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Synthesis and Characterization of $(NF_4)_2SnF_6$ and NF_4SnF_5

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Received April 8, 1976 AIC602700

The novel NF_4^+ salt $(NF_4)_2SnF_6$ was prepared by metathesis between Cs_2SnF_6 and NF_4SbF_6 in HF solution. It is a white solid, stable to above 200 °C. Based on its x-ray powder data, it crystallizes in the tetragonal system and is isotypic with $(NF_4)_2GeF_6$. Its composition was established by elemental analysis, and the presence of tetrahedral NF_4^+ and octahedral SnF_6^{2-} ions in the solid state and in BrF_5 solution was demonstrated by vibrational and ^{19}F NMR spectroscopy, respectively. The salt NF_4SnF_5 was obtained in quantitative yield from the displacement reaction between equimolar amounts of NF_4BF_4 and SnF_4 in HF solution. When a large excess of NF_4BF_4 was used, the main product was again NF_4SnF_5 and only a small amount of $(NF_4)_2SnF_6$ was formed. The NF_4SnF_5 salt was characterized by elemental analysis, vibrational and ^{19}F NMR spectroscopy, and x-ray powder data. The vibrational spectra of the solid and the ^{19}F NMR spectra of BrF_5 solutions show that SnF_5^- possesses a polymeric structure of cis-fluorine-bridged SnF_6 octahedra, analogous to that observed for GeF_5^- in NF_4GeF_5. The potential of $(NF_4)_2SnF_6$ for a "self-clinkering" NF_3–F_2 gas generator is briefly discussed.

Introduction

Perfluoroammonium salts are of significant interest owing to their potential for solid propellant NF_3–F_2 gas generators for chemical HF–DF lasers.[1] Salts are known of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6^-\cdot nSbF_5$, BiF_6^-, $BiF_6^-\cdot nBiF_5$, BF_4^-, GeF_5^-, and GeF_6^{2-}.[1,2] All of these salts are derived from Lewis acids which are volatile and either completely or at least partially monomeric at temperatures below the thermal decomposition temperature of their NF_4^+ salts. Since these volatile Lewis acids are undesirable for NF_3–F_2 gas generators, they must be removed by complexing (clinker formation) with a strong Lewis base, such as KF. Since the addition of a clinker-forming component degrades the performance of an NF_3–F_2 gas generator, the synthesis of NF_4^+ salts, derived from nonvolatile Lewis acids, became very desirable. However, this objective presented a synthetic challenge, since nonvolatile Lewis acids are highly polymeric and already possess favorable high coordination numbers. Consequently, these polymeric compounds are quite unreactive and do not behave like strong Lewis acids, thus rendering a direct synthesis[3] from NF_3, F_2, and the Lewis acid impossible. In this paper we report the synthesis of NF_4^+ salts derived from SnF_4, a doubly trans-fluorine-bridged polymer[4,5] subliming at 704 °C, using metathetical[6,7] and displacement[1,2] reactions.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those recently described.[1,2] The NF_4BF_4[1] and NF_4SbF_6[2] starting materials were prepared as previously reported. The SnF_4 (Ozark Mahoning) and $SnCl_4$ (Baker) were used as received. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[8] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. The CsF was fused in a platinum crucible and powdered in the drybox.

Synthesis of Cs_2SnF_6. Dry CsF (10.45 mmol) and $SnCl_4$ (5.22 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (10 mL of liquid) was added, and the mixture was agitated at 20 °C for several hours until HCl evolution had ceased and a clear solution was obtained. The volatile materials were pumped off at 50 °C. The white solid residue (2.604 g; weight calculated for 5.22 mmol of Cs_2SnF_6 2.600 g) was shown by infrared and Raman spectroscopy[9,10] and its x-ray diffraction powder pattern[11] to be of excellent purity.

If SnF_4 is readily available, the following synthesis of Cs_2SnF_6 was found to be somewhat more convenient. A mixture of CsF and SnF_4 (2:1 mole ratio) was fused in a covered platinum crucible until a clear melt was obtained. Alternately, CsF and SnF_4 (2:1 mole ratio) were agitated in anhydrous HF until a clear solution was obtained (SnF_4 is only very sparingly soluble in HF). In both cases the resulting products were shown by spectroscopic techniques to be undistinguishable from that obtained by the above method.

