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CHEMICALS

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STAUFFER CHEMICAL COMPANY

HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

Richmond Research Center  
Richmond, California

STAUFFER CHEMICAL COMPANY  
Richmond Research Center  
Richmond, California

"HIGH ENERGY OXIDIZERS"

CONTRACT Nonr-4019(00)

Project NR 093-035

ARPA No. 399-62

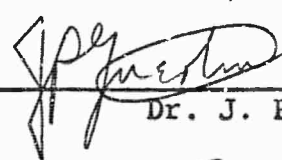
OFFICE OF NAVAL RESEARCH  
WASHINGTON, D. C .

Annual Technical Summary Report  
for the Period February 1, 1965 to January 31, 1966

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Foreword

This is the third annual Technical Summary Report on the investigation of complexes based on chlorinefluorides. It covers the period from February 1, 1965 to January 31, 1966. The work was conducted at the Richmond Research Center, Richmond, California, of Stauffer Chemical Company, under the sponsorship of the Advanced Research Projects Agency. The project was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, under ARPA No. 399-62.

In 1965, we filed a patent on the solid fuel oxidizers,  $\text{KClF}_2$ ,  $\text{RbClF}_2$ , and  $\text{CsClF}_2$  as reported in the ARPA Quarterly Report, June 1, 1965. This year, we intend to file a patent on the  $\text{NF}_4^+$  cation including the new compound,  $\text{NF}_4^+\text{AsF}_6^-$ . No other patent applications are contemplated.

Abstract

This abstract summarizes the data included under the form of five manuscripts in this report.

Low-temperature glow discharge of a mixture of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  results in the adduct, tetrafluoronitronium(V) hexafluoroarsenate(V),  $\text{NF}_4^+\text{AsF}_6^-$ . The white crystalline solid is the first known derivative of the hypothetical  $\text{NF}_5$ . It is stable and involatile at  $25^\circ$  and decomposes exothermally at temperatures greater than  $270^\circ$ . It is very hygroscopic and hydrolyzes to a pale blue solution producing  $\text{HF}$ ,  $\text{NF}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{F}_4$ , and  $\text{AsF}_5$ . The X-ray powder diffraction pattern can be indexed in the tetragonal system. Indications are that the structure is similar to that found for  $\text{PCl}_4^+\text{PCl}_6^-$ . Elemental and mass spectroscopic analyses indicate the 1:1:1 combining ratio of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$ . Vibrational spectroscopy (infrared and Raman) and  $\text{F}^{19}$  magnetic resonance measurements confirm the structure,  $\text{NF}_4^+\text{AsF}_6^-$ .

The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by the reaction of the corresponding fluorides with chlorine monofluoride or  $\text{NO}^+\text{ClF}_2^-$ . These white solids are the first known difluorochlorates(I) salts stable at  $25^\circ$ . They decompose exothermally at temperatures greater than  $230^\circ$ . Their composition and structure were established by elemental analysis, infrared, and X-ray studies. The salts are ionic and contain linear

$\text{ClF}_2^-$  anions. Attempts to prepare  $\text{LiClF}_2$  and  $\text{Ca}(\text{ClF}_2)_2$  failed, while  $\text{NaClF}_2$ ,  $\text{Ba}(\text{ClF}_2)_2$ , and  $\text{Sr}(\text{ClF}_2)_2$  may have formed to a very small extent.

Infrared and conductivity measurements show that  $\text{MClF}_4$  (where M = NO, Rb, or Cs) is ionic in the solid state and in solution, respectively. A square-planar structure (point group  $D_{4h}$ ) is assigned to the  $\text{ClF}_4^-$  anion in  $\text{Rb}^+\text{ClF}_4^-$  and  $\text{Cs}^+\text{ClF}_4^-$ . For the  $\text{ClF}_4^-$  anion in  $\text{NO}^+\text{ClF}_4^-$ , the low-temperature infrared measurement indicates a lower symmetry.



I. Manuscript of Paper: The Tetrafluoronitronium(V) Cation,  $\text{NF}_4^+$

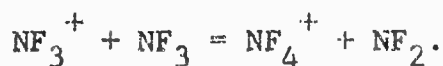
THE TETRAFLUORONITRONIUM(V) CATION,  $\text{NF}_4^+$

Karl O. Christe, Jacques P. Guertin and Attila E. Pavlath

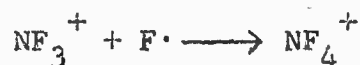
Contribution from the Western Research Center

Stauffer Chemical Company, Richmond, California

WHILE THE EXISTENCE OF  $\text{NF}_4^+$  has not previously been established, Wilson (1) estimated that  $\text{NF}_4^+ \text{BF}_4^-$  might have sufficient stability to exist at temperatures less than  $-120^\circ$ . However, mass spectroscopic analyses (1) did not show  $\text{NF}_4^+$  as a possible product of the ion-molecule reaction



Two possible mechanisms for the formation of  $\text{NF}_4^+$  from  $\text{NF}_3$  and  $\text{F}_2$  are shown by the following equations



In each case, a Lewis acid such as  $\text{AsF}_5$ , can react with the negatively charged species ( $\text{F}^-$  or  $e^-$ ). Thus, the resultant  $\text{AsF}_6^-$  stabilizes the  $\text{NF}_4^+$  cation. The overall reaction can be represented by the following equation



Either mechanism (through  $\text{NF}_3^+$  or  $\text{F}^+$  intermediates) requires a high activation energy (1, 2). This energy can be supplied in various ways: (i) the application of heat, (ii) glow discharge, (iii) microwave discharge, and (iv) radiation. Our attempts in using "method (i)" were not successful. But a mixture of  $\text{NF}_3$ ,  $\text{AsF}_5$ , and  $\text{F}_2$ , in mole ratio, 1:1:2, subjected to glow discharge at  $-78^\circ$ , yielded tetrafluoronitronium(V) hexafluoroarsenate(V),  $\text{NF}_4^+ \text{AsF}_6^-$  (only one mole of  $\text{F}_2$  consumed).

The compound is a white, crystalline, powdery solid, stable and involatile at  $25^\circ$ . It is very hygroscopic and easily hydrolyzes to a pale blue solution producing  $\text{HF}$ ,  $\text{NF}_3$ ,  $\text{NO}$ , and As-F containing species. Differential thermal analysis indicates initial decomposition at about  $270^\circ$ .

Tetrafluoronitronium(V) hexafluoroarsenate(V) was characterized using elemental analysis, infrared spectroscopy, Raman spectroscopy, mass spectroscopy,  $\text{F}^{19}$  magnetic resonance, and X-ray diffraction. The obtained data strongly indicate that the compound formed from the glow-discharge interaction of  $\text{F}_2$ ,  $\text{AsF}_5$ , and  $\text{NF}_3$ , is  $\text{NF}_4^+ \text{AsF}_6^-$ .

We have named the  $\text{NF}_4^+$  cation tetrafluoronitronium(V), as a derivative of hypothetical  $\text{NF}_5$ . The name tetrafluoroammonium is inappropriate due to the polarity of N-F bond. Detailed results and their interpretation will be published at a later date (3).

Acknowledgement - This work has been supported by the  
Advanced Research Projects Agency and the Office of Naval Research.

References

1. J. N. WILSON, Paper presented at the Symposium on Advanced Propellant Chemistry, American Chemical Society, Detroit, Mich., April, 1965.
2. Electronic Interpretation of Organic Chemistry, John Wiley and Sons, Inc., New York, N.Y., 2nd ed., 1949, p. 122.
3. K. O. CHRISTE, J. P. GUERTIN and A. E. PAVLATH, to be published.

II. Manuscript of Paper: Tetrafluoronitronium(V) Cation,  $\text{NF}_4^+$ .  
Synthesis and Properties of  $\text{NF}_4^+\text{AsF}_6^-$

Contribution from the Western Research Center,  
Stauffer Chemical Company, Richmond, California

Tetrafluoronitronium(V) Cation,  $\text{NF}_4^+$ . Synthesis  
and Properties of  $\text{NF}_4^+\text{AsF}_6^-$

By Jacques P. Guertin, Karl O. Christe, and Attila E. Pavlath

Received , 1966

Abstract

Nitrogen trifluoride,  $\text{AsF}_5$ , and  $\text{F}_2$  when subjected to low-temperature glow discharge, react in 1:1:1 mole ratio, forming tetrafluoronitronium(V) hexafluoroarsenate(V),  $\text{NF}_4^+\text{AsF}_6^-$ . This complex is the first known derivative of hypothetical  $\text{NF}_5$ . The white, crystalline powder is stable and non-volatile at 25°. Differential thermal analysis indicates initial decomposition at about 270°. The compound is very hygroscopic and easily hydrolyzes to a pale blue solution with the evolution of gas. Its composition was established by quantitative vacuum synthesis and elemental analysis. Mass spectral analysis of the decomposition and hydrolysis products supports this composition. The X-ray powder diffraction pattern can be indexed in the tetragonal system. The unit cell dimensions are  $a = 7.70 \text{ \AA}$ . and  $c = 5.73 \text{ \AA}$ .

Density measurements indicate two molecules per unit cell. The crystal structure seems similar to that of  $\text{PCl}_4^+\text{PCl}_6^-$ .

### Introduction

Previously, the existence of a stable compound containing the  $\text{NF}_4^+$  cation was considered unlikely. For example, Price et al.<sup>1</sup> claim that the ionization potential is too high and that the dimensions are too large for  $\text{NF}_4^+$  to give sufficient lattice energy to form crystalline salts. Wilson<sup>2</sup> estimated the heat of formation of  $\text{NF}_4^+$  as  $240 \pm 15 \text{ kcal. mole}^{-1}$  and thus concluded that  $\text{NF}_4^+\text{BF}_4^-$  might have sufficient stability (relative to its decomposition products) to exist at temperatures less than  $-120^\circ$ . Recently, in a preliminary paper,<sup>3</sup> we briefly described the preparation and identification of  $\text{NF}_4^+\text{AsF}_6^-$ . At about the same time, Tolberg et al.<sup>4</sup> prepared  $\text{NF}_4^+\text{SbF}_6^-$ .

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- (1) W. G. Price, T. R. Passmore, and D. M. Roessler, Disc. Faraday Soc., 35, 201 (1963).
  - (2) J. N. Wilson, Paper presented at the Symposium on Advanced Propellant Chemistry, American Chemical Society, Detroit, Mich., April, 1965.
  - (3) K. O. Christe, J. P. Guertin, and A. E. Pavlath, Inorg. Nucl. Chem. Letters, (1966).
  - (4) W. E. Tolberg, R. T. Rexick, R. S. Stringham, and M. E. Hill, *ibid*, (1966).

The following paper is a more detailed description of our findings dealing mainly with the synthesis and properties of  $\text{NF}_4^+\text{AsF}_6^-$ . In a subsequent paper,<sup>5</sup> spectroscopic data and their interpretation (including force constant calculations as well as  $\text{F}^{19}$  magnetic resonance spectra) will be discussed.

### Experimental Section

Materials and Apparatus. - Using a standard Pyrex-glass high-vacuum system (stopcocks and joints lubricated with Halocarbon grease of high-temperature grade), nitrogen trifluoride (98%, Air Products) and arsenic pentafluoride (98%, Ozark-Mahoning Co.) were purified by several low-temperature vacuum distillations. Fluorine (98%, Matheson Co., Inc.) was passed through an HF absorber and used without further purification. These three gases were then stored separately at 25° in 300 ml. Monel cylinders equipped with Monel valves (Whitey, M6TS6) and Monel Helicoid pressure gauges (American Chain and Cable Co., Inc., 460-R, 30 in. vacuum to 300 p.s.i.). These were connected to a metal vacuum system (copper tubing and Monel fittings used to minimize corrosion) equipped with bellows-seal valves (Hoke Inc., M482M) and copper to Pyrex-glass seals where necessary. Pressures were measured

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(5) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny,  
Inorg. Chem., (1966).



using a precision-dial manometer (0-30 in.  $\pm$  0.02 in., Wallace and Tiernan, Inc., FA145). Only the glow-discharge apparatus had glass parts.

The glow-discharge apparatus of Schreiner et al.<sup>6</sup> has been slightly modified. Instead of using a single solenoid coil to drive a piston vertically in one direction and a stainless steel spring (subject to corrosion) to pull it back, we have used two solenoids to propel the piston horizontally, thus eliminating the spring.<sup>7</sup> The two air-cooled solenoids are identical, each 4 cm. long, 1.5 cm. thick (including insulation), with a 2.3 cm. diameter hollow core; the design allows continuous operation on a 120 volt A.C. line without overheating. A selenium rectifier (single ph. Bridge No. J116B1) changes A.C. to D.C. A Flexopulse timer (Eagle Signal Co., range 0-120 seconds) coupled with a Mercury-column type relay (Kerman Electric, rating: 1 ma. at 115v.) provides the means of operating one solenoid at a time. A convenient operating condition is 12 strokes/min.

A transformer (Jefferson luminous tube outdoor type, primary 120v. 60 cycles, secondary 15 kv., 30 ma. with midpoint of secondary

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(6) F. Schreiner, J. G. Malm, and J. G. Hindman, J. Am. Chem. Soc., 87, 25 (1965).

