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Complex Fluoro Cations. II.[1] Tetrafluoronitrogen(V) Cation, NF_4^+. Synthesis and Properties of $NF_4^+AsF_6^-$

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Nitrogen trifluoride, AsF_5, and F_2 when subjected to low-temperature glow discharge react in a 1:1:1 mole ratio, forming tetrafluoronitrogen(V) hexafluoroarsenate(V), $NF_4^+AsF_6^-$. This complex is considered a derivative of hypothetical NF_5. The white, crystalline powder is stable and nonvolatile at 25°. Differential thermal analysis indicates decomposition at about 270°. The compound is very hygroscopic and easily hydrolyzes to an initially pale blue solution with the evolution of gas. Mass spectral analysis of the decomposition and hydrolysis products and elemental analysis support the composition of the complex. The X-ray powder diffraction pattern can be indexed in the tetragonal system. The unit cell dimensions are $a = 7.70$ A and $c = 5.73$ A. Density measurements indicate two molecules per unit cell. The crystal structure seems similar to that of $PCl_4^+PCl_6^-$.

Introduction

Previously, a compound containing the NF_4^+ cation was considered unlikely to exist at room temperature. For example, Price, *et al.*,[2] claim that the ionization potential is too high and that the dimensions are too large for NF_4^+ to give sufficient lattice energy to form crystalline salts. Wilson[3] estimated the heat of formation of NF_4^+ as 240 ± 15 kcal mole^{-1} and thus concluded that $NF_4^+BF_4^-$ might have sufficient stability (relative to its decomposition products) to exist at temperatures less than $-120°$. Recently, in a preliminary paper,[4] we briefly described the preparation and identification of $NF_4^+AsF_6^-$. At the same time, Tolberg, *et al.*,[5] reported the preparation of $NF_4^+SbF_6^-$ and $NF_4^+AsF_6^-$ by a different method.

The following paper is a more detailed description of our findings dealing mainly with the synthesis and properties of $NF_4^+AsF_6^-$. In a subsequent paper,[6] spectroscopic data and their interpretation (including force constant calculations as well as F^{19} nuclear 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 psi). These cylinders 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 using a precision-dial manometer (0–30 ± 0.02 in., Wallace and Tiernan, Inc., FA145). Only the glow-discharge apparatus had glass parts.

The glow-discharge apparatus of Schreiner, *et al.*,[7] 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.[8] The two air-cooled solenoids are identical, each 4 cm long and 1.5 cm thick (including insulation), with a 2.3-cm diameter hollow core; the design allows continuous operation on a 120-v ac line without overheating. A selenium rectifier (single-phase bridge No. J116B1) changes ac to dc. A Flexopulse timer (Eagle Signal Co., range 0–120 sec) coupled with a mercury-column type of relay (Kerman Electric; rating: 1 ma at 115 v) 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 120 v, 60 c, secondary 15 kv, 30 ma, with midpoint of secondary 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 $NF_4^+AsF_6^-$.—A mixture of NF_3, AsF_5, and 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 $-78°$, and a 15-kv potential was placed across the copper electrodes. If the discharge did not occur at this pressure, a Tesla coil was used for initiation. If this also failed, then the pressure was reduced somewhat and the procedure was repeated until discharge occurred.

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 7 hr was required between fillings, and five or six fillings were needed for the production of ~1 g of $NF_4^+AsF_6^-$. No appreciable etching of the glass discharge vessel could be observed, and only small quantities of SiF_4 could be detected by infrared spectroscopy.

In a typical experiment, the glow discharge of a mixture of NF_3, AsF_5, and 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

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[1] Part I of this series: K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).

[2] W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.*, **35**, 201 (1963).

[3] J. N. Wilson, paper presented at the Symposium on Advanced Propellant Chemistry, American Chemical Society, Detroit, Mich., April 1965.

[4] K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Letters*, **2**, 83 (1966).

[5] W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *ibid.*, **2**, 79 (1966).

[6] K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, to be published.

[7] F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Am. Chem. Soc.*, **87**, 25 (1965).

[8] W. R. Bennett, Jr., *Rev. Sci. Instr.*, **28**, 1092 (1957).