Synthesis of $(NF_4)_2SnF_6$. The small-scale metathetical reactions were carried out in the apparatus depicted in Figure 1. It consisted of three Teflon FEP U-traps interconnected by Monel unions (Swagelok) and closed off at both ends by a Monel valve. The union between trap II and trap III contained a Teflon filter (porous Teflon sheet, $^1/_{16}$-in. thickness from Russel Assoc. Inc.) and was held in place by a press fit. The passivated apparatus was taken to the drybox and Cs_2SnF_6 and NF_4SbF_6 (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous HF, in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the Cs_2SnF_6 solution to run into trap II containing the NF_4SbF_6 solution. Upon contact of the two solutions, copious amounts of a white precipitate ($CsSbF_6$) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to −80 °C. After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of $CsSbF_6$, whereas the solid collected in trap III was mainly the desired $(NF_4)_2SnF_6$.

The following example gives a typical product distribution obtainable with the above procedure and apparatus: starting materials NF_4SbF_6 (9.72 mmol), Cs_2SnF_6 (4.86 mmol); weight of solid on filter 4.24 g; weight of solid in trap III 1.36 g (weight calculated for 4.86 mmol of $(NF_4)_2SnF_6$ 2.01 g). Anal. Calcd for solid from trap III, a mixture of 82.8% $(NF_4)_2SnF_6$, 12.9% NF_4SbF_6, and 4.3% $CsSbF_6$: NF_3, 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43. Found: NF_3, 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3.

Synthesis of NF_4SnF_5. A mixture of NF_4BF_4 and SnF_4 (9.82 mmol each) was placed into a passivated Teflon–FEP ampule containing a Teflon-coated magnetic stirring bar. Anhydrous HF (10 mL of

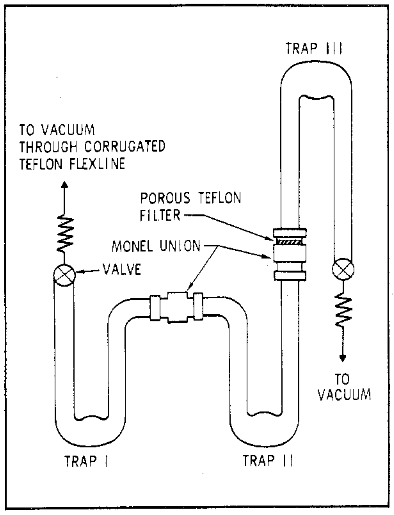

Figure 1. Apparatus for small-scale metathetical reactions consisting of three interconnected Teflon–FEP U-traps.

liquid) was added at −78 °C, and the resulting suspension was stirred at 25 °C for 2 h. The volatile material was pumped off at 35 °C leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol % NF_4SnF_5 and 17 mol % unreacted starting materials. The HF treatment was repeated (again for 2 h) and the nonvolatile residue (2.980 g; weight calculated for 9.82 mmol of NF_4SnF_5 2.982 g) was shown by infrared, Raman, and ^{19}F NMR spectroscopy to be essentially pure NF_4SnF_5. Anal. Calcd for NF_4SnF_5: NF_3, 23.38; Sn, 39.08. Found: NF_3, 23.6; Sn, 38.7.

When a mixture of NF_4BF_4 and SnF_4 in a mole ratio of 2:1 was treated eight times, as described above, with liquid HF for a total of 35 days, the resulting nonvolatile residue consisted mainly of NF_4SnF_5, unreacted NF_4BF_4, and a small amount of $(NF_4)_2SnF_6$.

Results and Discussion

Syntheses. As pointed out in the Introduction, SnF_4 is polymeric with Sn being hexacoordinated. Consequently, solid SnF_4 does not act as a strong Lewis acid. This was experimentally confirmed by demonstrating that mixtures of NF_3, F_2, and SnF_4, when heated to temperatures of up to 300 °C at autogenous pressures of about 150 atm, did not show any evidence for NF_4^+ formation.