(7) W. R. Bennett, Jr., Rev. Sci. Instr., 28, 1092 (1957).

grounded; Jefferson Electronic Co.) provides the necessary voltage to discharge across the copper electrodes (5 cm. apart). Ignition wire (Packard 440) is used throughout the high-voltage circuit.

Hygroscopic nonvolatile compounds were manipulated in the dry nitrogen atmosphere of a glove box.

Preparation of  $\text{NF}_4^+\text{AsF}_6^-$ . - A mixture of  $\text{NF}_3$ ,  $\text{AsF}_5$ , and  $\text{F}_2$ , in 1:1:~2 mole ratio, was introduced into the glow-discharge vessel at a maximum pressure of 80 mm. The circulating pump was started, the glow-discharge vessel was cooled to  $-78^\circ$ , and a 15 kv. potential was placed across the copper electrodes. Should discharge not occur at this pressure, a Tesla coil is used for initiation. Should this also fail, then the pressure is reduced somewhat and the procedure is repeated until discharge occurs.

The extent of reaction was indicated by pressure vs. time readings. When the pressure had decreased to a sufficiently low value (usually ~10 mm.), the rate of reaction had also decreased; therefore, another quantity of the mixture was introduced to a pressure of 80 mm. Usually about seven hours were required between fillings and five or six fillings were needed for the production of ~1 g. of  $\text{NF}_4^+\text{AsF}_6^-$ . No appreciable etching of the glass discharge vessel could be observed and only small quantities of  $\text{SiF}_4$  could be detected by infrared spectroscopy.

In a typical experiment, the glow discharge of a mixture of  $\text{NF}_3$ ,

$\text{AsF}_5$ , and  $\text{F}_2$ , in 1:1:2 mole ratio at a pressure of 80 mm. produced a white nonvolatile solid and a residual gas pressure of  $\sim 19$  mm. The infrared spectrum of this gaseous residue showed only traces of  $\text{SiF}_4$  ( $\sim 1$  mm.). Therefore, it is reasonable to assume that the remaining 18 mm. of pressure is due to  $\text{F}_2$ . And assuming that  $\sim 2$  mm. of  $\text{F}_2$  could have been consumed by interaction with parts of the discharge vessel, it is clear that  $\text{NF}_3$  (20 mm.),  $\text{AsF}_5$  (20 mm.) and  $\text{F}_2$  (20 mm.) have reacted in 1:1:1 mole ratio producing  $\text{NF}_4^+ \text{AsF}_6^-$ .

Anal. Calcd. for  $\text{NAsF}_{10}$ : As, 26.9; F, 68.1. Found: As, 26.9; F, 66.2.

Nitrogen trifluoride was introduced into a vessel containing liquid  $\text{AsF}_5$  at  $-78^\circ$  until a total pressure of 740 mm. was attained. With liquid  $\text{AsF}_5$  still present in quantity and the pressure remaining constant, no interaction between these components could be detected. Had interaction occurred, the total pressure would have decreased appreciably (vapor pressure of  $\text{AsF}_5$  at  $-78^\circ$  is  $\sim 150$  mm.).

Finally,  $\text{NF}_3$  (0.1 mole),  $\text{AsF}_5$  (0.1 mole), and  $\text{F}_2$  (excess) were introduced into a 100 ml. Monel cylinder equipped with a Monel Helicoid pressure gauge (0-4000 p.s.i.) and a Monel Whitey valve (see "materials and apparatus" section). A pressure of 960 p.s.i. was observed at  $25^\circ$ . The cylinder was heated electrically to  $485^\circ$  and a pressure of 2400 p.s.i. developed. These conditions were maintained for 12 hours, after which the cylinder was cooled to  $25^\circ$ . The pressure returned to almost its original value to 920 p.s.i. indicating

that no appreciable interaction had occurred. After removing the volatile material the cylinder was disassembled and only a small amount of pale yellow solid ( $\sim 2$  g.) was found. Elemental analysis indicated that this solid was  $\text{Ni}(\text{AsF}_6)_2$ . This may account for the slightly lower final pressure (lower by 30 p.s.i.) observed.

Anal. Calcd. for  $\text{NiAs}_2\text{F}_{12}$ : Ni, 13.5; As, 34.3; F, 52.2. Found: Ni, 13.9; As, 32.5; F, 53.7.

Elemental Analysis. - In general, products were analyzed for fluorine, arsenic, and nitrogen. The sample was fused using the Parr bomb technique ( $\text{Na}_2\text{O}_2$  and a trace of starch). Fluorine was determined by titration with  $\text{ThNO}_3$  using alizarine red as indicator, arsenic by the iodometric titration of As(V), and nitrogen by the Kjeldahl method. The latter method was not suitable for small sample size.

Mass Spectra. - Mass spectra were recorded on an EAI QUAD 200 mass spectrometer at sample temperatures in the range  $-196$  to  $+440^\circ$ . Good spectra were generally obtained using a controlled sample pressure of  $\sim 5 \times 10^{-6}$  mm.

Pure  $\text{NF}_4^+\text{AsF}_6^-$  ( $\sim 20$  mg.) was introduced into a small stainless steel tube equipped with a control valve. Since the mass spectrometer used was not equipped for placing a sample directly into the ionization chamber and  $\text{NF}_4^+\text{AsF}_6^-$  can not be sublimed without decomposition, only the decomposition and/or dissociation products of the com-

plex were observed. A second sample was prepared by introducing two drops of water over  $\text{NF}_4^+\text{AsF}_6^-$  ( $\sim 20$  mg.), maintained at  $-196^\circ$  to prevent the escape of any volatile products. After connecting the control valve (closed) to the stainless steel tube, the hydrolysis was allowed to occur at  $25^\circ$ . The products of this reaction were similarly recorded on the mass spectrometer.

X-Ray Powder Data. - Debye-Sherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper  $K_\alpha$  radiation and a nickel filter. Samples were sealed in Lindeman glass tubes ( $\sim 0.3$  mm. o.d.).

Density Measurements. - The density of  $\text{NF}_4^+\text{AsF}_6^-$  was found using the displacement method.<sup>8</sup> A perfluorinated amine (3M Co., FC-43) was used to fill the pycnometer. Attempts to obtain a density using a perfluorinated ether (3M Co., FC-75) were not successful due to interaction of the adduct with the ether.

Differential Thermal Analysis. - A Perkin-Elmer differential scanning calorimeter Model DSC-1 was used to obtain the DTA of  $\text{NF}_4^+\text{AsF}_6^-$ . The sample was sealed in aluminum pans. A heating rate of  $10^\circ \text{ min.}^{-1}$  and an argon purge of  $30 \text{ ml. min.}^{-1}$  were used.

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(8) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, J. Am. Chem. Soc., 86, 2583 (1964).

### Results

Synthesis. - Nitrogen trifluoride,  $\text{AsF}_5$ , and  $\text{F}_2$  (in excess), when subjected to low-temperature glow discharge, react in 1:1:1 mole ratio forming the complex,  $\text{NF}_4^+\text{AsF}_6^-$ . In experiments not using excess fluorine, a considerable quantity of undesired  $\text{NO}^+\text{AsF}_6^-$  was formed. Poor cooling of the glow-discharge vessel had a similar effect.

In a separate experiment, thermal activation and high pressure conditions ( $485^\circ$  and 2400 p.s.i., respectively) did not result in any interaction of the components,  $\text{NF}_3$ ,  $\text{AsF}_5$ , and  $\text{F}_2$  (in excess) except for the formation of  $\text{Ni}(\text{AsF}_6)_2$  due to corrosion of the Monel reaction vessel. Also, vapor pressure measurements did not indicate any interaction when gaseous  $\text{NF}_3$  was mixed with liquid  $\text{AsF}_5$  at  $-78^\circ$ .

Properties. - The complex is a hygroscopic, crystalline powder, storeable indefinitely in glass at  $25^\circ$  and fairly soluble in liquid HF ( $\sim 0.2$  g. ml. $^{-1}$  at  $25^\circ$ ). Attempts to sublime  $\text{NF}_4^+\text{AsF}_6^-$  were unsuccessful. Heating the solid in the glow-discharge vessel (under vacuum) to a temperature of  $250^\circ$  did not result in appreciable transfer of solid to cooler sections. Infrared measurements on the small amount of gaseous product from this "decomposition" indicated silicon tetrafluoride only.

Mass spectra of  $\text{NF}_4^+\text{AsF}_6^-$  (s) at temperatures  $-196$  to  $400^\circ$  revealed the following data: mass number (m/e), ion species: 19,  $\text{F}^+$ ;

33,  $\text{NF}^+$ ; 52,  $\text{NF}_2^+$ ; 71,  $\text{NF}_3^+$ ; 75,  $\text{As}^+$ ; 94,  $\text{AsF}^+$ ; 113,  $\text{AsF}_2^+$ ; 132,  $\text{AsF}_3^+$ ; 151,  $\text{AsF}_4^+$ . The spectra also showed trace quantities of other species: mass number (m/e), ion species: 28,  $\text{N}_2^+$ ; 30,  $\text{NO}^+$ ; 44,  $\text{CO}_2^+$ ; 47,  $\text{N}_2\text{F}^+$ ; 49,  $\text{NOF}^+$ ; 66,  $\text{N}_2\text{F}_2^+$ ; 85,  $\text{N}_2\text{F}_3^+$ . This data clearly indicates that the thermal decomposition products of  $\text{NF}_4^+\text{AsF}_6^-$  are  $\text{NF}_3$  and  $\text{AsF}_5$ . Fluorine is probably a product as well, but it can not easily be detected in these mass spectra. The impurities in the sample seem to be NO (from NOF),  $\text{N}_2\text{F}_4$ , and possibly  $\text{N}_2\text{F}_2$ . The peak at m/e 44 is due to  $\text{CO}_2$  always present in the mass spectrometer. The relative abundance of the ion species is not given due to sudden variances in the rate of decomposition of the sample. However, the mass spectra do show that the decomposition proceeds rapidly at temperatures higher than  $150^\circ$ .

Differential thermal analysis indicates exothermic decomposition at  $270^\circ$ .

Hydrolysis. - Qualitatively,  $\text{NF}_4^+\text{AsF}_6^-$  is very hygroscopic and readily hydrolyzes to a pale blue solution with the evolution of gas. On standing, the solution becomes colorless. This suggests the initial formation of nitrogen-oxygen containing radicals. Also, the gas evolved had a slight brown color indicative of one or more nitrogen oxide species.

Mass spectra of hydrolyzed  $\text{NF}_4^+\text{AsF}_6^-$  at temperatures  $-196$  to  $+440^\circ$  show the following: mass number (m/e), ion species: 14,  $\text{N}^+$ ; 16,  $\text{O}^+$ ;

17,  $\text{CH}^+$ ; 18,  $\text{H}_2\text{O}^+$ ; 19,  $\text{F}^+$ ; 20,  $\text{HF}^+$ ; 28,  $\text{N}_2^+$ ; 30,  $\text{NO}^+$ ; 32,  $\text{O}_2^+$ ; 33,  $\text{NF}^+$ ; 44,  $\text{CO}_2^+$ ; 45,  $\text{NO}_2^+$ ; 47,  $\text{N}_2\text{F}^+$ ; 49,  $\text{NOF}^+$ ; 52,  $\text{NF}_2^+$ ; 65,  $\text{NO}_2\text{F}^+$ ; 66,  $\text{N}_2\text{F}_2^+$ ; 71,  $\text{NF}_3^+$ ; 75,  $\text{F}_2^+$ ; 85,  $\text{N}_2\text{F}_3^+$ ; 94,  $\text{AsF}^+$ ; 101, ?; 104,  $\text{N}_2\text{F}_4^+$ ; 113,  $\text{AsF}_2^+$ ; 132,  $\text{AsF}_3^+$ . As before, the relative abundance of the ion species is not given for the same reason. The noteworthy products are  $\text{HF}$ ,  $\text{NO}$  (from  $\text{NOF}$ ),  $\text{NO}_2$  (from  $\text{NO}_2\text{F}$ ),  $\text{NF}_3$ ,  $\text{N}_2\text{F}_4$ ,  $\text{AsF}_5$  (only at temperatures higher than  $100^\circ$ ), and possibly  $\text{N}_2$ . Also, there is some indication of small amounts of  $\text{AsOF}_3$  (m/e, ion species: 91,  $\text{AsO}^+$ ; 110,  $\text{AsOF}^+$ ; 129,  $\text{AsOF}_2^+$ ; 148,  $\text{AsOF}_3^+$ ). The peak at m/e 44 is again due to  $\text{CO}_2$ .

X-Ray Powder Data. - Table I lists calculated and observed X-ray powder diffraction data (indexed in the tetragonal system) for  $\text{NF}_4^+\text{AsF}_6^-$ .<sup>9</sup> From these data, the calculated unit cell dimensions are  $a = 7.70 \text{ \AA}$ . and  $c = 5.73 \text{ \AA}$ . For comparison, Table I also lists the d spacings for  $\text{PCl}_4^+\text{PCl}_6^-$ .

Density measurements using the perfluorinated ether, FC-75, as ballast fluid, were not successful. This ether reacts with  $\text{NF}_4^+\text{AsF}_6^-$ .