~19 mm. The infrared spectrum of this gaseous residue showed only traces of SiF_4 (~1 mm). Therefore, the remaining 18 mm of pressure is due to an infrared-inactive gas such as F_2. Assuming that ~2 mm of F_2 could have been consumed by interaction with parts of the discharge vessel, it is probable that NF_3 (20 mm), AsF_5 (20 mm), and F_2 (20 mm) have reacted in 1:1:1 mole ratio producing $NF_4^+AsF_6^-$. *Anal.* Calcd for $NAsF_{10}$: As, 26.9; F, 68.1. Found: As, 26.9; F, 66.2.

Nitrogen trifluoride was introduced into a vessel containing liquid AsF_5 at −78° until a total pressure of 740 mm was attained. With liquid AsF_5 still present in quantity and the pressure remaining constant, no solid compound could be detected.

Finally, NF_3 (0.1 mole), AsF_5 (0.1 mole), and F_2 (excess) were introduced into a 100-ml Monel cylinder equipped with a Monel Helicoid pressure gauge (0–4000 psi) and a Monel Whitney valve (see section on Materials and Apparatus). A pressure of 960 psi was observed at 25°. The cylinder was heated to 485° and a pressure of 2400 psi developed. These conditions were maintained for 12 hr, after which the cylinder was slowly cooled to 25°. The pressure returned to 920 psi, almost its original value, 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 (~2 g) was found. Elemental analysis indicated that this solid was $Ni(AsF_6)_2$. This may account for the slightly lower final pressure (low by 40 psi) observed. *Anal.* Calcd for $NiAs_2F_{12}$: 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 (Na_2O_2 and a trace of starch). Fluorine was determined by titration with $Th(NO_3)_4$ 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°. Good spectra were generally obtained using a controlled sample pressure of $\sim 5 \times 10^{-6}$ mm.

A quantity (~20 mg of at least 95% purity) of $NF_4^+AsF_6^-$ 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 $NF_4^+AsF_6^-$ cannot be sublimed without decomposition, only the decomposition and/or dissociation products of the complex were observed. Another 20 mg from the same sample was introduced into a second tube, maintained at −196° to prevent the escape of any volatile products formed by the addition of two drops of water. After connecting the control valve (closed) to the stainless steel tube, the hydrolysis was allowed to occur at 25°. The products of this reaction were similarly recorded on the mass spectrometer.

X-Ray Powder Data.—Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (~0.3-mm o.d.).

Density Measurements.—The density of $NF_4^+AsF_6^-$ was found using the displacement method.[9] 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, empirical formula: $C_8F_{16}O$) were not successful owing to interaction of the complex with the ether.

Differential Thermal Analysis.—A Perkin-Elmer differential scanning calorimeter, Model DSC-1, was used to obtain the dta of $NF_4^+AsF_6^-$. The sample was sealed in aluminum pans. A heating rate of 10°/min and an argon purge of 30 ml/min were used.

Results

Synthesis.—Nitrogen trifluoride, AsF_5, and F_2 (in excess), when subjected to low-temperature glow discharge, react in 1:1:1 mole ratio forming the complex, $NF_4^+AsF_6^-$. Using proper conditions, a product containing at least 95% $NF_4^+AsF_6^-$ (shown by the over-all results of mass spectral, X-ray, and elemental analyses) was obtained. This sample was used for all measurements. In experiments not using excess fluorine, some undesired $NO^+AsF_6^-$ was formed. Poor cooling of the glow-discharge vessel had a similar effect.

In a separate experiment, thermal activation and high-pressure conditions (485° and 2400 psi, respectively) did not result in any interaction of the components NF_3, AsF_5, and F_2 (in excess), except for the formation of $Ni(AsF_6)_2$ due to corrosion of the Monel reaction vessel. Also, no solid compound could be detected when gaseous NF_3 was mixed with liquid AsF_5 at −78°.