Since a direct synthesis of an NF_4^+ salt derived from SnF_4 was not possible, we have studied metathetical and displacement reactions. Because it has previously been shown[12] that SnF_6^{2-} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. On the basis of the reported solubilities of $CsSbF_6$ (5.6 g/100 g of HF),[6] NF_4SbF_6 (280 g/100 g of HF),[6] and Cs_2SnF_6 (~250 g/100 g of HF)[12] and the predicted high solubility of $(NF_4)_2SnF_6$ (the analogous $(NF_4)_2GeF_6$ is very soluble in HF),[2] the metathetical reaction

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

should be capable of producing $(NF_4)_2SnF_6$ in a purity of about 93 mol %. The soundness of these predictions was experimentally verified. A product was obtained which based on its elemental analysis had the following composition (mol %): $(NF_4)_2SnF_6$, 82.8; NF_4SbF_6, 12.9; $CsSbF_6$, 4.3. Whereas the amount of $CsSbF_6$ found in the product approximates that predicted, the presence of about 13% NF_4SbF_6 indicates the loss of some Cs_2SnF_6. This was probably caused by the hold up of some of the Cs_2SnF_6 solution in trap I (see Figure 1) during its transfer to trap II. It should be possible to eliminate most of the NF_4SbF_6 from the product either by minimizing the relative loss of Cs_2SnF_6 during transfer by scaling up the reaction or by recrystallization of the product. However, both approaches were beyond the scope of the present study.

Whereas SnF_4 is quite insoluble in anhydrous HF (contrary to a previous literature report[13]), it dissolves reasonably fast in HF solutions containing an excess of an alkali metal fluoride with formation of the corresponding alkali metal SnF_6^{2-} salt. SnF_4 has also been reported to act as a relatively strong acid in HF solution.[13] Furthermore, GeF_4 is capable of displacing BF_4^- in NF_4BF_4,[2] and the strength of a Lewis acid generally increases within a group of the periodic system with increasing atomic weight of the central atom. Consequently, SnF_4 in HF might be expected to also be capable of displacing BF_4^- in NF_4BF_4.

When equimolar mixtures of NF_4BF_4 and SnF_4 were stirred in anhydrous HF, the following quantitative reaction occurred

$$NF_4BF_4 + SnF_4 \xrightarrow{HF} NF_4SnF_5 + BF_3$$

However, BF_3 interacts with HF and the above reaction appears to be an equilibrium reaction. Consequently, it was found advantageous to pump off the volatile products and to repeat the HF treatment at least once to obtain complete conversion to NF_4SnF_5. No evidence for SnF_6^{2-} formation was observed under these conditions. The quantitative formation of SnF_5^- was surprising, since for the alkali metal fluoride–SnF_4 systems exclusive SnF_6^{2-} formation was observed during our study. We could not find any previous literature reports on SnF_5^-, except for a recent low-temperature ^{19}F NMR study by Dean[14] which demonstrated the presence of polyanions in SO_2 solutions of mixtures of SnF_6^{2-} and SnF_4.

The possibility of preparing $(NF_4)_2SnF_6$ from a 2:1 mixture of NF_4BF_4 and SnF_4 was examined. However, even after eight HF treatments for a total of 35 days only a small amount of SnF_6^{2-} had formed. The main products were NF_4SnF_5 and unreacted NF_4BF_4. These results indicate that the Lewis acid strength of SnF_5^- in HF is insufficient to displace most of the BF_4^- from its NF_4^+ salt and that, in agreement with Dean's observation for SO_2 solutions,[14] the equilibrium is shifted far to the right.

