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Synthesis and Characterization of $(NF_4)_2NiF_6$

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The NF_4^+ cation has successfully been coupled with the energetic NiF_6^{2-} anion in the form of the stable $(NF_4)_2NiF_6$ salt. The salt was prepared from Cs_2NiF_6 and NF_4SbF_6 by metathesis in HF. It was characterized by elemental analysis, vibrational spectroscopy, and its x-ray powder diffraction pattern. Its hydrolysis and thermal decomposition were studied.

Introduction

A large number of strongly oxidizing complex fluoro cations and anions are known. However, their potential application as energetic oxidizers had been handicapped by the fact that they formed stable salts only with nonenergetic counterions. The recent syntheses[1-3] of several stable NF_4^+ salts, derived from relatively weak Lewis acids, indicated that the NF_4^+ cation might possess the necessary stability required for its successful combination with energetic anions.

In this paper we report the synthesis and properties of $(NF_4)_2NiF_6$ which, to our knowledge, is the first known example of a stable salt containing both a strongly oxidizing complex fluoro cation and anion. The NiF_6^{2-} anion is well-known[4-19] and is a strong oxidizer owing to the fact that the parent molecule NiF_4 is unstable and decomposes to lower nickel fluorides and elemental fluorine.[17,18]

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those previously described.[2,3] The NF_4SbF_6 was prepared as previously[20] reported. The HF (Matheson) was dried by F_2 treatment[21] and was stored over K_2NiF_6 (Ozark Mahoning) prior to use. The Cs_2NiF_6 was prepared by heating a finely ground 2:1 molar mixture of dried CsF and $NiCl_2$ (Alfa) with 15 mol of F_2/mol of $NiCl_2$ in a nickel cylinder to 250 °C for 16 h. The volatile products were pumped off at room temperature. The solid product was finely powdered in the drybox and the fluorination step was repeated as described above. The weight and the vibrational spectra of the resulting crimson red solid were in excellent agreement with those expected[9,15,16] for Cs_2NiF_6.

In the infrared spectrum of Cs_2NiF_6 several relatively intense previously unreported combination bands (cm^{-1}) were observed. These were $\nu_1 + \nu_3$ (1205 w, 1187 mw), $\nu_2 + \nu_3$ (1164 mw, 1144 m), $\nu_3 + \nu_5$ (954 sh, 936 w), $\nu_1 + \nu_4$ (884 vw), and $\nu_2 + \nu_4$ (842 vw). From these combination bands a splitting of ν_3 into two components with frequencies of 660 and 641 cm^{-1} can be deduced. The observed frequencies (cm^{-1}) and relative intensities of the fundamentals were as follows: infrared, ν_3 (645 vs, br), ν_4 (331 s); Raman, ν_1 [545 (10)], ν_2 [503 (7.5)], ν_5 [294 (4)].

Synthesis of $(NF_4)_2NiF_6$. In the glovebox a mixture of Cs_2NiF_6 (13.50 mmol) and NF_4SbF_6 (27.94 mmol) was placed in a $^3/_4$-in. o.d. Teflon FEP U-trap which was connected through a 180 °C coupling to a second U-trap. This coupling contained a porous Teflon filter (Pall Corp.). The free ends of both U-traps were closed off by valves. Both valves were connected through flexible, corrugated Teflon FEP tubing to a vacuum manifold. Dry HF (10 mL of liquid) was added at −78 °C to the trap containing the reactants. The mixture was warmed to 25 °C and stirred with a Teflon-coated magnetic stirring bar for 30 min. The U-tube and filter coupling were cooled to −78 °C and the trap was inverted. The receiving trap was also cooled to −78 °C and the solution above the filter was pressurized by 2 atm of dry nitrogen to accelerate the filtration. After completion of the filtration, the HF solvent was removed by pumping for 12 h at 25 °C. The filter cake consisted of 10.15 g of a light brown solid (weight calcd for 27.0 mmol of $CsSbF_6$ 9.95 g) which was identified by analysis and vibrational spectroscopy as mainly $CsSbF_6$ containing a small amount of NF_4^+ and NiF_6^{2-} salts. The filtrate residue consisted of 4.36 g of a deep red solid (weight calcd for 13.5 mmol of $(NF_4)_2NiF_6$ 4.76 g) which on the basis of elemental and spectroscopic analyses had the following composition (wt %): $(NF_4)_2NiF_6$, 82.35; NF_4SbF_6, 13.98; $CsSbF_6$, 3.56. Anal. Calcd: Ni, 13.71; Sb, 6.40; Cs, 1.28; NF_3, 36.20. Found: Ni, 13.70; Sb, 6.44; Cs, 1.31; NF_3, 36.19. The method for purifying this material by recrystallization from anhydrous HF at ambient temperature has previously been described[20] for NF_4BF_4.