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- (9) The observed diffraction pattern was somewhat poor in quality since relatively brief exposures had to be used to avoid decomposition of the sample by X-rays. Thus the patterns obtained were either of low intensity free of lines due to decomposition products or of higher intensity but containing interfering lines from decomposition products. Therefore, the observed intensities are not so accurate.



Table I

X-ray Powder Data for  $\text{NF}_4^+\text{AsF}_6^-$  and  $\text{PCl}_4^+\text{PCl}_6^-$

Intensity	d (obsd.), Å.	$\text{NF}_4^+\text{AsF}_6^-$		Intensity	$\text{PCl}_4^+\text{PCl}_6^-$		hkl
		$\sin^2 \theta$ (obsd.)	$\sin^2 \theta$ (calcd.)		d (obsd.), Å.		
mw	5.46	0.0199	0.0200	3	6.7		110
ms	4.57	0.0284	0.0284	13	5.8		101
vs	3.93	0.0384	0.0384	100	4.99		111
s	3.84	0.0400	0.0400	75	4.70		200
s	3.22	0.0576	0.0584	20	3.99		201
mw	2.94	0.0685	0.0684	5	3.67		211
mw	2.82	0.0745	0.0736	15	3.48		002
m	2.66	0.0840	0.0836	50	2.96		102
w	2.52	0.0934	0.0936				112
w	2.360	0.1022	0.1000				310
vw	2.197	0.1226	0.1236	25	2.88		202, 301
vw	2.030	0.1565	0.1584	100	2.79		212
vw	1.926	0.1596	0.1600	20	2.44		321
vw	1.903	0.1634	0.1636	10	2.32		400
mw	1.817	0.1793	0.1800				302
mw	1.768	0.1894	0.1884				330
							411

<sup>a</sup> "Powder Diffraction File," ASTM Special Technical Publication 48-M2, American Society for Testing and Materials, Pa., 1964, No. 1-0250.

However, only slight interaction was observed using the perfluorinated amine, FC-43, and a density,  $d^{25^\circ} = 2.98 \text{ g. cm.}^{-3}$  was found. This density value indicates two "molecules" of  $\text{NF}_4^+\text{AsF}_6^-$  per unit cell ( $d_{\text{calcd.}} = 2.72 \text{ g. cm.}^{-3}$ ).

When  $\text{NF}_4^+\text{AsF}_6^-$  was prepared using proper experimental conditions, the X-ray powder pattern did not show even a trace of the impurity,  $\text{NO}^+\text{AsF}_6^-$ .

### Discussion

Synthesis. - (i) The existence of the corresponding  $\text{M}_x\text{F}_y$  species had always been known in the case of ionic complexes containing  $\text{M}_x\text{F}_{(y-1)}^+$ . Thus, such complexes could easily be prepared from  $\text{M}_x\text{F}_y$  and a suitable acceptor species such as the strong Lewis acids,  $\text{AsF}_5$  or  $\text{SbF}_5$ . Since  $\text{NF}_5$  has never been prepared (and is unlikely to be due to the validity of the octet rule for the first row elements of the periodic system),  $\text{NF}_4^+$  can not be synthesized in this manner. (ii) A theoretically possible halogen exchange reaction,  $\text{NX}_4^+$  (where X = Cl, Br, or I)  $\longrightarrow$   $\text{NF}_4^+$  is improbable for similar reasons, i.e.,  $\text{NX}_4^+$  has never been prepared. (iii) Finally,  $\text{NH}_4^+$  to  $\text{NF}_4^+$  by direct fluorination is unlikely. In this case, the intermediates would be

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- (10) A. Young, T. Hirata, and S. Morrow, J. Am. Chem. Soc., 86, 20 (1964).

unstable and would likely decompose with the elimination of HF analogous to the partially fluorinated amines.<sup>11,12</sup> Therefore, a more promising method for the preparation of  $\text{NF}_4^+$  considers the use of the next lower fluoride,  $\text{NF}_3$ , and fluorine (either through  $\text{NF}_3^+ + \text{F} \cdot$  or  $\text{NF}_3 + \text{F}^+$ ). This requires a high activation energy.

The formation of  $\text{NF}_4^+$  from  $\text{NF}_3$  and  $\text{F}_2$  will be favored by the following: (i) sufficient activation energy which might be supplied by radiation (X-rays or radioactive fission products, etc.), flash photolysis, thermal activation, or glow discharge; (ii) lowering this activation energy through the formation of an intermediate activated complex (including a solvation effect using a suitable solvent); (iii) stabilizing  $\text{NF}_4^+$  by the simultaneous formation of highly symmetrical anions, such as  $\text{AsF}_6^-$  or  $\text{SbF}_6^-$ , stable and energetically favored. In addition, the formation of a solid or a complex in solution will result in a gain of lattice energy or solvation energy, respectively.

Our use of thermal activation, simply by heating a mixture of  $\text{NF}_3$ ,  $\text{AsF}_5$ , and  $\text{F}_2$  under autogenous pressure to a temperature of  $485^\circ$ , failed to produce  $\text{NF}_4^+$ . From the possible remaining energy sources

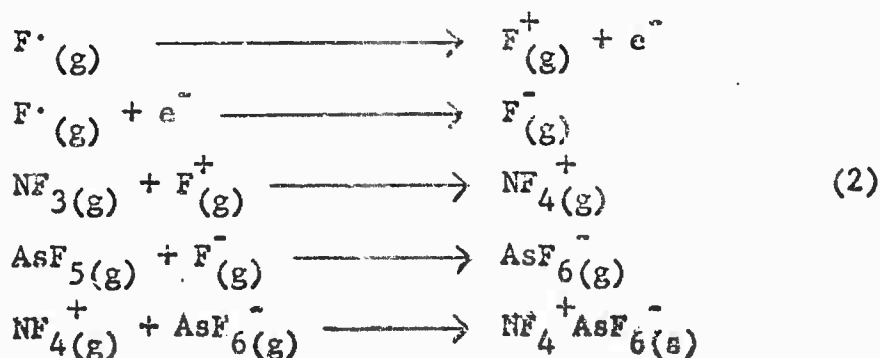
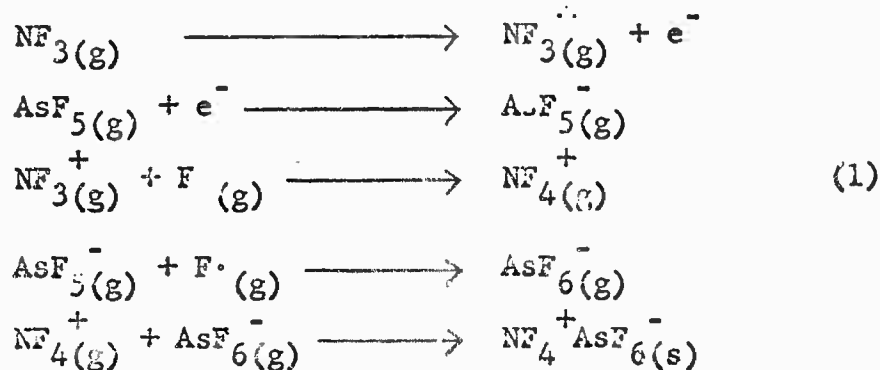
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(11) H. Dubb, R. Greenough, and E. C. Curtis, *Inorg. Chem.*, 4, 648 (1965).

(12) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, 62, 1 (1962).

we chose glow discharge at  $-78^\circ$  for the following reasons: (i)  $\text{NF}_3$  and  $\text{AsF}_5$  were observed not to interact at  $-78^\circ$ , which is not surprising since  $\text{NF}_3$  and  $\text{BF}_3$  were not observed to interact at low temperature;<sup>13</sup> (ii) the vapor pressures of the starting materials are sufficient at  $-78^\circ$ ; (iii) the hoped for product,  $\text{NF}_4^+\text{AsF}_6^-$ , could have a low thermal stability.

Two possible mechanisms are proposed. Mechanism 1 is based on the ionization of  $\text{NF}_3$  to  $\text{NF}_3^+$  and Mechanism 2 involves the heterolytic fission of a fluorine molecule (to  $\text{F}^+$  and  $\text{F}^-$ ) aided by the presence of a Lewis acid ( $\text{AsF}_5$ ) and a Lewis base ( $\text{NF}_3$ ).




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(13) A. D. Craig, Inorg. Chem., 3, 1628 (1964).

Mechanism 1 may be slightly favored since the ionization potential of  $\text{NF}_3$  (13.2 e.v.)<sup>14</sup> is less than that of the fluorine atom,  $\text{F}^\bullet$  (17.34 e.v.).<sup>15</sup> However, the energy supplied by glow discharge using 15 kv. is likely considerably greater than either ionization potential. Kinetic measurements will probably be necessary to formulate the true mechanism.

Properties. - It is surprising, in view of previously reported estimations,<sup>1,2</sup> that  $\text{NF}_4^+\text{AsF}_6^-$  does not decompose appreciably at temperatures less than 150°. As expected, the complex can not be sublimed without irreversible decomposition. The heat of formation of  $\text{NF}_4^+\text{AsF}_6^-(\text{s})$  could be estimated using a Born-Haber cycle. This would give a measure of the stability of the complex relative to its decomposition products,  $\text{NF}_3$ ,  $\text{AsF}_5$ , and  $\text{F}_2$ . The heat of formation of  $\text{NF}_4^+(\text{g})$  has been estimated<sup>2</sup> and an estimate of the lattice energy of  $\text{NF}_4^+\text{AsF}_6^-(\text{s})$  can be obtained from experimental X-ray data (using the Kapustinskii equation<sup>16</sup>). However, little data are available in order to estimate the heat of formation of  $\text{AsF}_6^-(\text{g})$ .

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(14) R. M. Reese and V. H. Dibeler, J. Chem. Phys., 24, 1175 (1956).

(15) Handbook of Chemistry and Physics, 45th edition, The Chemical Rubber Co., Cleveland, Ohio, 1964, p. E-41.

(16) A. F. Kapustinskii, Quart. Rev., 10, 283 (1956).

Mass Spectra. - Mass spectrometry was used mainly to identify qualitatively the thermal decomposition and hydrolysis products of  $\text{NF}_4^+\text{AsF}_6^-$ . Generally, there was no difficulty in assignment of ion species to corresponding mass number. The peaks at  $m/e$  28 and 85 could be due to  $\text{Si}^+$  and  $\text{SiF}_3^+$  (from  $\text{SiF}_4$ ), respectively; however, if this were correct the peak at  $m/e$  85 ( $\text{N}_2\text{F}_3^+$ ) would be much more intense than it actually is. In fact the peaks at  $m/e$  47 ( $\text{N}_2\text{F}^+$ ) and 66 ( $\text{N}_2\text{F}_2^+$ ) have about the same intensity as that of the peak at  $m/e$  85, in agreement with the observed intensities for the mass spectrum of  $\text{N}_2\text{F}_4$ .<sup>17</sup> We have assigned the peak at  $m/e$  44 to  $\text{CO}_2^+$  not to  $\text{N}_2\text{O}^+$  since the latter assignment would imply the presence of appreciable quantities of  $\text{NO}^+$  as well. But  $\text{NO}^+$  was observed only in an extremely small amount and only at two temperatures, 120 and 180°, whereas the peak at  $m/e$  44 was present in all spectra. The peaks assigned to  $\text{NF}_3$  agree well with the previously obtained mass spectrum of  $\text{NF}_3$ .<sup>12,14</sup> The parent ion,  $\text{AsF}_5^+$ , at  $m/e$  170, was not observed since only the dissociation and/or decomposition products entered the mass spectrometer. This peak is absent in the mass spectrum of pure  $\text{AsF}_5$ <sup>18</sup> and in the mass spectrum of the thermal decomposition products of

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(17) J. T. Herron and V. H. Dibeler, J. Chem. Phys., 33, 1595 (1960).

(18) R. P. Nielsen, Shell Development, Emeryville, California, Private communication.

$\text{O}_2^+ \text{AsF}_6^-$ .<sup>10</sup> The parent ion peak is also lacking in the mass spectrum of  $\text{KrF}_2$ .<sup>6,19</sup>

No peak at  $m/e$  38 ( $\text{F}_2^+$ ) occurs. However, this does not necessarily mean that  $\text{F}_2$  is not a decomposition product since the mass spectrometer had not been passivated prior to the measurements on  $\text{NF}_4^+ \text{AsF}_6^-$ . The peak at  $m/e$  19 ( $\text{F}^+$ ) is too intense by a factor of about seven to be entirely due to  $\text{NF}_3$  (intensity ratio  $\text{NF}_2^+/\text{F}^+ = 20/1$ )<sup>14</sup> and consequently,  $\text{F}_2$  may contribute to its abnormally high intensity. However, the fragmentation of  $\text{AsF}_5$  no doubt also produces  $\text{F}^\bullet$  which can ionize easily to  $\text{F}^+$ .