Properties.—The complex is a hygroscopic, crystalline powder, storable indefinitely in glass at 25° and moderately soluble in liquid HF. Attempts to sublime $NF_4^+AsF_6^-$ were unsuccessful. Heating the solid in the glow-discharge vessel (under vacuum) to a temperature of 250° 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 $NF_4^+AsF_6^-$(s) at temperatures of −196 to 440° revealed the following data [mass number (*m/e*), ion species]: 19, F^+; 33, NF^+; 52, NF_2^+; 71, NF_3^+; 75, As^+; 94, AsF^+; 113, AsF_2^+; 132, AsF_3^+; 151, AsF_4^+. The spectra also showed *trace* quantities of other species [mass number (*m/e*), ion species]: 28, N_2^+; 30, NO^+; 44, CO_2^+; 47, SiF^+; 49, NOF^+; 66, SiF_2^+; 85, SiF_3^+. These data clearly indicate that the thermal decomposition products of $NF_4^+AsF_6^-$ are NF_3 and AsF_5. Fluorine is probably a product as well, but it cannot easily be detected in these mass spectra. Therefore, the observed impurities in the sample seem to be traces of NO, NOF, and SiF_4.[10] The peak at *m/e* 44 is due to CO_2 always present in the mass spectrometer. The relative abundance of the ion species is not given owing to sudden variances in the rate of decomposition of the sample.

Although the mass spectra show that decomposition of $NF_4^+AsF_6^-$ occurs at a temperature as low as 50°, it only becomes appreciable at temperatures higher than 150°. Differential thermal analysis indicates decomposition at 270°. This temperature difference is not unreasonable if one considers the relative sensitivities of the two techniques.

Hydrolysis.—Tetrafluoronitrogen(V) hexafluoroarsenate(V) 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 $NF_4^+AsF_6^-$ at temperatures of −196 to +440° show the following [mass number (*m/e*), ion species]: 14, N^+; 16, O^+; 17,

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[9] E. D. Whitney, R. O. MacLaren, C. E. Fogle, and T. J. Hurley, *J. Am. Chem. Soc.*, **86**, 2583 (1964).

[10] J. T. Herron and V. H. Dibeler, *J. Chem. Phys.*, **33**, 1595 (1960).

OH^+; 18, H_2O^+; 19, F^+; 20, HF^+; 28, N_2^+; 30, NO^+; 32, O_2^+; 33, NF^+; 44, CO_2^+; 46, NO_2^+; 47, SiF^+; 49, NOF^+; 52, NF_2^+; 65, NO_2F^+; 66, SiF_2^+; 71, NF_3^+; 75, As^+; 85, SiF_3^+; 94, AsF^+; 104, SiF_4^+; 113, AsF_2^+; 132, AsF_3^+. As before, the relative abundance of the ion species is not given for the same reason. The noteworthy products are HF, NO, NOF, NO_2, NO_2F, NF_3, SiF_4, and AsF_5 (only at temperatures higher than 100°). The very large quantities of nitrogen oxides or nitrogen oxygen fluorides in the hydrolyzed sample clearly show that these products are due to hydrolysis of $NF_4^+AsF_6^-$ and not to trace impurities present in the nonhydrolyzed sample. Also, at these higher temperatures, there is some indication of trace amounts of $AsOF_3$[11] (m/e, ion species: 91, AsO^+; 110, $AsOF^+$; 129, $AsOF_2^+$; 148, $AsOF_3^+$). The peak at m/e 44 is again due to CO_2.

X-Ray Powder Data.—Table I lists calculated and observed X-ray powder diffraction data (indexed in the tetragonal system) for $NF_4^+AsF_6^-$. From these data, the calculated unit cell dimensions are $a = 7.70$ A and $c = 5.73$ A.

TABLE I

X-RAY POWDER DATA FOR $NF_4^+AsF_6^-$

d (obsd), A	d (calcd), A	Intens	$h\ k\ l$
5.47	5.48	mw	1 1 0
4.57	4.57	ms	1 0 1
3.93	3.93	vs	1 1 1
3.85	3.85	s	2 0 0
3.21	3.19	s	2 0 1
2.94	2.94	mw	2 1 1
2.82	2.84	mw	0 0 2
2.66	2.66	m	1 0 2
2.52	2.52	w	1 1 2
2.40	2.43	w	3 1 0
2.197	2.191	vw	2 1 2
2.030	1.999	vvw	3 2 1
1.926	1.926	vvw	4 0 0
1.903	1.904	vw	3 0 2
1.817	1.815	mw	3 3 0
1.773	1.775	mw	4 1 1

Density measurements using the perfluorinated ether, FC-75, as ballast fluid were not successful. This ether reacts with $NF_4^+AsF_6^-$. However, only slight interaction was observed using the perfluorinated amine, FC-43, and a density, d^{25} 2.98 g cm^{-3}, was found. This density value indicates two "molecules" of $NF_4^+AsF_6^-$ per unit cell ($d_{\text{calcd}} = 2.72$ g cm^{-3}).