Hydrolysis of $(NF_4)_2NiF_6$. *Caution*! The reaction of $(NF_4)_2NiF_6$ with water is very violent and can result in explosions. About 5 mL of distilled water was frozen out at −196 °C in the upper section of a Teflon FEP U-trap containing about 1 mmol of $(NF_4)_2NiF_6$. The frozen water was knocked down into the bottom section of the tube containing the sample and the ice and sample were mixed by agitation at low temperature. After good mixing was achieved, the mixture was carefully warmed toward room temperature and as soon as interaction was noticeable, the mixture was chilled again by liquid N_2. This procedure was repeated until the color of the sample had completely changed from red to the green color characteristic for divalent nickel. The products volatile at −78 °C consisted of O_2, NF_3, and OF_2. The oxygen was separated from the NF_3 and OF_2 at −210 °C, and the NF_3:OF_2 ratio was determined by infrared spectroscopy. The hydrolysate was analyzed for Ni, Cs, Sb by both x-ray fluorescence and atomic absorption spectroscopy. The mole ratio of O_2 to OF_2 was found to vary somewhat from experiment to experiment, but approached 2:1 with the total amount being close to that expected for the reduction of N(+V) and Ni(+IV) to N(+III) and Ni(+II), respectively. Control experiments on the hydrolysis of Cs_2NiF_6 under indentical conditions resulted in the evolution of O_2 only in amounts corresponding to the reduction of Ni(+IV) to Ni(+II).

Pyrolysis of $(NF_4)_2NiF_6$. A sample of $(NF_4)_2NiF_6$ (296 mg) was placed into a prepassivated (with ClF_3, followed by F_2 at 130 °C) $^1/_4$-in. o.d. stainless steel U-tube (volume 10.46 cm^3) closed off on both ends by Hoke valves (3132M25). One side of the U was connected to a pressure transducer (Validyne, Model AP10) and the other side to the vacuum line. The U-tube was kept at a constant temperature with an oil bath and the pressure build-up was measured as a function of time. Periodic evacuation of the system revealed that the decomposition rate was not influenced by the pressure of the gaseous decomposition products. The decomposition rates of $(NF_4)_2NiF_6$ were determined over the temperature range 80–128 °C. All measurements were carried out on one sample starting at the lowest temperature. At the highest temperature (128 °C), an exhaustive pyrolysis of the remaining undecomposed 82% of the original sample was carried out until gas evolution practically ceased. The evolved gas was shown by infrared and mass spectroscopy to be a mixture of NF_3 and F_2 in a mole ratio of about 2:3. On the basis of its weight loss and vibrational spectrum, the solid residue from the exhaustive pyrolysis was shown to consist of the thermally more stable NF_4SbF_6 and $CsSbF_6$ impurities and the previously described[9,17] nonstoichiometric brown nickel fluoride $NiF_{2.x}$.