The trace impurities (indicated by the mass spectra) in  $\text{NF}_4^+ \text{AsF}_6^-$  are easily accountable. The starting material,  $\text{NF}_3$ , may contain traces of  $\text{N}_2\text{F}_2$ , thus forming the complex,  $\text{N}_2\text{F}^+ \text{AsF}_6^-$ .<sup>20</sup> Also, under glow discharge conditions, traces of  $\text{N}_2\text{F}_4$  could form, probably resulting in complex formation between  $\text{N}_2\text{F}_4$  and  $\text{AsF}_5$  (in analogy to the corresponding  $\text{SbF}_5$  compound<sup>21</sup>). This species could also form during the decomposition of  $\text{NF}_4^+ \text{AsF}_6^-$ . Present in even smaller quantity,  $\text{NO}^+$  and  $\text{NOF}^+$  ion species are no doubt due to  $\text{NO}^+ \text{AsF}_6^-$ . This compound was a substantial impurity in experiments in which excess  $\text{F}_2$  was not used in the glow discharge vessel or in experiments

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(19) E. N. Sloth and M. H. Studier, *Science*, 141, 528 (1963).

(20) D. Moy and A. R. Young, *J. Am. Chem. Soc.*, 87, 1889 (1965).

(21) J. K. Ruff, *ibid.* 87, 1140 (1965).

in which the glow discharge vessel was not sufficiently cooled. It was identified by infrared spectroscopy ( $\text{NO}^+$  stretching vibration at  $2300 \text{ cm.}^{-1}$ )<sup>22</sup> and X-ray powder diffraction data.<sup>10</sup> The formation of  $\text{NO}^+\text{AsF}_6^-$  can be due to either the interaction of  $\text{NF}_4^+\text{AsF}_6^-$  with the glass walls of the glow-discharge vessel, represented by the following equation:



or reaction involving the formation of NOF as follows:



Since fluorine can react with NOF (or NO) to form  $\text{NF}_3$ ,<sup>12,23</sup> excess fluorine will suppress the formation of NOF. An excess of fluorine is also desirable to replenish that which is consumed by interaction with the glass walls<sup>24</sup> or copper electrodes of the glow-discharge vessel and by interaction with any traces of nitrogen (impurity in the  $\text{NF}_3$ ) present forming  $\text{NF}_3$ .<sup>25</sup>

The mass spectra of hydrolyzed  $\text{NF}_4^+\text{AsF}_6^-$  show the expected ion

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- (22) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, 4, 905 (1965).
  - (23) O. Glemser, *Angew. Chem. (Int. Ed.)*, 4, 446 (1965).
  - (24) A. G. Streng and A. V. Grosse, *J. Am. Chem. Soc.*, 88, 169 (1966).
  - (25) W. Maya, *Inorg. Chem.*, 3, 1063 (1964).



species, notably  $\text{HF}^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{NOF}^+$ ,  $\text{NO}_2\text{F}^+$ ,  $\text{AsO}^+$ ,  $\text{AsOF}^+$ ,  $\text{AsOF}_2^+$ , and  $\text{AsOF}_3^+$ . Since the ions species,  $\text{AsF}_3^+$ ,  $\text{AsF}_2^+$ , and  $\text{AsF}^+$ , are detected in substantial quantity, the lack of a peak at  $m/e$  151 ( $\text{AsF}_4^+$ ) is difficult to explain. The fact that  $\text{NF}_3$  is not easily hydrolyzed<sup>12</sup> accounts for its presence in substantial quantity.

In summary, the mass spectra showed that  $\text{NF}_4^+\text{AsF}_6^-$ , prepared using the proper experimental conditions as previously described, contained only small amounts of impurities. In addition, the thermal decomposition and hydrolysis products of the complex were identified.

Structure of  $\text{NF}_4^+\text{AsF}_6^-$ . - Since the 1:1:1 mole ratio of the complex formed from  $\text{NF}_3$ ,  $\text{AsF}_5$ , and  $\text{F}_2$ , and the ionic structure,  $\text{NF}_4^+\text{AsF}_6^-$ , were established by quantitative vacuum synthesis and elemental analysis and by vibrational and  $\text{F}^{19}$  magnetic resonance spectroscopy,<sup>5</sup> respectively, we have taken the liberty of using this ionic structure throughout the text. Further evidence for this structure is the high thermal stability of the complex.

X-ray powder data (Table I) indicate that  $\text{NF}_4^+\text{AsF}_6^-$  has a crystal structure similar to that of  $\text{PCl}_4^+\text{PCl}_6^-$ .<sup>26</sup> This is not too surprising since both compounds have comparable anion radius to cation radius ratio and have ions of similar shape. As expected,  $\text{PCl}_4^+\text{PCl}_6^-$  has

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(26) D. Clark, H. M. Powell, and A. F. Wells, J. Chem. Soc., 642 (1942).

a somewhat larger unit cell ( $a = 9.22 \text{ \AA}$ ,  $c = 7.44 \text{ \AA}$ ) and a lower density ( $d = 2.12 \text{ g. cm.}^{-3}$ ); however,  $a/c$  is similar for both compounds, i.e., 1.23 and 1.34 for  $\text{PCl}_4^+ \text{PCl}_6^-$  and  $\text{NF}_4^+ \text{AsF}_6^-$ , respectively. Also, both compounds have two "molecules" per unit cell. In both X-ray powder patterns,  $hk0$  diffraction lines are absent for  $h + k =$  odd integer, indicative of a similar space group. The structure is essentially the cesium chloride type; however, the nonspherical ions of  $\text{NF}_4^+ \text{AsF}_6^-$  and  $\text{PCl}_4^+ \text{PCl}_6^-$  cause a distortion (i.e., from simple cubic to tetragonal). Each ion ( $\text{NF}_4^+$  or  $\text{AsF}_6^-$ ) has eight neighboring ions of opposite charge.

Nomenclature. - Previously used names such as "tetrafluoroammonium" or "perfluoroammonium" cation for  $\text{NF}_4^+$  are inappropriate since the polarity of the bond in  $\text{NF}_4^+$  is different from that in  $\text{NF}_4^+$ . Whereas for  $\text{NF}_4^+$  the nitrogen atom has a formal oxidation number, +V, it is -III for  $\text{NH}_4^+$ . Therefore,  $\text{NF}_4^+$  is named "tetrafluoronitronium(V)", as a derivative of hypothetical  $\text{NF}_5$ .

Acknowledgment. - We thank Drs. J. N. Wilson and R. P. Nielsen of Shell Development, Emeryville, California, for the use of the mass spectrometer. This work was supported by the Office of Naval Research.

III. Manuscript of Paper: Tetrafluoronitronium(V) Cation,  $\text{NF}_4^+$ .  
Vibrational and  $\text{F}^{19}$  Magnetic Resonance Spectra of  $\text{NF}_4^+\text{AsF}_6^-$

Contribution from the Western Research Center,  
Stauffer Chemical Company, Richmond, California

Tetrafluoronitronium(V) Cation,  $\text{NF}_4^+$ . Vibrational and  
 $\text{F}^{19}$  Magnetic Resonance Spectra of  $\text{NF}_4^+\text{AsF}_6^-$

By Karl O. Christe, Jacques P. Guertin,  
Attila E. Pavlath, and Wolfgang Sawodny<sup>1</sup>

Received , 1966

Abstract

Infrared, Raman, and  $\text{F}^{19}$  magnetic spectroscopy confirm the ionic structure,  $\text{NF}_4^+\text{AsF}_6^-$ , for the compound formed by the addition of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  in 1:1:1 mole ratio. The  $\text{NF}_4^+$  cation, with four equivalent fluorine atoms, has a tetrahedral structure (point group  $T_d$ ). The force constants of  $\text{NF}_4^+$  are calculated and compared with that of  $\text{NF}_3$  and isoelectronic species,  $\text{BF}_4^-$  and  $\text{CF}_4$ .

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Technische Hochschule, Stuttgart, Germany.

### Introduction

Recently, we have reported the existence of  $\text{NF}_4^+\text{AsF}_6^-$ .<sup>2</sup> In the preceding paper<sup>3</sup> the synthesis and properties of this complex have been described. The object of this paper is to support the proposed ionic structure,  $\text{NF}_4^+\text{AsF}_6^-$ , by spectroscopic data and to compare the bonding in  $\text{NF}_4^+$  with that of  $\text{NF}_3$  and isoelectronic  $\text{BF}_4^-$  and  $\text{CF}_4$ .

### Experimental Section

The preparation of  $\text{NF}_4^+\text{AsF}_6^-$  by the glow discharge of a 1:1 mole mixture of  $\text{NF}_3$  and  $\text{AsF}_5$  in the presence of excess fluorine has been described in the preceding paper.<sup>3</sup> In the sample used for the spectroscopic investigations, none of the possible impurities, such as  $\text{NO}^+\text{AsF}_6^-$  or complex copper salts, could be detected by either X-ray or infrared measurements. Manipulations outside the vacuum line were done in the dry nitrogen atmosphere of a glove box.

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- (2) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Letters*, (1966).
- (3) J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, 5, (1966).

Infrared Spectra. - Infrared spectra were recorded on a Beckman Model IR-9 grating spectrophotometer in the range 4000-420  $\text{cm}^{-1}$ . A sample of  $\text{NF}_4^+\text{AsF}_6^-$ , as a dry powder, was placed between AgCl windows. These were held in place by a screw cap metal cell equipped with neoprene O-rings.

Raman Spectra. - The Raman spectra were recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 Å.) as the exciting line and a saturated  $\text{KNO}_2$  solution as the filter. A Pyrex-glass tube (7 mm. o.d.) having an inner hollow glass cone for variable sample thickness or a glass-plunger type of reflection cell was used. Due to the very fine particle size of the sample, the better spectra were obtained using the latter technique.

$\text{F}^{19}$  Magnetic Resonance Spectra. - A Varian Associates Model HA-100 spectrometer was used to record the  $\text{F}^{19}$  magnetic resonance spectra. Solid  $\text{NF}_4^+\text{AsF}_6^-$  (0.15 g.) was placed into a Teflon FEP tube equipped with a Monel bellows-seal valve (Hoke, M482M). The tube was connected to a vacuum line having only Monel and Teflon FEP construction. Purified liquid HF ( $\sim 0.5$  ml.) was condensed into the tube. After allowing one hour for complete mixing at  $25^\circ$ , the clear solution above some undissolved material was transferred mechanically (decanted) into a Teflon FEP n.m.r. tube ( $\sim 4$  mm. o.d.). The n.m.r. tube was "heat sealed" under vacuum (using a hot Pyrex-glass rod) and inserted into a standard 5 mm. o.d. glass n.m.r. tube to facilitate

the spinning of the sample. Fluorocarbon-11 ( $\text{CFCl}_3$ ) was used as an external standard ( $\delta = 0.0$  p.p.m.).

### Results

$\text{F}^{19}$  Magnetic Resonance Spectrum. - The  $\text{F}^{19}$  magnetic resonance spectrum of a solution of  $\text{NF}_4^+\text{AsF}_6^-$  in liquid HF is shown in figure 1. The following chemical shifts were obtained: (i) a strong singlet at  $\delta = +196.1$  p.p.m. (HF solvent), (ii) a broad multiplet at  $\delta = +69.5$  p.p.m. ( $\text{AsF}_6^-$ ), and (iii) a triplet at  $\delta = -213.5$  p.p.m. ( $\text{NF}_4^+$ ) having a coupling constant,  $J_{\text{NF}} = 234$  c.p.s. For comparison,  $\text{F}_2$  in liquid HF and  $\text{NF}_3$  have chemical shifts,  $\delta = -428.7$  and  $-146.9$  p.p.m.,<sup>4</sup> respectively.

Vibrational Spectra. - Figure 2 shows the infrared spectrum of  $\text{NF}_4^+\text{AsF}_6^-$ . The band at  $406 \text{ cm}^{-1}$  does not actually have as high an intensity as shown in the figure, since the AgCl windows begin to absorb in this range. The Raman spectrum was rather weak and could be obtained only under very extreme conditions. There are two certain bands, one at  $813 \text{ cm}^{-1}$ , and a very broad one at about  $500 \text{ cm}^{-1}$ . The latter seems to consist of two separate bands at  $520$  and  $488 \text{ cm}^{-1}$ . The other lines reported are somewhat doubtful, but coincide well with

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(4) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, J. Chem. Phys., 37, 182 (1962).