When $NF_4^+AsF_6^-$ was prepared using proper experimental conditions, the X-ray powder pattern did not show even a trace of the possible impurities, $NO^+AsF_6^-$[12] and CuF_2.[13]

Discussion

Synthesis.—The existence of the corresponding M_xF_y species had always been known in the case of ionic complexes containing $M_xF_{y-1}^+$. Thus, such complexes could easily be prepared from M_xF_y and a suitable acceptor species such as the strong Lewis acids AsF_5 or SbF_5. Since NF_5 had never been prepared (and is unlikely to be for various reasons one of which is the validity of the octet rule for the first row elements of the periodic system), NF_4^+ cannot be synthesized in this manner. Therefore, a more promising method for the preparation of NF_4^+ considers the use of the next lower fluoride, NF_3, and fluorine.

The formation of NF_4^+ from NF_3 and 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 NF_4^+ by the simultaneous formation of highly symmetrical anions, such as AsF_6^- or 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 NF_3, AsF_5, and F_2 under autogenous pressure to a temperature of 485°, failed to produce NF_4^+. From the possible remaining energy sources we chose glow discharge. Low temperature was used for the following reasons: (i) NF_3 and AsF_5 were observed not to form a solid compound at −78°, which is not surprising since NF_3 and BF_3 were not observed to interact at low temperature;[14] (ii) the vapor pressures of the starting materials are sufficient at −78°; (iii) the hoped for product, $NF_4^+AsF_6^-$, could have a low thermal stability.

Except for perhaps small amounts of CuF_2 and SiF_6^{2-} salts, the only noticeable (by mass spectrometry) trace impurity in $NF_4^+AsF_6^-$ was $NO^+AsF_6^-$. This impurity was substantial in experiments in which excess F_2 was not used in the glow-discharge vessel or in experiments in which the glow-discharge vessel was not sufficiently cooled. It was identified by infrared spectroscopy (NO^+ stretching vibration at 2300 cm^{-1})[15] and X-ray powder diffraction data.[12] The formation of $NO^+AsF_6^+$ can be due to either the interaction of $NF_4^+AsF_6^-$ with the glass walls of the glow-discharge vessel, represented by the equation

$$2NF_4^+AsF_6^- + SiO_2 \longrightarrow 2NO^+AsF_6^- + SiF_4 + 2F_2$$

or reaction involving the formation of NOF as

$$2NF_3 + SiO_2 \longrightarrow 2NOF + SiF_4$$

and

$$NOF + AsF_5 \longrightarrow NO^+AsF_6^-$$

Since fluorine can react with NOF (or NO) to form NF_3,[16,17] 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[18] or copper electrodes of the glow-dis-

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charge vessel and by interaction with any traces of nitrogen (impurity in the NF_3) forming NF_3.[19]

Simultaneously, the preparation of $NF_4^+SbF_6^-$ and $NF_4^+AsF_6^-$ was reported by another research group.[5] They used liquid HF as a solvent as well as high temperature and pressure. Whereas the glow-discharge method results in a product containing at least 95% $NF_4^+AsF_6^-$ (Results section), it is not practical for the preparation of $NF_4^+SbF_6^-$ owing to the low volatility of SbF_5. On the other hand, the "solvation" method is satisfactory for preparing $NF_4^+SbF_6^-$, although the product is contaminated with substantial quantities (~25%) of metal fluorides. In the case of $NF_4^+AsF_6^-$, however, this method seems to be less suitable owing to the volatility of $Ni(AsF_6)_2$ at 200°. Both methods require special equipment.

Possible mechanisms for the formation of NF_4^+ from NF_3 and F_2 are shown by the equations

$$NF_3^+ + F_2 \longrightarrow NF_4^+ + F\cdot \qquad (1)$$

$$NF_3^+ + F\cdot \longrightarrow NF_4^+ \qquad (2)$$

$$NF_3 + F_2^+ \longrightarrow NF_4^+ + F\cdot \qquad (3)$$

$$NF_3 + F^+ \longrightarrow NF_4^+ \qquad (4)$$

In each case, a Lewis acid such as AsF_5 can react with the negatively charged species (F^- or e^-, the latter followed by reaction with F_2 or $F\cdot$). Thus, the resultant AsF_6^- stabilizes the NF_4^+ cation. The overall reaction could be represented by the equation

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4^+AsF_6^- \qquad (5)$$

This equation is the heterolytic fission of the fluorine molecule.