The thermal decomposition was also visually followed by heating a sample of $(NF_4)_2NiF_6$ in a sealed glass capillary. At 130 °C the color of the sample changed from dark red to brown ($NiF_{2.x}$) which at higher temperatures changed to gray. Vibrational spectra of the final decomposition product and those obtained from the yellow pyrolysis product of Cs_2NiF_6 showed that in both cases the main product was NiF_2 (Raman, 520 vs, 425 s; IR, 520 sh, 425 s, br).

Results and Discussion

Synthesis and Properties. Since the NiF_6^{2-} anion is stable in anhydrous HF solution,[9,12,17] the synthesis of $(NF_4)_2NiF_6$ by metathesis appeared feasible. Both NF_4SbF_6 and Cs_2NiF_6 are highly soluble in HF, whereas $CsSbF_6$ is of relatively low solubility, particularly at lower temperature. Consequently, the following reaction was used to prepare $(NF_4)_2NiF_6$:

$$2NF_4SbF_6 + Cs_2NiF_6 \xrightarrow[-78\ ^\circ C\ filtr]{HF} 2CsSbF_6\downarrow + (NF_4)_2NiF_6$$

Table I. X-Ray Powder Data for $(NF_4)_2NiF_6$[a]

d(obsd), Å	d(calcd), Å	Intens	hkl
5.46	5.49	vs	002
3.42	3.45	ms	103
3.31	3.31	s	310
2.880	2.878	ms	213
2.742	2.738	mw	004
2.407	2.405	mw	331
2.150	2.150	s	422
1.954	1.954	w	502 432
1.846	1.849	m	440

[a] Tetragonal; $a = 10.457$ Å, $c = 10.953$ Å; Cu Kα radiation, Ni filter.

Table II. Crystallographic Data of $(NF_4)_2NiF_6$ Compared to Those of Other $(NF_4)_2MF_6$ Salts[a]

	Tetragonal unit cell dimensions				
	a, Å	c, Å	V, Å^3	Vol/F, Å^3	Calcd density, g/cm^3
$(NF_4)_2TiF_6$[b]	10.715	11.114	1276.0	17.09	2.37
$(NF_4)_2NiF_6$	10.457	10.953	1197.7	16.04	2.61
$(NF_4)_2GeF_6$[c]	10.627	11.114	1255.1	16.81	2.59
$(NF_4)_2SnF_6$[d]	10.828	11.406	1337.4	17.91	2.73

[a] For all compounds $Z = {}^{16}/_3$. [b] Reference 1. [c] Reference 3. [d] Reference 2.

The optimization of a NF_4SbF_6–cesium salt based metathetical process and the possible product purification have previously been discussed in detail for the corresponding NF_4BF_4 process[20] and hence are not being reiterated.

The resulting $(NF_4)_2NiF_6$ is a deep red hygroscopic solid, stable at room temperature. In the absence of fuels, the compound is not shock sensitive. It crystallizes in the tetragonal system (see Table I) and is isotypic with the other known $(NF_4)_2MF_6$ (M = Ge, Sn, Ti)[1-3] salts (see Table II). As expected, the size of the unit cell decreases from $(NF_4)_2TiF_6$ to $(NF_4)_2NiF_6$ owing to the transition metal contraction and then increases again when going from Ni to the main-group elements.

The vibrational spectra of $(NF_4)_2NiF_6$ are shown in Figure 1 and the observed frequencies and their assignments are summarized in Table III. The observed frequencies and intensities are in excellent agreement with those previously reported for other NF_4^+ salts[1-3] and K_2NiF_6[9,15] and Cs_2NiF_6 (see Experimental Section), thus establishing the ionic nature of $(NF_4)_2NiF_6$.

Thermal Decomposition. The thermal decomposition of $(NF_4)_2NiF_6$ was investigated by DSC and visual observation of samples sealed in glass melting point capillaries. The DSC curves of samples sealed in aluminum pans indicated the onset of very slow endothermic decomposition between 110 to 120 °C, which increased with increasing temperture and became rapid between 200 and 210 °C. The fact that $(NF_4)_2NiF_6$ undergoes appreciable decomposition well below 200 °C was confirmed by visual observation of samples sealed in glass melting point capillaries. Heating to 130 °C resulted in the formation of the brown nonstoichiometric $NiF_{2.x}$[9,17] (see Experimental Section). As previously discussed,[1-3] these data are only qualitative.