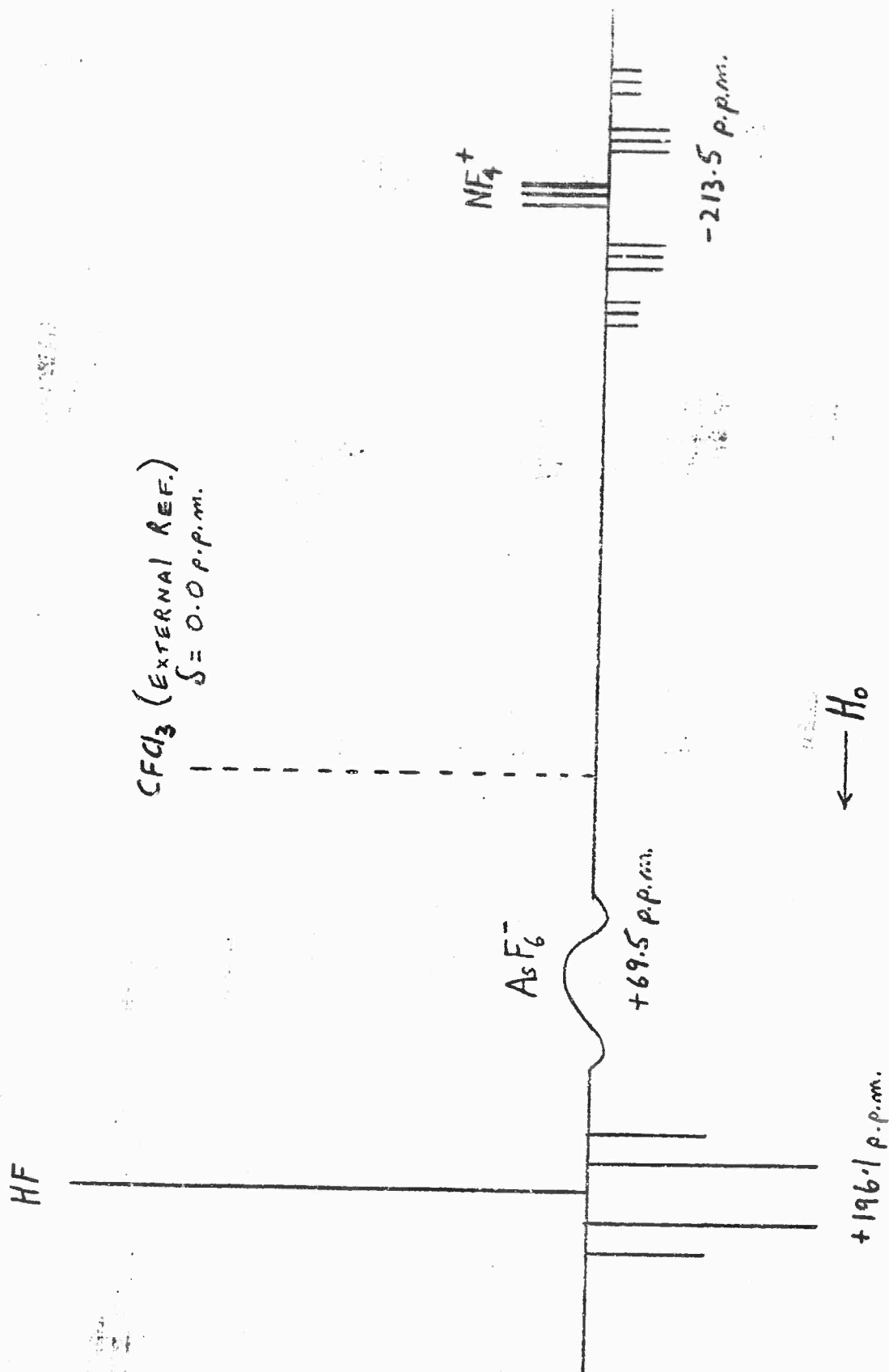
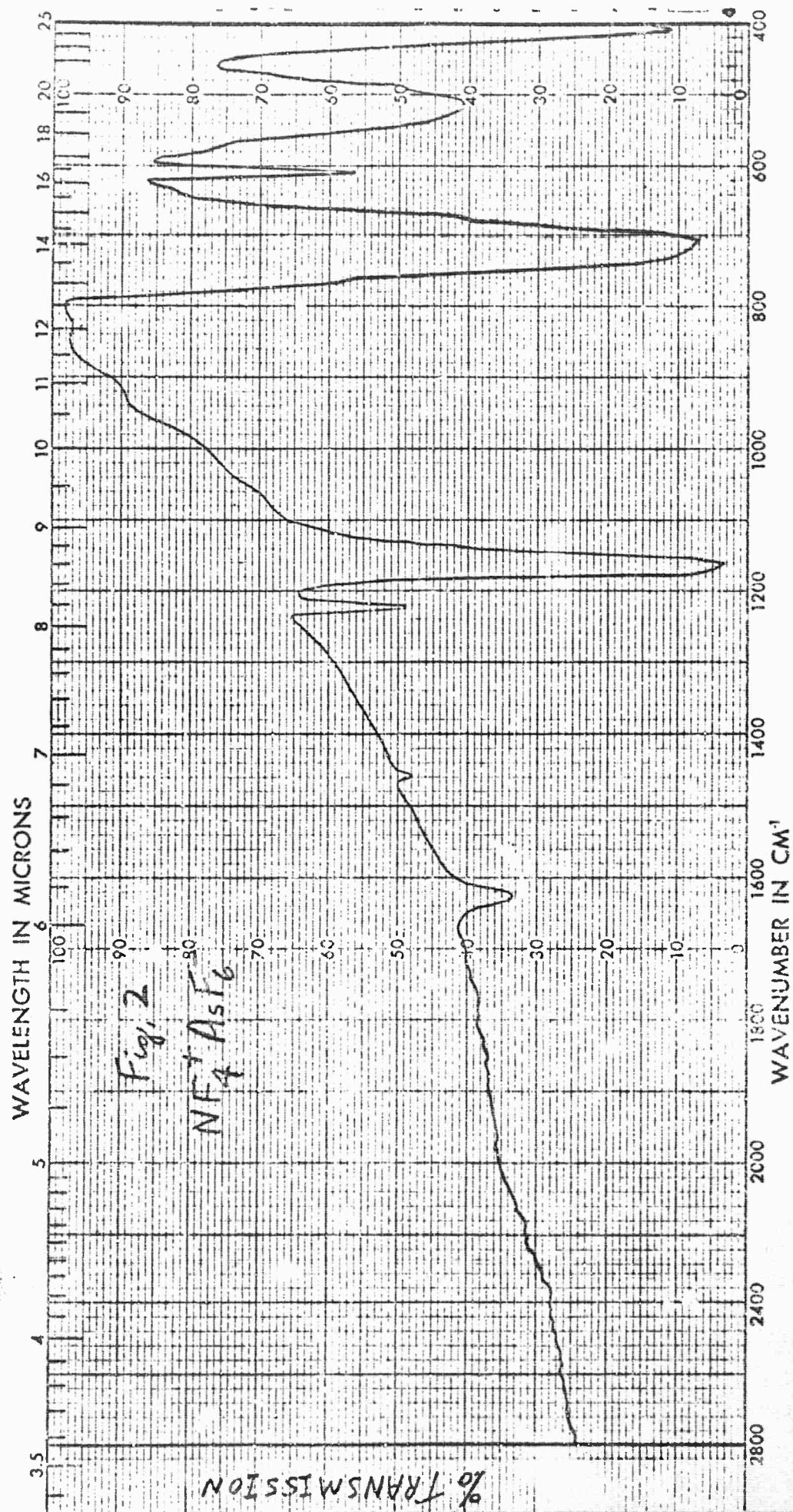


Fig. 1.  
 $\text{F}^{19}$  MAGNETIC RESONANCE OF  $\text{NF}_4^+\text{AsF}_6^-$  IN LIQUID HF.





with the strongest Raman lines expected for  $\text{AsF}_6^-$ .

Table I lists the observed frequencies (and their assignments) of the infrared and Raman spectra of  $\text{NF}_4^+\text{AsF}_6^-$ .

Calculation of Force Constants. - The force constants of  $\text{NF}_4^+$  were calculated by a recently published method.<sup>5</sup> Using this method, the normal vibrations are sufficient data to allow the calculation of a complete set of constants. Table II compares the force constants obtained by this method with the force constants of the General Valence Force Field (GVFF). A good approximation of the GVFF values is expected especially for the fluorides of the first row elements of the

Table II

Comparison of Valence Force Constants (mdynes/Å.)

	<u>GVFF</u>	<u>Our Method</u>
$\text{NF}_3$	4.36 <sup>6</sup>	4.39 <sup>7</sup>
$\text{CF}_4$	6.97 <sup>8</sup>	6.88 <sup>7</sup>
$\text{BF}_3$	7.10 <sup>9</sup>	7.29 <sup>5</sup>

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(5) W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, 21, 995 (1965).

(6) P. M. Schatz, *J. Chem. Phys.*, 29, 481 (1958).

(7) W. Sawodny, unpublished.

(8) J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, 20, 1089 (1964).

(9) J. L. Duncan, *J. Mol. Spectr.*, 13, 338 (1964).

Table I

Vibrational Spectra of  $\text{NF}_4^+ \text{AsF}_6^-$  and their Assignment

Observed frequencies,  $\text{cm}^{-1}$

Assignment (point group)  
 $\text{NF}_4^+$  ( $T_d$ )       $\text{AsF}_6^-$  ( $O_h$ )

Infrared

Raman

1628 vw

1458 vvw

1223 w

1159 s

} overtones or combination vibrations

$\nu$  asym.,  $\nu_3$  ( $F_2$ )

$\nu$  sym.,  $\nu_1$  ( $A_1$ )

813 m

709 vs

$\nu$  asym.,  $\nu_3$  ( $F_{1u}$ )

687 w (?)

$\nu$  sym.,  $\nu_1$  ( $A_{1g}$ )

611 mw

$\nu_3$ ,  $\nu_4$  or  $\nu$  sym.,  $\nu_2$  ( $E_g$ )

518 m

$\delta$  asym.,  $\nu_4$  ( $F_2$ )

488 w (?)

$\delta$  sym.,  $\nu_2$  (E)

406 m

$\delta$  asym.,  $\nu_4$  ( $F_{1u}$ )

378 vw (?)

$\delta$  sym.,  $\nu_5$  ( $F_{2g}$ )

periodic system. The symmetry force constants of  $\text{NF}_4^+$  (Table III) were calculated using the set of normal vibrations obtained from Table I.

Table III

Symmetry Force Constants of  $\text{NF}_4^+$  (mdynes/Å.)

$A_1$	$F_{11}$	7.396		
E	$F_{22}$	0.888		
$F_2$	$F_{33}$	5.415	$F_{34}$	0.495
			$F_{44}$	0.694

Hence, the valence force constant (fr) and coupling force constant (frr) are 5.910 and 0.495 mdynes/Å., respectively. Because of the redundancy condition in  $A_1$ , it is not possible to give explicit data for the deformation constants.

### Discussion

Few structural possibilities exist for a 1:1:1 adduct formed from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$ . If we exclude very unlikely structures requiring either more than eight valence electrons for the nitrogen atom or extremely unusual oxidation and coordination numbers for the arsenic atom, such as a hypothetical  $\text{AsF}_8^-$ , the only remaining plausible structure is  $\text{NF}_4^+\text{AsF}_6^-$ . This structure satisfies the octet rule for the nitrogen atom and results in two highly symmetrical

and saturated (based on coordination number) ions of high stability. Since the octet rule is strictly applicable only to the first row elements of the periodic system, it is expected that  $\text{NF}_4^+$  is an ideal  $\text{sp}^3$ -hybrid (tetrahedron), analogous to isoelectronic  $\text{BF}_4^-$  and  $\text{CF}_4$ .

$\text{F}^{19}$  Magnetic Resonance Spectrum. - An ideal tetrahedral species,  $\text{XF}_4^+$ , should exhibit only a single  $\text{F}^{19}$  magnetic resonance line since the four fluorine atoms are equivalent. However, a nitrogen atom has a quadrupole moment. Thus, the expected singlet splits into a triplet ( $J_{\text{NF}} = 234$  c.p.s.). Similar quadrupole coupling is observed in the  $\text{F}^{19}$  magnetic resonance spectrum of  $\text{NF}_3$  (a triplet  $J_{\text{NF}} = 155$  c.p.s.)<sup>4</sup> and  $\text{N}_2\text{F}^+$  (a triplet,  $J_{\text{NF}} = 328$  c.p.s.).<sup>10</sup> Thus, the obtained triplet for  $\text{NF}_4^+\text{AsF}_6^-$  is entirely consistent with a tetrahedral  $\text{NF}_4^+$  cation possessing equivalent fluorine atoms.

Vibrational Spectra. - Table I shows the vibrational spectra of  $\text{NF}_4^+\text{AsF}_6^-$ . The following section discusses the assignment of the observed frequencies. An octahedral anion of the type  $\text{XY}_6^-$ , such as  $\text{AsF}_6^-$ , has  $\text{O}_h$  symmetry. The five normal modes of vibration are classified as ( $\text{A}_{1g} + \text{E}_g + \text{F}_{2g} + 2 \text{F}_{1u}$ ). Of these, only the two  $\text{F}_{1u}$  modes will be infrared active, while only the  $\text{A}_{1g}$ ,  $\text{E}_g$ , and  $\text{F}_{2g}$  modes will be Raman active, assuming that the selection rules are valid

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(10) D. Moy and A. R. Young, II, J. Am. Chem. Soc., 87, 1839 (1965).

and that the octahedron is not distorted. Accordingly, the normal modes associated with  $\text{AsF}_6^-$  can be assigned without difficulty. Assignment of four of the five expected fundamental vibrations was done with assurance, whereas the assignment of  $\nu_2 (E_g)$  to the infrared band at  $611 \text{ cm}^{-1}$  is uncertain. For example, this band could also be assigned to  $\nu_3 - \nu_4$  of  $\text{NF}_4^+$ . The  $\nu_2 (E_g)$  mode should not be infrared active; however, it is known that slight distortion of the  $\text{AsF}_6^-$  octahedron or crystal field effects could result in this mode becoming active. The observed frequencies and intensities are in good agreement with that of similar complexes containing  $\text{AsF}_6^-$ , such as  $\text{AsCl}_4^+ \text{AsF}_6^-$ <sup>11</sup> or  $\text{ClF}_2^+ \text{AsF}_6^-$ <sup>12</sup>.

