrared spectra of solid Cs_2TiF_6, $Cs_2Ti_2F_{10}$, $CsTi_2F_9$, and prefluorinated TiF_4 as dry powders in AgCl disks.

The vibrational spectra of $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$ are shown in Figures 1 and 2, respectively, and the observed frequencies are listed in Table V. Again, the presence of NF_4^+ is clearly established.

For a better characterization of the anion bands, the vibrational spectra of several cesium salts and of solid TiF_4 were also recorded (see Figures 3 and 4, and Tables IV–VI). Since Cs_2TiF_6 can be prepared in high purity and since higher polytitanate impurities preferentially underwent hydrolysis, no problems were encountered with defining the principal bands belonging to each anion. The single most useful band for the identification of a poly(perfluorotitanate(IV)) anion is the symmetric, in-phase, terminal TiF stretching mode. This mode results in a narrow and very intense Raman band, the frequencies of which have been denoted in Figures 1–3. As can be seen, the frequency of this band increases with increasing TiF_4 content and decreasing negative charge of the anion, i.e., $TiF_6^{2-} < Ti_2F_{10}^{2-} < Ti_2F_9^- < Ti_3F_{13}^- < Ti_6F_{25}^- < (TiF_4)_n$.

The structure of $Ti_2F_{10}^{2-}$ (I) has been established[12] by ^{19}F



I

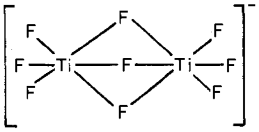
NMR spectroscopy as the cis fluorine-bridged dimer and a

Table VI. Vibrational Spectra of Solid $Cs_2Ti_2F_{10}$ and Prefluorinated TiF_4

$Cs_2Ti_2F_{10}$			TiF_4	
Obsd freq (cm^{-1}) and rel intens[a]		Assignments[b] for point group D_{2h}	Obsd freq and rel intens[a]	
IR	Raman		IR	Raman
	703 (10)	ν_1 (A_g) ν_{17} (B_{2g})		829 (5.0) 817 (0.4)
	620 (0.2)	ν_9 (B_{1g})	840–730 vs, br	807 (10)
	577 (3)	ν_2 (A_g)		761 (1.7)
730–600 vs, br		ν_{13} (B_{1u}) ν_{26} (B_{3u}) ν_{20} (B_{2u}) ν_{27} (B_{3u})	580 vs, br 481 vs	731 (0.4) 471 (0.5)
468 m		ν_{28} (B_{3u})		370 (1.7)
441 s		ν_{21} (B_{2u})		291 (0.9)
	335 (0.5)	ν_{18} (B_{2g}) ν_{11} (B_{1g})		239 (1.8) 221 (0+)
	284 (1.7)	ν_4 (A_g)		201 (2.0)
	248 (4.8)	ν_{24} (B_{3g})		179 (6.1)
	218 (2.8)	ν_5 (A_g)		140 (2.0)
	199 (0.8)	ν_{12} (B_{1g})		99 (0+)
				87 (0+)
				70 (0+)

[a] Uncorrected Raman intensities. [b] Using the symmetry coordinates of ref 21.

thorough vibrational analysis has previously been carried[21,22] out for the isostructural molecule Nb_2Cl_{10}. Consequently, sufficient information was available to allow some tentative assignments for $Ti_2F_{10}^{2-}$. These assignments are summarized in Table VI and are based on the symmetry coordinates defined for Nb_2Cl_{10} by Beattie and co-workers.[21] No attempts were made to assign the spectra of the remaining poly(perfluorotitanate(IV)) anions and TiF_4 itself, although some data are available for $Ti_2F_9^-$. Dean suggested[12] on the basis of ^{19}F NMR data for $Ti_2F_9^-$ the triply fluorine-bridged structure II



II

and Beattie has analyzed[21] the vibrational spectrum of the isostructural $Tl_2Cl_9^{3-}$ anion. Our spectra of prefluorinated TiF_4 (see Figures 3 and 4) significantly differ from those of untreated TiF_4 and those[23-25] previously reported in the literature.

Summary

The synthesis of NF_4^+ salts has successfully been extended to a subgroup element. The results of this study show that TiF_4 can act as a much stronger Lewis acid than predicted on the basis of previous literature data.[13] Thus, stable NF_4^+ salts derived from TiF_4 can be prepared either directly or indirectly. Of all the presently known NF_4^+ salts, $(NF_4)_2TiF_6$ contains the highest percentage of usable fluorine.

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Registry No. $(NF_4)_2TiF_6$, 61128-92-5; Cs_2TiF_6, 16919-28-1; $CsTi_2F_9$, 61128-93-6; $NF_4Ti_2F_9$, 61128-94-7; $NF_4Ti_3F_{13}$, 61267-52-5; $NF_4Ti_6F_{25}$, 61303-83-1; $Cs_2Ti_2F_{10}$, 61128-95-8; NF_4BF_4, 15640-93-4; CsF, 13400-13-0; TiF_4, 7783-63-3; NF_3, 7783-54-2; F_2, 7782-41-4.

References and Notes

(1) K. O. Christe, R. D. Wilson, and A. E. Axworthy, *Inorg. Chem.*, **12**, 2478 (1973).
(2) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **15**, 1275 (1976).
(3) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, in press.
(4) K. O. Christe, R. D. Wilson, and C. J. Schack, *Inorg. Chem.*, in press.
(5) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **14**, 2224 (1975).
(6) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966); J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).
(7) S. M. Sinel'nikov and V. Ya. Rosolovskii, *Dokl. Akad. Nauk SSSR*, **194**, 1341 (1970).
(8) C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, D. C. Wagner, and J. N. Wilson, *Inorg. Chem.*, **11**, 1696 (1972).
(9) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Nucl. Chem. Lett.*, **2**, 79 (1966); *Inorg. Chem.*, **6**, 1156 (1967).
(10) K. O. Christe and I. B. Goldberg, to be submitted for publication.
(11) S. P. Mishra, M. C. R. Symons, K. O. Christe, R. D. Wilson, and R. I. Wagner, *Inorg. Chem.*, **14**, 1103 (1975).
(12) P. A. W. Dean, *Can. J. Chem.*, **51**, 4024 (1973).
(13) A. F. Clifford, H. C. Beachell, and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).
(14) R. I. Wagner, unpublished results.
(15) A. Kigoshi, *Thermochim. Acta*, **11**, 35 (1975).
(16) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, **6**, 533 (1967).
(17) P. A. W. Dean and D. F. Evans, *J. Chem. Soc. A*, 698 (1967).
(18) K. O. Christe and D. Pilipovich, *Inorg. Chem.*, **10**, 2803 (1971).
(19) D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc. A*, 100 (1967).
(20) D. Breitinger and K. Köhler, *Inorg. Nucl. Chem. Lett.*, **8**, 957 (1972).
(21) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. A*, 2765 (1968).
(22) R. D. Werder, R. A. Frey, and Hs. H. Günthard, *J. Chem. Phys.*, **47**, 4159 (1967).
(23) D. J. Reynolds, *Adv. Fluorine Chem.*, **7**, 54 (1971).
(24) L. E. Alexander and I. R. Beattie, *J. Chem. Soc., Dalton Trans.*, 1745 (1972).
(25) F. E. Dickson, *J. Inorg. Nucl. Chem.*, **31**, 2636 (1969).