Since the thermal stability of a powerful oxidizer, such as $(NF_4)_2NiF_6$, is of great practical importance, its rate of decomposition was quantitatively studied by total pressure measurements over the temperature range 80–128 °C. The decomposition follows the equation

$$(NF_4)_2NiF_6 \rightarrow 2NF_3 + (3 - x/2)F_2 + NiF_{2.x}$$

Table III. Vibrational Spectra of Solid $(NF_4)_2NiF_6$

Obsd freq, cm^{-1}, and rel intens[a]		Assignments (point group)[b]	
IR	Raman	NF_4^+ (T_d)	NiF_6^{2-} (O_h)
2301 vw		$2\nu_3$ ($A_1 + E + F_2$)	
1998 w		$\nu_1 + \nu_3$ (F_2)	
1756 vw		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)	
1460 vw		$\nu_1 + \nu_4$ (F_2)	
1218 m		$2\nu_4$ ($A_1 + E + F_2$)	
1156 vs	1157 (0.1)	ν_3 (F_2)	
1055 vw		$\nu_2 + \nu_4$ ($F_1 + F_2$)	
854 vw	854 (1)	ν_1 (A_1)	
648 vs			ν_3 (F_{1u})
609 m	609 (0.5)	ν_4 (F_2)	
604 sh			
556 vw	555 (10)		ν_1 (A_{1g})
512 vw	512 (7)		ν_2 (E_g)
	457 (0.5)	ν_2 (E)	
	454 (0.5)		
443 vw			
332 mw			ν_4 (F_{1u})
	307 (1.5)		ν_5 (F_{2g})
	298 (4)		
	90 (0.1)	Lattice vib	
	60 (0+)		

[a] Uncorrected Raman intensities. [b] The actual site symmetries of NF_4^+ and NiF_6^{2-} in this salt are probably lower than T_d and O_h, respectively, as indicated by the large unit cell ($Z = {}^{16}/_3$) and the observed slight deviations from the selection rules and the lifting of the degeneracy for some of the modes; however, since the actual site symmetries are unknown, the assignments are given for the idealized point groups.

Table IV. Rate Constants Observed for the Thermal Decompositon of $(NF_4)_2NiF_6$

T, °C	k, s^{-1}	T, °C	k, s^{-1}
80	8.279×10^{-8}	110	4.197×10^{-6}
90	2.739×10^{-7}	128	3.012×10^{-5}
99	1.165×10^{-6}		

The decomposition rate was found to be independent of the gas pressure, as expected for an irreversible reaction involving the decomposition of the thermodynamically unstable NiF_4 to $NiF_{2.x}$. Owing to the limited amount of sample available, all measurements were carried out on the same sample. From 80 to 110 °C the decomposition rates were measured only for low α (fraction of material decomposed) values. At 128 °C an exhaustive decomposition was carried out for the α range 0.18–1. Plots of α as a function of time t resulted in straight lines for the α range 0–0.18 from 80 to 110 °C and for α = 0.18–0.6 at 128 °C. From these straight lines, rate constants, k, were calculated for each temperature (see Table IV). An Arrhenius plot of log k vs. $1/T$ resulted in a straight line. The fact that this plot included the data points obtained for both low and high α values strongly suggests that the decomposition rates are independent of α at $\alpha < 0.6$. From the Arrhenius plot, the following expressions can be derived for the specific reaction rate constant (s^{-1}) and activation energy of the $(NF_4)_2NiF_6$ decomposition

$$k = 4.840 \times 10^{14} e^{-35161/RT(\mathrm{K})}$$

$$\Delta H_a = 35.161 \text{ kcal/mol}$$

A detailed study of the exact decomposition mechanism was beyond the scope of this study. However, the failure to observe significant sigmoid character for the decomposition curves indicates that the decomposition is not autocatalytic. Furthermore, the fact that the decomposition rates were independent of α over a large range of α suggests that the decomposition occurs at active sites and that the number of these sites is fixed.[22] In view of the experimental limitations (only one sample was used and the sample contained impurities, although these were more stable than the compound of interest), the above kinetic data will have to be verified in a more