The remaining bands of the  $\text{NF}_4^+ \text{AsF}_6^-$  spectra, therefore, should be due to the  $\text{NF}_4^+$  cation. A tetrahedral cation of the type  $\text{XY}_4^+$ , such as  $\text{NF}_4^+$ , has  $T_d$  symmetry. The four normal modes of vibration are classified as  $(A_1 + E + 2 F_2)$ . While all four modes are Raman active, only the two  $F_2$  modes are infrared active. The two infrared bands at  $1159$  and  $518 \text{ cm}^{-1}$  are obviously the triple degenerate asymmetric stretching and the triple degenerate asymmetric deformation vibration,  $\nu_3 (F_2)$  and  $\nu_4 (F_2)$ , respectively, of  $\text{NF}_4^+$ . Of the remaining Raman

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(11) J. Weidlein and K. Dehnicke, Z. anorg. allg. Chem., 337, 113 (1965).

(12) K. O. Christe and W. Sawodny, Inorg. Chem., in press.

bands the one with the highest intensity at  $813\text{ cm.}^{-1}$  is clearly the symmetric stretching vibration of the  $\text{NF}_4^+$  cation. If the very broad Raman band at  $\sim 500\text{ cm.}^{-1}$  is actually two bands at 520 and  $488\text{ cm.}^{-1}$ , the former corresponds to the  $518\text{ cm.}^{-1}$  band of the infrared spectrum, and therefore, is assigned to the asymmetric deformation vibration,  $\nu_4$  ( $F_2$ ), of  $\text{NF}_4^+$ . The  $488\text{ cm.}^{-1}$  band can tentatively be assigned to the symmetric deformation vibration,  $\nu_2$  (E), of  $\text{NF}_4^+$ , although the difference between  $\nu_2$  and  $\nu_4$  is rather small, compared with that of similar molecules such as  $\text{CF}_4$ <sup>13</sup> or  $\text{BF}_4^-$ .<sup>14</sup> The infrared spectrum shows three additional bands of low intensity. Their frequencies are too high to be fundamental vibrations and consequently, these bands are assigned to overtones or combination bands. They could also be due to slight impurities in the sample. In summary, the vibrational spectra strongly support the proposed structure,  $\text{NF}_4^+\text{AsF}_6^-$ , and are consistent with the predictions made for this type of complex.

Force Constants. - The  $\text{NF}_4^+$  cation is isoelectronic with  $\text{CF}_4$  and the  $\text{BF}_4^-$  anion. Woodward<sup>15</sup> compared force constants of species

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- (13) J. Goubeau, W. Bues, and F. W. Kampmann, Z. anorg. allg. Chem., 283, 123 (1956).
- (14) J. Goubeau and W. Bues, Z. anorg. allg. Chem., 268, 221 (1952).
- (15) L. A. Woodward, Trans. Farad. Soc., 54, 1271 (1958).

within similar isoelectronic series and suggested that the force constant increases as the magnitude of the positive charge of the central atom increases assuming only single bonds are involved. This theory should also apply to the isoelectronic series:  $\text{BF}_4^-$ ,  $\text{CF}_4$ ,  $\text{NF}_4^+$ . In this series, bonding orbitals of the central atom have the same hybridization ( $\text{sp}^3$ ). Also, partial double bond character is not possible due to the strict validity of the octet rule for the first row elements of the periodic system. However, Table IV indicates that Woodward's suggestion does not apply to the series:  $\text{BF}_4^-$ ,  $\text{CF}_4$ ,  $\text{NF}_4^+$ . The valence force constant does increase from  $\text{BF}_4^-$  to  $\text{CF}_4$ ; however, it decreases from  $\text{CF}_4$  to  $\text{NF}_4^+$ . In Table IV, the bond

Table IV

Force Constants of the Isoelectronic Species,  
 $\text{BF}_4^-$ ,  $\text{CF}_4$ , and  $\text{NF}_4^+$ ; Also Those of  $\text{NF}_3$  (mdynes/Å.)

	<u><math>\text{BF}_4^-</math></u>	<u><math>\text{CF}_4</math></u>	<u><math>\text{NF}_4^+</math></u>	<u><math>\text{NF}_3</math></u>
fr	5.28 <sup>7</sup>	6.88 <sup>7</sup>	5.91	4.39 <sup>7</sup>
$f_1$	5.06	6.08	7.09	4.25
n	1.04	1.13	0.83	1.03

orders ( $n = \text{fr}/f_1$ ) were calculated following the rules of Siebert<sup>16</sup>

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(16) H. Siebert, Z. anorg. allg. Chem., 273, 170 (1953).



and Goubeau.<sup>17</sup> The value of "n" is greater than one except for that of  $\text{NF}_4^+$ . The force constant (fr) of  $\text{NF}_4^+$  is larger than that of  $\text{NF}_3$ , but not as large as it should be according to Siebert's single bond values,  $f_1$ . Perhaps, the positively charged nitrogen atom combined with highly electronegative fluorine atoms results in considerable polarity of the N-F bond, thus decreasing the force constant and bond order.

Acknowledgments. - We thank Dr. W. E. Tolberg and co-workers of Stanford Research Institute, Menlo Park, California, for the use of equipment necessary to obtain the  $\text{F}^{19}$  magnetic resonance spectrum. We are also indebted to Dr. A. C. Jones of Shell Development, Emeryville, California, for the use of a Raman spectrometer. This work was supported by the Office of Naval Research.

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(17) J. Goubeau, *Angew. Chem.*, 69, 77 (1957).

IV. Manuscript of Paper: Difluorochlorates(I) of Cesium, Rubidium,  
and Potassium

Contribution from the Western Research Center  
Stauffer Chemical Company, Richmond, California

Difluorochlorates(I) of Cesium, Rubidium, and Potassium

By Karl O. Christe and Jacques P. Guertin

Abstract

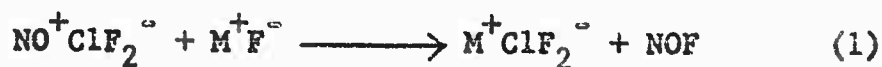
The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by the reaction of the corresponding fluorides with chlorine monofluoride or  $\text{NO}^+\text{ClF}_2^-$ . These white solids are the first known difluorochlorate(I) salts stable at 25°. They decompose exothermally at temperatures higher than 230°. Their composition and structure were established by elemental analysis, infrared, and X-ray studies. The salts are ionic and contain linear  $\text{ClF}_2^-$  anions. Attempts to prepare  $\text{LiClF}_2$  and  $\text{Ca}(\text{ClF}_2)_2$  failed, while  $\text{NaClF}_2$ ,  $\text{Ba}(\text{ClF}_2)_2$ , and  $\text{Sr}(\text{ClF}_2)_2$  may have formed to a very small extent.

### Introduction

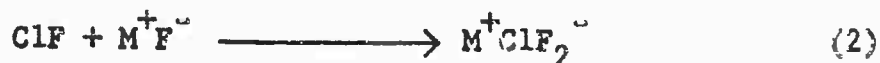
The existence of ionic complexes containing species such as  $\text{ClF}_2^+ 1-5$  and  $\text{ClF}_4^- 6-9$ , derived from chlorine trifluoride, is well established. However, complexes containing such species as  $\text{Cl}^+$  and  $\text{ClF}_2^-$ , formed from chlorine monofluoride, have not been investigated until recently. Schmeisser<sup>10</sup> isolated  $\text{Cl}^+\text{AsF}_6^-$  and

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- (1) F. Seel and O. Detmer, *Angew. Chem.*, 70, 163 (1958).
  - (2) F. Seel and O. Detmer, *Z. anorg. allgem. Chem.*, 301, 113 (1959).
  - (3) N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 5253 (1962).
  - (4) H. Selig and J. Shamir, *Inorg. Chem.*, 3, 294 (1964).
  - (5) K. O. Christe and A. E. Pavlath, *Z. anorg. allgem. Chem.*, 335, 210 (1965).
  - (6) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Am. Chem. Soc.*, 83, 2955 (1961).
  - (7) D. H. Kelly, B. Post, and R. W. Mason, *J. Am. Chem. Soc.*, 85, 307 (1963).
  - (8) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, *J. Am. Chem. Soc.*, 86, 2583 (1964).
  - (9) E. Whitney, R. MacLaren, T. Hurley, and C. Fogle, *J. Am. Chem. Soc.*, 86, 4340 (1964).
  - (10) Summary Report on the Inorganic Fluorine Chemistry Meeting, Argonne, 1963, *Science*, 143, 1058 (1964).

$\text{Cl}^+\text{SbF}_6^-$ , prepared by the interaction of  $\text{ClF}$  with the corresponding Lewis acid,  $\text{AsF}_5$  or  $\text{SbF}_5$ . We<sup>11</sup> have reported the existence of the  $\text{ClF}_2^-$  anion in the form of its nitrosyl salt,  $\text{NO}^+\text{ClF}_2^-$ . Nitrosyl difluorochlorate(I) was shown to be ionic in solution and in the solid state. The  $\text{ClF}_2^-$  anion was assigned a linear structure based on infrared investigation. Since  $\text{NO}^+\text{ClF}_2^-$  is stable only at low temperature we have investigated the replacement of the  $\text{NO}^+$  cation by an alkali or alkaline earth metal cation with the hope of obtaining more stable complex salts. This paper describes the results obtained from (1) the metathetical reaction shown by the equation,



and (2) the direct reaction shown by the equation,



where  $\text{M}^+$  is an alkali metal cation.

### Experimental

**Materials and Apparatus.** - The materials used in this work were manipulated in a standard pyrex-glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Reactions at overatmospheric pressure

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(11) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, 4, 905 (1965).

and elevated temperature were carried out in Monel containers equipped with a Monel pressure gauge and a Monel valve (Whitey, M6TS6). This valve could be connected to the glass vacuum line by Swagelock fittings and Kovar metal to graded glass seals. Chlorine monofluoride, nitrosyl fluoride (both from Ozark-Mahoning Company), and hexafluoroacetone (Allied Chemical) were purified by several low-temperature vacuum distillations. The purity of the volatile starting materials was determined by measurement of their vapor pressures, molecular weights, and infrared spectra. Little etching of the vacuum line could be observed. The alkali and alkaline earth metal fluorides (CsF 99.9% and RbF 99%, both from K & K Laboratories, Inc.) were used without further purification. Hygroscopic nonvolatile compounds were handled in the dry nitrogen atmosphere of a glove box.

**Infrared Spectra.** - Infrared spectra were recorded on a Beckman Model IR-9 grating spectrophotometer in the range  $4000-420\text{ cm}^{-1}$ . Screw cap metal cells equipped with neoprene O-rings and AgCl windows were used for solid samples. The solids were either milled with dry hexafluorobenzene or dry nujol, or they were used directly as dry powders.

**X-ray Powder Data.** - Debye-Scherrer powder patterns were taken using a Philips Norelco Instrument, Type No. 12046, with copper  $K_{\alpha}$  radiation and a nickel filter. Samples were sealed in Lindeman glass tubes ( $\sim 0.5\text{ mm. O.D.}$ ).

**Density Measurements.** - Density measurements were carried out by the displacement method<sup>8</sup> using a perfluorinated cyclic ether to fill the pycnometer.

**Differential Thermal Analysis.** - A Perkin-Elmer differential scanning calorimeter Model DSC-1 was used to obtain the DTA of the new compounds. These were sealed in aluminum pans. A heating rate of 10°/min. and an argon purge of 30 ml./min. was used.

**Elemental Analysis.** - Products were analyzed for fluorine, chlorine, and alkali or alkaline earth metal. Fluorine was determined by direct alkaline hydrolysis or by Parr bomb fusion of the sample, each followed by titration with  $\text{ThNO}_3$  using alizarine red as indicator. Chlorine was reduced to  $\text{Cl}^-$  either by Parr bomb fusion with  $\text{Na}_2\text{O}_2$  or by direct alkaline hydrolysis of the sample followed by reduction with  $\text{TiSO}_4$ . Finally, the resultant  $\text{Cl}^-$  was potentiometrically titrated with  $\text{AgNO}_3$ . Both methods compared favorably, yielding results with negligible deviations. The alkali metal content was determined by direct aqueous hydrolysis of the sample followed by flame spectroscopy. Gravimetric analysis yielded the alkaline earth metal content of a sample.

**Preparation of the Alkali Metal Difluorochlorates(I).** - Chlorine monofluoride and an alkali metal fluoride were mixed under different conditions at temperatures from 25 to 230° under autogenous pressures. In some reactions agitation and/or  $\text{NOF}$  (as a catalyst) were employed. Also,  $\text{CsF}$  was sometimes pretreated with  $\text{CF}_3\text{COCF}_3$ .