$$SnF_6^{2-} + SnF_4 \rightleftarrows 2SnF_5^-$$

Properties. Both salts, $(NF_4)_2SnF_6$ and NF_4SnF_5, are white, stable, crystallinic, moisture-sensitive solids. As previously pointed out,[2] the onset of thermal decomposition is difficult to define for NF_4^+ salts owing to the absence of a sharp decomposition point. For the SnF_4 salts, one of the decomposition products is nonvolatile solid SnF_4 and, therefore, no melting point could be observed. Visual observation for $(NF_4)_2SnF_6$ in sealed glass capillaries indicated the first signs of decomposition at about 240 °C. The occurrence of decomposition in this temperature range was confirmed by a DSC study which showed the onset of an irreversible endotherm at about 225 °C which was accompanied by F_2 evolution. Furthermore, sealed glass capillaries, when heated above 300 °C, exploded due to pressure buildup from the gaseous decomposition products. For NF_4SnF_5 in a sealed glass capillary, slight shrinkage of the solid was observed at about 120 °C. The DSC curve did not show any evidence for a sharp change in slope up to a temperature of about 270 °C, where a large exotherm started. It should be kept in mind, however, that for powerful oxidizers, such as NF_4^+ salts, exotherms can be caused by reaction of the oxidizer with the aluminum sample container.

The hydrolysis of $(NF_4)_2SnF_6$ and NF_4SnF_5 proceeds, as previously established for other NF_4^+ salts,[2,15] with quantitative NF_3 evolution. This reaction was also used for the elemental analyses. In anhydrous HF, the $(NF_4)_2SnF_6$ salt is highly soluble, whereas NF_4SnF_5 is of moderate solubility. Both salts are also soluble in BrF_5; however the solubilities are considerably lower than those in HF.

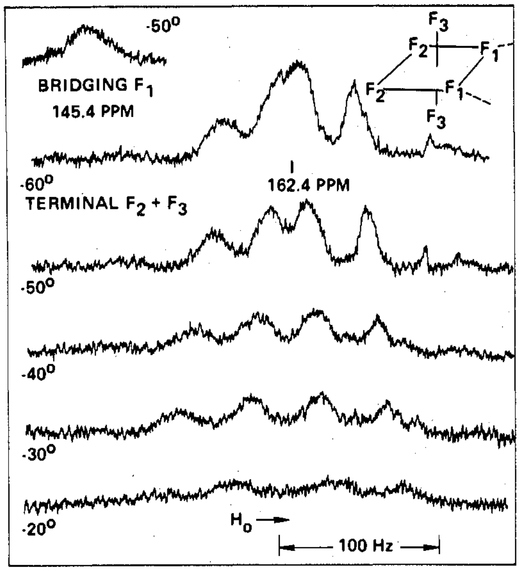

Figure 2. Temperature dependence of the ^{19}F NMR spectrum of the $(SnF_5)_n^{n-}$ part of NF_4SnF_5 in BrF_5 solution, recorded at 56.4 MHz using $CFCl_3$ as external standard.

Table I. Crystallographic Data of $(NF_4)_2SnF_6$ Compared to Those of Other NF_4^+ Salts

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

[a] Reference 1. [b] Reference 2.

X-Ray Powder Data. The powder pattern of $(NF_4)_2SnF_6$ is given as supplementary material. The observed pattern, after correction for several weak lines due to the presence of the metathesis by-products NF_4SbF_6[1] and $CsSbF_6$,[16] is very similar to that[2] of $(NF_4)_2GeF_6$, indicating that the two compounds are isotypic. The pattern was indexed for a tetragonal unit cell, and the resulting crystallographic parameters of $(NF_4)_2SnF_6$ are compared in Table I with those of other NF_4^+ salts. As can be seen, the agreement is excellent. Since $(NF_4)_2GeF_6$ has been prepared in high purity and is well characterized,[2] the x-ray powder data establish beyond doubt that the major crystalline product from the NF_4SbF_6 + Cs_2SnF_6 metathesis is indeed $(NF_4)_2SnF_6$.