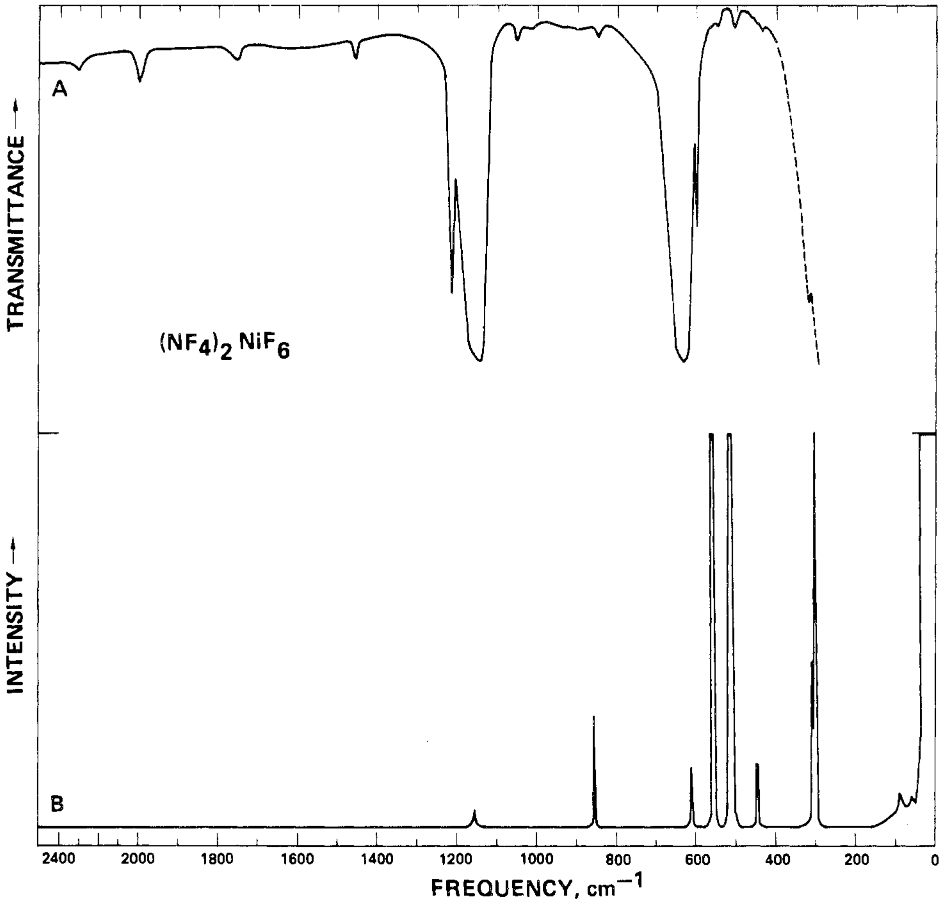


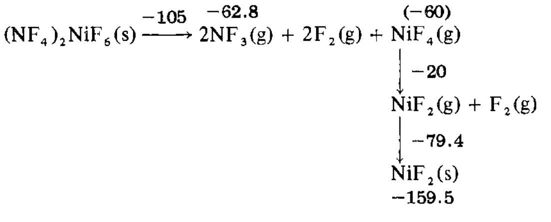
Figure 1. Vibrational spectra of solid $(NF_4)_2NiF_6$: trace A, infrared spectrum of the dry powder in a silver chloride disk, the absorption below 400 cm^{-1} (broken line) being due to the AgCl windows; trace B, Raman spectrum, recorded on a Cary Model 83 using the 6471-Å line of a Kr ion laser and a spectral slit width of 2 cm^{-1}.

detailed study on pure $(NF_4)_2NiF_6$.