In a typical experiment, CsF (0.204 mole) was introduced into a 300 ml. Monel cylinder having NPT openings (0.5 in.) on both ends to facilitate removal of solid products. One end of the cylinder was capped with a Swagelock fitting and the other end was connected by Monel high-pressure tubing to a Monel pressure gauge (0-2000 p.s.i.) and a Monel control valve (Whitey, M6TS6). The cylinder was connected to the vacuum system and  $\text{CF}_3\text{COCF}_3$  (0.350 mole) was condensed into it. The mixture was vigorously shaken for 12 hours at 25° under autogenous pressure, after which all volatile material was removed by vacuum pumping on the cylinder (warmed to 150°) for two hours. Now, excess ClF (0.700 mole) was condensed at -196° over the CsF. The mixture was heated for 48 hours at 175° in an electric tube furnace equipped with an automatic temperature control. An internal pressure of 800 p.s.i. developed. After cooling to 25°, the volatile material was similarly removed (except in this case the cylinder was warmed only to 100°). The nonvolatile, white, crystalline product was removed from the cylinder and the increase in weight of the starting material (CsF) was determined (Table I).

### Results and Discussion

**Synthesis.** - The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by (1) metathetical reaction, or (2) direct interaction of ClF with the corresponding fluoride. Table I lists the results of several experiments. A 100% conversion



TABLE I

Syntheses of  $\text{CsClF}_2$ ,  $\text{RbClF}_2$ , and  $\text{KClF}_2$ <sup>a</sup>

Reactants, moles			Reaction Temperature, °C	Reaction Time, Hours	Reaction Pressure, p.s.i.	Conversion to $\text{ClF}_2$ salt based on weight increase of starting material, %	Calcd., % <sup>b</sup>				Found, %		
Fluoride	$\text{ClF}$	$\text{NOF}$					Metal	$\text{Cl}$	$\text{F}$		Metal	$\text{Cl}$	$\text{F}$
$\text{CsF}$							Cs						
0.200 <sup>c</sup>	0.700	-	175	48	800	55		74.8	9.4	15.8	73.6	9.1	16.0
0.035	0.210	0.012	175	48	1100	80		69.0	13.7	17.2	69.5	8.7	17.4
$\text{RbF}$							Rb						
0.047 <sup>d</sup>	0.200	0.047	25	24	1100	49		68.1	10.9	21.0	68.1	10.8	20.7
0.036	0.220	-	230	60	1300	73		61.4	16.3	22.4	60.6	15.0	22.3
0.028 <sup>e</sup>	0.240	0.015	230	60	1580	87		57.4	19.4	23.2	58.2	8.2	22.4
$\text{KF}$							K						
0.069	0.390	0.031	150	14	2200	27		58.5	8.5	33.0	58.2	6.5	33.7

<sup>a</sup>All reactions were done in 30 ml. Monel cylinders, except the first row reaction (done in a 300 ml. Monel cylinder).

<sup>b</sup>Calculated from the weight increase of the starting material assuming the product to be a mixture of metal fluorides and metal difluorochlorates(I) only.

<sup>c</sup> $\text{CsF}$  was pretreated with excess  $\text{CF}_3\text{COCF}_3$  at 25°.

<sup>d</sup>This mixture was vigorously agitated.

<sup>e</sup>A small amount of  $\text{Rb}_2\text{NiF}_6$  impurity caused the product to have a slight pink color.

of starting material to the difluorochlorate(I) was never achieved. After reaction at elevated temperature and pressure, the product usually was a fused solid and was difficult to remove from the reactor. The temperature of reaction could not be increased much higher than 230° due to the limited thermal stability of the products and interaction of the compounds with the Monel reactor resulting in the formation of some dark red alkali metal hexafluoronickelate(IV). This impurity was easily identified by its known X-ray diffraction pattern<sup>12-15</sup> and by analysis of the product for nickel.

No difficulties were expected for the metathetical reaction. The low thermal stability of  $\text{NO}^+\text{ClF}_2^-$ <sup>11</sup> assured the complete removal of the complex from the product. Since NOF is regenerated during the reaction [equation (1)], only catalytic amounts are required. Generally, the use of NOF resulted in higher conversions of the starting material; however, analyses indicated too low a chlorine content compared with the alkali metal and fluorine content and the percent conversion found from the weight increase of starting material. Therefore, the reaction of CsF with NOF in the

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- (12) W. Klemm and E. Huss, Z. anorg. allgem. Chem., 258, 221 (1949).
  - (13) H. Bode, Naturwissenschaften, 37, 477 (1950).
  - (14) I. R. Scholder and W. Klemm, Angew. Chem., 66, 461 (1954).
  - (15) H. Bode and E. Voss, Z. anorg. allgem. Chem., 286, 136 (1956).

absence of ClF was investigated. A weight increase was obtained; however, the analytical results were inconclusive. The X-ray pattern showed only alkali metal bifluoride and starting material. No  $\text{CsNO}_3$  was found in the product. Impurities in or decomposition of NOF to nitrogen oxides could have produced this nitrate. Therefore, no conclusions can presently be made concerning the type of interaction observed. In several experiments the CsF was pre-treated with excess  $\text{CF}_3\text{COCF}_3$ . However, no significant activation effect was observed. On this basis, the direct reaction of ClF with the corresponding alkali metal fluoride seems to be the preferred method for preparing the difluorochlorate(I) salts.

The difluorochlorates(I) of lithium and calcium could not be prepared at 25 and 150° even using high autogenous ClF pressures ( $\sim 2000$  p.s.i.). No weight increase of the starting material was observed and the X-ray diffraction pattern showed no new products. Similarly, the reaction of NaF with ClF at 25° yielded negative results. Increasing the reaction temperature to 150° and using NOF as a catalyst resulted in a slight weight increase of the starting material. However, analysis indicated no chlorine in the product. From similar observations,  $\text{SrF}_2$  and  $\text{BaF}_2$  reacted with a mixture of ClF and NOF at 25 and 150° to an equally small extent. Again, no chlorine was found in the product. The greater tendency of CsF, RbF, and KF to form stable complex salts compared with the other alkali and alkaline earth metal fluorides was also ob-

served in the case of tetrafluorochlorates(III)<sup>6-8</sup> and salts containing the  $\text{CF}_3\text{O}^-$  anion<sup>16</sup>.

Properties of cesium, rubidium, and potassium difluorochlorates(I)<sup>17</sup>. - The compounds are white solids having good thermal stability. Differential thermal analysis indicated exothermic decompositions at 262, 248, and 237°, respectively. This stability order,  $\text{CsClF}_2 > \text{RbClF}_2 > \text{KClF}_2$ , follows the same sequence found for the  $\text{ClF}_4^-$ <sup>8</sup> and  $\text{CF}_3\text{O}^-$ <sup>16</sup> alkali salts. The decrease in cation size and the increase in polarizing power from  $\text{Cs}^+$  to  $\text{Li}^+$ <sup>18</sup> (in Group 1a of the periodic table of elements) probably accounts for this order of stability. By comparison, the difluorochlorates(I)

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- (16) D. C. Bradley, M. E. Redwood, and C. J. Willis, Proc. Chem. Soc., 416 (1964).
- (17) These compounds were not obtained pure. They invariably contained a certain percentage of the corresponding fluoride due to incomplete conversion of the starting material. Therefore, the properties given refer to mixtures of metal fluoride and metal difluorochlorates(I).
- (18) I. G. Ryss, "The Chemistry of Fluorine and its Inorganic Compounds", State Publishing House for Scientific, Technical, and Chemical Literature, Moscow (1956), English translation, Vol. 1, 1960, p. 217.

have lower oxidizing power and are somewhat less stable than the corresponding tetrafluorochlorates(III)<sup>6-8</sup>. This is in agreement with the reported stabilities of  $\text{NO}^+\text{ClF}_2^-$  and  $\text{NO}^+\text{ClF}_4^-$ <sup>11</sup>.

Structure of cesium, rubidium, and potassium difluorochlorates(I). - The infrared spectrum of  $\text{CsClF}_2$  in the range 4000 to 420  $\text{cm}^{-1}$  showed its strongest absorption at 636  $\text{cm}^{-1}$  in agreement with the 635  $\text{cm}^{-1}$  value found for the asymmetric stretching of the  $\text{ClF}_2^-$  anion in  $\text{NO}^+\text{ClF}_2^-$ <sup>11</sup>. Based on the suggested linearity of the  $\text{ClF}_2^-$  anion in  $\text{NO}^+\text{ClF}_2^-$ , a similar structure is assumed for the  $\text{ClF}_2^-$  anion in the alkali metal difluorochlorates(I).

The X-ray diffraction patterns of the products were of low intensity and resembled strongly those reported for the  $\alpha$ -modifications of the corresponding alkali metal bifluorides<sup>19,20</sup>. Since the found unit cell dimensions were nearly identical to those reported for the corresponding bifluorides, density measurements on the products were carried out. The large deviations between the found and calculated densities [for mixtures of metal fluoride and metal difluorochlorate(I)] indicated that the observed patterns

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- (19) R. Kruh, K. Fuwa, and T. E. McEver, J. Am. Chem. Soc., 78, 4256 (1956).
- (20) "Powder Diffraction File", ASTM Special Technical Publication 48-M2, American Society for Testing and Materials, Philadelphia, U.S.A., No. 1-1095 (1964).

are probably due to small amounts of the corresponding bifluoride as impurity, the difluorochlorate(I) salts being either amorphous or exhibiting only very low-intensity X-ray patterns.

The linear configuration of the  $\text{ClF}_2^-$  anion, supported by infrared analysis, may be explained by either of the following models:

(i) a hybridization model<sup>21</sup>, assuming mainly  $\text{sp}^3\text{d}$ -hybridization of the orbitals of the chlorine atom resulting in a trigonal bipyramid with the two fluorine atoms at the apexes, the chlorine atom at the center, and the three free electron-pairs at the remaining corners,

or perhaps more probably

(ii) a semi-empirical molecular orbital model<sup>21</sup> involving mainly  $\text{p}\sigma$  atomic orbitals for the formation of semi-ionic bonds.

Acknowledgement. - We thank Dr. A. E. Pavlath for helpful discussions. This work was supported by the Advanced Research Project Agency and the Office of Naval Research.

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(21) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, Chem. Rev. 199 (1965).

V. Manuscript of Paper: On the Structure of the Tetrafluorochlorate(III)  
Anion,  $\text{ClF}_4^-$

On the Structure of the  
Tetrafluorochlorate(III) Anion,  $\text{ClF}_4^-$

Abstract

Infrared and conductivity measurements show that  $\text{MClF}_4$  (where M is NO, Rb, or Cs) is ionic in the solid state and in solution, respectively. A square-planar structure (point group  $D_{4h}$ ) is assigned to the  $\text{ClF}_4^-$  anion in  $\text{Rb}^+\text{ClF}_4^-$  and  $\text{Cs}^+\text{ClF}_4^-$ . For the  $\text{ClF}_4^-$  anion in  $\text{NO}^+\text{ClF}_4^-$ , the low-temperature infrared measurement indicates a lower symmetry.

Introduction

While the existence of  $\text{MClF}_4$  (where M is NO, K, Rb, or Cs) is well known<sup>1-4</sup>, no reports on the ionic character of the  $\text{NOF-ClF}_3$

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- (1) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, J. Am. Chem. Soc., 83, 2955 (1961).
  - (2) D. H. Kelly, B. Post, and R. W. Mason, *ibid.*, 85, 307 (1963).
  - (3) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, *ibid.*, 86, 2583 (1964).
  - (4) E. Whitney, R. MacLaren, T. Hurley, and C. Fogle, *ibid.*, 86, 4340 (1964).



adduct and on the structure of the  $\text{ClF}_4^-$  anion have been published. Asprey<sup>1</sup> et al. obtained the infrared spectrum of  $\text{BrF}_4$ ; however, the absorptions reported by them occur at much higher frequencies than expected for the fundamental vibrations of the  $\text{ClF}_4^-$  anion. Therefore, they could have obtained only overtones and combination frequencies.

The structure of the  $\text{ClF}_4^-$  anion can be expected to be similar to that of the  $\text{BrF}_4^-$  anion, since both  $\text{KClF}_4$ <sup>2</sup> and  $\text{KBrF}_4$ <sup>5</sup> crystallize in the tetragonal system and have similar unit cell dimensions. Siegel interpreted the X-ray diffraction pattern of  $\text{KBrF}_4$  in terms of a tetrahedral configuration of the  $\text{BrF}_4^-$  anion. However, the pattern can be interpreted in terms of a planar  $\text{BrF}_4^-$  anion<sup>6,7</sup> as well. The tetrafluoroiodates(III) of potassium, rubidium, and cesium have been prepared<sup>8</sup>, but the structure of the anion has not been investigated. However, it was reported<sup>8</sup> that the X-ray powder diagrams are complex and that the  $\text{IF}_4^-$  compounds are probably not isostructural with the corresponding  $\text{BrF}_4^-$  compounds. Therefore, the evidence reported previously in the literature is insufficient

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(5) S. Siegel, *Acta Cryst.*, 9, 493 (1956).

(6) W. G. Sly and R. E. Marsh, *ibid.*, 10, 378 (1957).

(7) S. Siegel, *ibid.*, 10, 380 (1957).