Nitrogen trifluoride, F_2, and $F\cdot$ have similar ionization potentials (13.2,[20] 15.7,[21] and 17.4[21] ev, respectively). The energy supplied by glow discharge using 15 kv is likely considerably greater than these ionization potentials; therefore, any difference in the activation energy of the previous equations (1–4) is insufficient to favor any one mechanism. Kinetic measurements will probably be necessary to formulate the true mechanism.

It is surprising, in view of previously reported estimations,[2,3] that $NF_4^+AsF_6^-$ does not decompose appreciably at temperatures of less than 150°. As expected, the complex cannot be sublimed without irreversible decomposition.

Mass Spectra.—Mass spectrometry was used mainly to identify qualitatively the thermal decomposition and hydrolysis products of $NF_4^+AsF_6^-$. Generally, there was no difficulty in assignment of ion species to corresponding mass number. The peak assigned to NF_3 agrees well with the previously obtained mass spectrum of NF_3.[20] The parent ion, 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 AsF_5[22] and in the mass spectrum of the thermal decomposition products of $O_2^+AsF_6^-$.[12] No peak at *m/e* 38 (F_2^+) occurs. However, this does not necessarily mean that F_2 is not a decomposition product since the mass spectrometer had not been passivated prior to the measurements on $NF_4^+AsF_6^-$. The peak at *m/e* 19 (F^+) is too intense by a factor of about 7 to be entirely due to NF_3 (intensity ratio $NF_2^+:F^+ = 20:1$)[20] and, consequently, F_2 may contribute to its abnormally high intensity. However, the fragmentation of AsF_5 no doubt also produces $F\cdot$ which can ionize easily to F^+. Trace amounts of NO^+ and NOF^+ ion species are no doubt due to $NO^+AsF_6^-$.

The mass spectra of hydrolyzed $NF_4^+AsF_6^-$ show the expected ion species. The fact that NF_3 is not easily hydrolyzed[17] accounts for its presence in substantial quantity.

Structure of $NF_4^+AsF_6^-$.—Since the 1:1:1 mole ratio of the complex formed from NF_3, AsF_5, and F_2 and the ionic structure, $NF_4^+AsF_6^-$, were established by elemental and mass spectral analyses and by vibrational and F^{19} magnetic resonance spectroscopy,[6] respectively, we have used this ionic structure throughout the text. Perhaps equally strong evidence for this structure is the high thermal stability of the complex and the following X-ray data.

X-Ray powder data (Table I) indicate that NF_4^+-AsF_6^- has a crystal structure similar to that of PCl_4^+-PCl_6^-.[23,24] This is not too surprising since both compounds have comparable anion radius to cation radius ratios and have ions of similar shape. As expected, $PCl_4^+PCl_6^-$ has a somewhat larger unit cell ($a = 9.22$ A, $c = 7.44$ A) and a lower density (d 2.12 g cm^{-3}); however, a/c is similar for both compounds, *i.e.*, 1.23 and 1.34 for $PCl_4^+PCl_6^-$ and $NF_4^+AsF_6^-$, respectively. Also, both compounds have two "molecules" per unit cell. In both X-ray powder patterns, *hk*0 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 $NF_4^+AsF_6^-$ and $PCl_4^+PCl_6^-$ cause a distortion (*i.e.*, from simple cubic to tetragonal). Each ion (NF_4^+ or AsF_6^-) has eight neighboring ions of opposite charge.

Nomenclature.—Previously used names such as "tetrafluoroammonium" or "perfluoroammonium" cation for NF_4^+ could be used; however, the polarity of the bonds in NF_4^+ is different from that in NH_4^+. Whereas for NF_4^+ the nitrogen atom has a formal oxidation number, +5, it is −3 for NH_4^+. Therefore, NF_4^+ is named "tetrafluoronitrogen(V)," as a derivative of hypothetical NF_5.

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