The thermal decomposition of $(NF_4)_2NiF_6$ differs strongly from that previously reported[23] for NF_4AsF_6. Contrary to our findings for $(NF_4)_2NiF_6$, the decomposition of NF_4AsF_6 was found to be pressure dependent indicating the equilibrium

$$NF_3 + F_2 + AsF_5 \rightleftarrows NF_4AsF_6$$

Because of the irreversibility of the $(NF_4)_2NiF_6$ decomposition, the heat of dissociation and thereby the heat of formation of solid $(NF_4)_2NiF_6$ cannot be computed. However, in view of its importance for performance calculations, the heat of formation of solid $(NF_4)_2NiF_6$ was estimated to be about −230 kcal/mol based on the sequence (where all values are in kcal/mol)



$$\begin{tikzcd}(NF_4)_2NiF_6(s) \arrow[r, "-105"] & \overset{-62.8}{2NF_3(g)} + 2F_2(g) + \overset{(-60)}{NiF_4(g)} \arrow[d, "-20"] \\ & NiF_2(g) + F_2(g) \arrow[d, "-79.4"] \\ & \underset{-159.5}{NiF_2(s)}\end{tikzcd}$$

The values for the heat of formation[24] and heat of sublimation[25] of solid NiF_2 and for the heat of formation of gaseous NF_3[26] are literature values. The heats of decomposition of gaseous NiF_4 and solid $(NF_4)_2NiF_6$ are estimates. The latter estimate[27] is based on the known[28] value of −34.6 kcal/mol of the reaction $NF_4BF_4(s) \rightarrow NF_3(g) + F_2(g) + BF_3(g)$. A value for the heat of formation of $(NF_4)_2NiF_6$ being slightly more negative than −222 kcal/mol ($\Delta H_f°(NiF_2(s)) + 2\Delta H_f°(NF_3(g))$) is supported by our DSC measurements which showed the decomposition of $(NF_4)_2NiF_6$ to be mildly endothermic.

Hydrolysis. The hydrolysis of $(NF_4)_2NiF_6$ can be described approximately by the equation

$$2(NF_4)_2NiF_6 + 5H_2O \rightarrow 4NF_3 + 10HF + 2O_2 + OF_2 + 2NiF_2$$

Whereas the NF_3 evolution and formation of +II Ni were quantitative, the ratio of O_2:OF_2 varied from experiment to experiment. The observation of significant amounts of OF_2 was quite unexpected since neither NF_4^+ nor NiF_6^{2-} alone produces OF_2 during hydrolysis. This was verified by studying the hydrolysis of Cs_2NiF_6 which, in agreement with a previous report,[9] produced only O_2 according to

$$2NiF_6^{2-} + 2H_2O \rightarrow 4HF_2^- + 2NiF_2 + O_2$$

The hydrolyses of NF_4^+ salts containing nonoxidizing anions have been studied previously. Although O_2 evolution had not always been quantitative, H_2O_2 and not OF_2 had been the only observed by-product.[3] It thus appears that the combination of NF_4^+ and NiF_6^{2-} is required to produce significant amounts of OF_2. A plausible explanation for the formation of OF_2 is the fluorination of HOF, a likely intermediate in the rapid hydrolysis of NF_4^+,[3] by the hydrolytically more stable NiF_6^{2-} according to