(8) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 2373 (1960).

to prove the structure of any of the tetrafluorohalogenate(III) anions. However, based on the known square-planar structure of the  $\text{ICl}_4^-$  anion<sup>9</sup> and of the isoelectronic  $\text{XeF}_4$ <sup>10</sup>, the square-planar structure seems most likely.

The knowledge of the structure of interhalogen complexes such as the tetrafluorochlorates(III) is important for theoretical bonding considerations, since a certain symmetry of a compound could rule out certain theoretical bond models. If, for example, the tetrafluorochlorate(III) anion were tetrahedral, the semi-ionic bond model<sup>10</sup> would be incorrect.

#### Experimental

The compounds examined were prepared as described in the literature<sup>3,4</sup>. The infrared spectra of  $\text{RbClF}_4$ ,  $\text{CsClF}_4$ , and  $\text{NOClF}_4$  were taken with a Beckman IR-9 spectrophotometer in the range 4000 - 400  $\text{cm}^{-1}$ . The spectrum of  $\text{RbClF}_4$  was also recorded on a Beckman IR-11 spectrophotometer in the range 800 - 33  $\text{cm}^{-1}$ . Nujol mulls or dry powder between AgCl or polyethylene disks were employed. The low-temperature spectrum of  $\text{NOClF}_4$  was taken using

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(9) R. C. L. Mooney, Z. Krist. 98, 377 (1938).

(10) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, Chem. Rev., 65, 199 (1965).

the same technique described earlier for  $\text{NO}^+\text{ClF}_2^-$ <sup>11</sup> and  $\text{ClF}_2^+\text{AsF}_6^-$ <sup>12</sup>. The conductivity measurements were done using the method reported earlier<sup>11</sup>.

### Results

Conductivity. - The solubility of  $\text{NOClF}_4$  in liquid  $\text{ClF}_3$  at  $-23^\circ$  was quite low. Table I shows the results obtained for a saturated solution of  $\text{NOClF}_4$  in liquid  $\text{ClF}_3$ .

Table I

Conductivity of  $\text{NOClF}_4$  in liquid  $\text{ClF}_3$

Compound	Temp., $^\circ\text{C}$	Specific conductance, $\sigma$ $\text{ohm}^{-1} \text{ cm}^{-1}$
$\text{ClF}_3$	$-23$	$9.2 \times 10^{-9}$
$\text{NOF}$	$-79$	$5.4 \times 10^{-5}$
Saturated solution of $\text{NOClF}_4$ in liquid $\text{ClF}_3$	$-23$	$2.1 \times 10^{-7}$

Assuming complete solubility of the  $\text{NOClF}_4$  in  $\text{ClF}_3$  (not actually the case) the solution would have had a molarity of  $0.079 \text{ mole l}^{-1}$ , and thus a minimum equivalent conductance,  $\Lambda = 3.69 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^2$ .

(11) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 985 (1965).

(12) K. O. Christe and A. E. Pavlath, *Z. anorg. allgem. Chem.*, **335**, 210 (1965).

Infrared Spectra. - Table II shows the absorption frequencies of  $\text{NOClF}_4$ ,  $\text{RbClF}_4$ , and  $\text{CsClF}_4$ . The frequencies of the pure solid starting materials,  $\text{NOF}^{11}$  and  $\text{ClF}_3^{12}$ , have previously been reported. The  $\text{NOClF}_4$  sample was prepared directly on a cold  $\text{AgCl}$  window using excess  $\text{NOF}$  or excess  $\text{ClF}_3$ . It was found more convenient to remove unreacted  $\text{NOF}$  from  $\text{NOClF}_4$ , due to its greater volatility. Figure 1 shows the low-temperature infrared spectrum of solid  $\text{NOClF}_4$ .

Table II

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  $\text{MClF}_4$   
and vibrational assignments for  $\text{RbClF}_4$  and  
 $\text{CsClF}_4$  in the point group  $D_{4h}$

$\text{RbClF}_4$	$\text{CsClF}_4$	assignment for $\text{RbClF}_4$ and $\text{CsClF}_4$ in the point group $D_{4h}$	$\text{NOClF}_4$
1242 mw		$\nu_6 + \nu_7$	2298 m $\nu_{\text{NO}}^+$
745 vs	742 vs	$\nu_6 (\text{E}_u)$	676 ms 541 vs
486 s	478 s	$\nu_2 (\text{A}_{2u})$	498 m
430 m	425 m	$\nu_7 (\text{E}_u)$	434 s
118 m		lattice vibration	

### Discussion

NOClF<sub>4</sub>, Ionic Character. - Three reasonable structures for the complex are: coordination complex, ClF<sub>3</sub>·NOF(I); ClF<sub>2</sub><sup>+</sup>NOF<sub>2</sub><sup>-</sup>(II); NO<sup>+</sup>ClF<sub>4</sub><sup>-</sup>(III). Structure I should show no significant conductivity increase in ClF<sub>3</sub> solution and would require an infrared spectrum similar to that of ClF<sub>3</sub> superimposed on NOF with perhaps some shifting of absorption bands. The NO bond in structures I and II has double bond character and should absorb at 2000-1800 cm.<sup>-1</sup> 11. In structure III the NO bond has triple bond character and should absorb at 2350-2100 cm.<sup>-1</sup> 13. The solution containing the complex has an increased conductivity and the infrared spectrum shows the NO absorption at 2298 cm.<sup>-1</sup> indicative of the NO<sup>+</sup> cation. In addition, considering only symmetry, structure II would have required a higher number of infrared-active vibrations, the position of which would have to have been quite different. Thus, structure III is assigned to the complex.

Structure of the ClF<sub>4</sub><sup>-</sup> anion. - Table III shows the point groups taken into consideration as structural possibilities for the ClF<sub>4</sub><sup>-</sup> anion and the infrared-active fundamental vibrations expected for each group.

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- (13) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle,  
Inorg. Chem. 1, 661 (1962).

RbClF<sub>4</sub> and CsClF<sub>4</sub>. - Since  $\text{NO}^+\text{ClF}_4^-$  and the alkali metal tetrafluorochlorates(III) do not show the same number of absorption bands and do have somewhat different frequency positions, these compounds will be treated separately. The spectra of the alkali-metal tetrafluorochlorates(III) show only three infrared-active fundamental vibrations. The absorption at  $118\text{ cm}^{-1}$  in  $\text{RbClF}_4$  is too low to be a fundamental vibration, and therefore, is assigned to a lattice vibration, in agreement with values found for  $\text{K}_2\text{PtCl}_4$  and similar compounds<sup>14</sup>. The band at  $1242\text{ cm}^{-1}$  occurs at too high a frequency to be a  $\text{ClF}$  fundamental and consequently, is assigned to a combination vibration. Therefore, since only three infrared active-fundamentals were found, a square-planar structure can be assigned to the  $\text{ClF}_4^-$  anion and the other structural possibilities can be ruled out.

A square-planar molecule of the type  $\text{XY}_4$  has  $\text{D}_{4h}$  symmetry. The nine normal modes of vibration are classified as  $(\text{A}_{1g} + \text{A}_{2u} + \text{B}_{1g} + \text{B}_{1u} + \text{B}_{2g} + 2\text{E}_u)$ . Of these, only the  $\text{E}_u$  and  $\text{A}_{2u}$  modes will be infrared active in the isolated molecule, assuming that the selection rules in the solid are the same as they would be for the free gaseous ion.

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(14) A. Sabatini, L. Sacconi, and V. Schettino, *Inorg. Chem.*, 3, 1775 (1964).

Table III

Number of infrared-active fundamentals expected for the  $\text{ClF}_4^-$  anion  
in different point groups

<u>Point group</u>	<u>Structure</u>	<u>Total number of infrared- active fundamentals</u>	<u>Number of infrared- active stretching vibrations</u>	<u>Number of infra- red-active defor- mation vibrations</u>
$T_d$	Tetrahedral $\text{XY}_4$	2	1	1
$D_{4h}$	square-planar $\text{XY}_4$	3	1	2
$D_{2h}$	planar trans- $\text{XY}_2\text{Z}_2$	6	2	4
$C_{2v}$	non-planar $\text{XY}_2\text{Z}_2$	8	4	4

The bands within the range of possible fundamentals in the spectrum of  $\text{RbClF}_4$ , occur at 745, 486, and 430  $\text{cm}^{-1}$ . The band at 745  $\text{cm}^{-1}$  is undoubtedly the Cl-F  $E_u$  stretching mode. Out of the two expected infrared-active deformation vibrations the in-plane vibration likely has a lower frequency than the out-of-plane vibration. Therefore, the bands at 486  $\text{cm}^{-1}$  and 430  $\text{cm}^{-1}$  are assigned to the vibration of the  $A_{2u}$  species and the  $E_u$  species, respectively. Sabatini et al.<sup>14</sup> preferred the opposite assignment for the two deformation vibrations in  $\text{PtCl}_4^{2-}$  and similar square-planar anions. Our assignment, however, is in agreement with the assignments for other square-planar  $\text{AB}_4$  type molecules<sup>15,16</sup>,  $\text{ClF}_5$ <sup>17</sup>, and the iso-electronic  $\text{XeF}_4$ <sup>18</sup>. In addition, it can be assumed that the repulsion between the fluorine atoms in the  $\text{ClF}_4^-$  anion caused by the lone electron pairs is greater than the repulsion caused by the neighboring fluorine atoms. Therefore, the out-of-plane deformation vibration can be expected to show a higher frequency than the in-plane deformation vibration.

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(15) A. B. F. Duncan and J. W. Murray, J. Chem. Phys., 2, 636 (1934).

(16) E. B. Wilson, J. Chem. Phys., 3, 59 (1935).

(17) G. M. Begun, W. H. Fletcher, and D. F. Smith, J. Chem. Phys., 42, 2236 (1965).

(18) H. H. Claassen, C. L. Chernick, and J. G. Malm, J. Am. Chem. Soc., 85, 1927 (1963).



For  $\text{CsClF}_4$  slightly lower frequencies were obtained for these modes. Table II contains the vibrational assignments of the observed frequencies in the point group  $D_{4h}$  for both compounds.

$\text{NO}^+\text{ClF}_4^-$ . - The low-temperature infrared spectrum of  $\text{NO}^+\text{ClF}_4^-$  shows one more band in the observed range than that of the alkali-metal tetrafluorochlorates(III). In addition, the positions of the higher frequency band differ somewhat. The number of observed bands rules out the tetrahedral ( $T_d$  point group) structure. The square-planar ( $D_{4h}$  point group) structure should show one vibration less. However, since we are dealing with spectra of solids at low temperature, in which the anion does not necessarily behave ideally, it is possible that the symmetric stretching vibration of  $\text{ClF}_4^-$  might have become infrared active. Then the assignments could be made in analogy to the vibrations of the square-planar  $\text{ClF}_4$  part of the  $\text{ClF}_5$  molecule<sup>17</sup>. However, the found intensities do not agree so well with this assignment. The planar trans- $\text{XY}_2\text{Z}_2$  structure is also possible. In this case, the band at  $498\text{ cm}^{-1}$  would be a deformation vibration. However, the band at  $541\text{ cm}^{-1}$  is asymmetric and most infrared spectra of  $\text{NO}^+\text{ClF}_4^-$  showed a very weak shoulder at  $570\text{ cm}^{-1}$ . Based on this, and the fact that the position of the band at  $498\text{ cm}^{-1}$  does not exclude its interpretation as a stretching vibration, the possibility of assigning the  $\text{ClF}_4^-$  anion in  $\text{NO}^+\text{ClF}_4^-$  to the point group  $C_{2v}$  can not be eliminated. Regardless, the

symmetry of the  $\text{ClF}_4^-$  anion in  $\text{NO}^+\text{ClF}_4^-$  at low temperature appears to be lower than  $D_{4h}$  (found for  $\text{RbClF}_4$  and  $\text{CsClF}_4$ ).

Conclusion. -

- (i) The ionic structure,  $\text{NO}^+\text{ClF}_4^-$ , is assigned to the 1:1 adduct formed from NOF and  $\text{ClF}_3$ .
- (ii) The tetrafluorochlorate(III) anion in  $\text{RbClF}_4$  and  $\text{CsClF}_4$  is square-planar (symmetry  $D_{4h}$ ).
- (iii) The tetrafluorochlorate(III) anion in  $\text{NOClF}_4$  at low temperature has lower symmetry than  $D_{4h}$ .
- (iv) The square-planar structure found for the  $\text{ClF}_4^-$  anion in  $\text{RbClF}_4$  and  $\text{CsClF}_4$  is in agreement with either the semi-empirical molecular orbital model, assuming semi-ionic bonds, or the  $sp^3d^2$ -hybridization model.
- (v) Since  $\text{KClF}_4$  and  $\text{KBrF}_4$  are isostructural according to their x-ray data, the interpretation of  $\text{KBrF}_4$  in terms of a planar rather than a tetrahedral  $\text{BrF}_4^-$  anion seems more likely.

Acknowledgment. - We thank Dr. A. E. Pavlath for helpful discussions and Dr. J. Scherer and Mr. G. Bailey, of the U. S. Department of Agriculture, Albany, California, for the use of the Beckman IR-11 spectrophotometer. This work has been supported by the Advanced Research Projects Agency and the Office of Naval Research.

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March 2, 1966