$$NF_4^+ + 2HOH \rightarrow FOH + H_3O^+ + NF_3$$

$$FOH + NiF_6^{2-} \rightarrow FOF + HF + NiF_4^{2-}$$

Summary

The successful synthesis of $(NF_4)_2NiF_6$ is significant since, to our knowledge, it is the first combination of a strongly oxidizing complex fluoro cation with a strongly oxidizing complex fluoro anion in the form of a stable salt. Its potential as an oxidizer and an ingredient for a solid propellant NF_3–F_2 gas generator[2,29,30] for chemical HF–DF lasers becomes evident from the following comparison. On thermal decomposition, 1 cm^3 of solid $(NF_4)_2NiF_6$ is capable of producing 12% more useful fluorine values, i.e., in the form of F_2 and NF_3, than liquid F_2 at −187 °C. Furthermore, $(NF_4)_2NiF_6$ is a stable solid at ambient temperature which can be safely stored without requiring cryogenic cooling. The physical and spectroscopic properties of $(NF_4)_4NiF_6$ are in excellent agreement with those predicted for a solid containing NF_4^+ and NiF_6^{2-} ions. The only unexpected property was the observation of significant amounts of OF_2 during hydrolysis.

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Registry No. $(NF_4)_2NiF_6$, 63105-40-8; Cs_2NiF_6, 17218-49-4; NF_4SbF_6, 16871-76-4; NiF_2, 10028-18-9.

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Hydrogen Bonding. 10. Polyhedral Water–Fluoride Cluster Anions in Tetraethylammonium Fluoride Hydrates[1,2]

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We have prepared the previously unreported penta-, tri-, di-, and monohydrates of tetraethylammonium fluoride and have studied the water–anion complex species in these hydrates by deuterium labeling and infrared spectroscopy at 300 and 10 K. The pentahydrate contains normal clathrate water; however, the spectral properties of the trihydrate, dihydrate, and monohydrate suggest that they contain discrete polyhedral water–fluoride cluster anions. Deposition of well-formed needles of trihydrate from liquid pentahydrate affords the first macrocrystalline material containing such a cluster anion. Attempted preparation of the mixed hydroxide–fluoride $H_4O_3F^{3-}$ cluster fails via disproportionation to separate hydroxide and fluoride hydrates. Attendant decomposition of tetraethylammonium fluoride by Hofmann or S_N2 reactions competes with the formation of the lower hydrates.

Introduction

We have recently reported preparative and spectroscopic studies of the lower hydrates of tetrapropylammonium fluoride and tetramethylammonium fluoride and hydroxide. Tetrapropylammonium fluoride forms[4] hexa-, tri-, and dihydrates of the framework clathrate[5] type, in which there is an extended water–anion network; these materials have low crystallinity and melt in the vicinity of 30 °C. There is no monohydrate; further dehydration of the dihydrate results in rapid, exothermic Hofmann-type decomposition to tripropylamine, propene, and tetrapropylammonium hydrogen difluoride.[4] The tetrapropylammonium fluoride hydrates show an increase in energy for the broad librational band[6] of the structural water with decreasing hydration number, since increased framework charge density leads to tighter binding of water as the H_2O:F^- ratio is reduced.

Tetramethylammonium fluoride and hydroxide show quite different behavior. The fluoride forms a crystalline framework tetrahydrate[7] and the hydroxide a similar pentahydrate,[8] and we have found[9] that both salts form very stable, high-melting trihydrates containing strongly hydrogen-bonded water–anion networks. Unlike tetrapropylammonium fluoride, both tetramethylammonium fluoride and hydroxide form monohydrates. The water in these monohydrates is extraordinarily tightly bound, and the infrared spectra of the water–anion moieties, which show the characteristic sharp and intense rocking bands[6] of strongly coordinated trivalent oxygens, are completely different from those of compounds containing water bound in framework clathrate structures.

We have demonstrated that tetramethylammonium fluoride and hydroxide monohydrates contain discrete water–anion clusters rather than extended networks and have postulated on the basis of infrared spectra, deuterium labeling, steric limitations on anion size, internal coordinate analysis of predicted spectra, topological equivalent-orbital considerations, and spectral–crystal structure correlations that these clusters are dinegative anions based on a tetrahedral arrangement of electronegative atoms.[9,10] The hydroxide monohydrate would