The powder pattern of NF_4SnF_5 was also recorded and is given as supplementary material. It did not contain any lines which could be attributed to either NF_4BF_4,[2] SnF_4, or

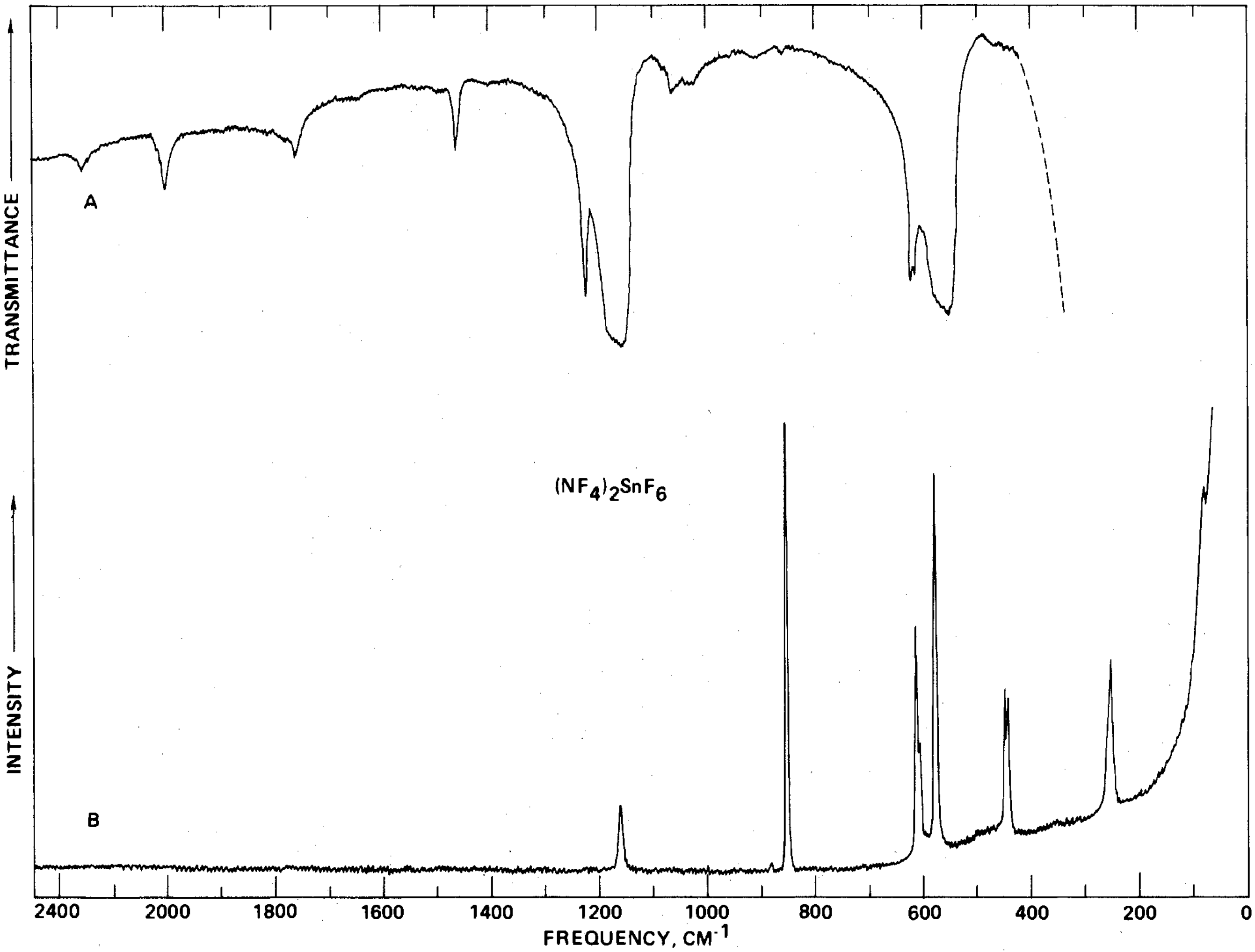

Figure 3. Vibrational spectra of solid $(NF_4)_2SnF_6$: trace A, infrared spectrum of the dry powder in a silver chloride disk, the absorption below 400 cm^{-1} (broken line) being due to the AgCl windows; trace B, Raman spectrum recorded at a spectral slit width of 3 cm^{-1}. Weak bands due to SbF_6^- were deleted from the spectra.

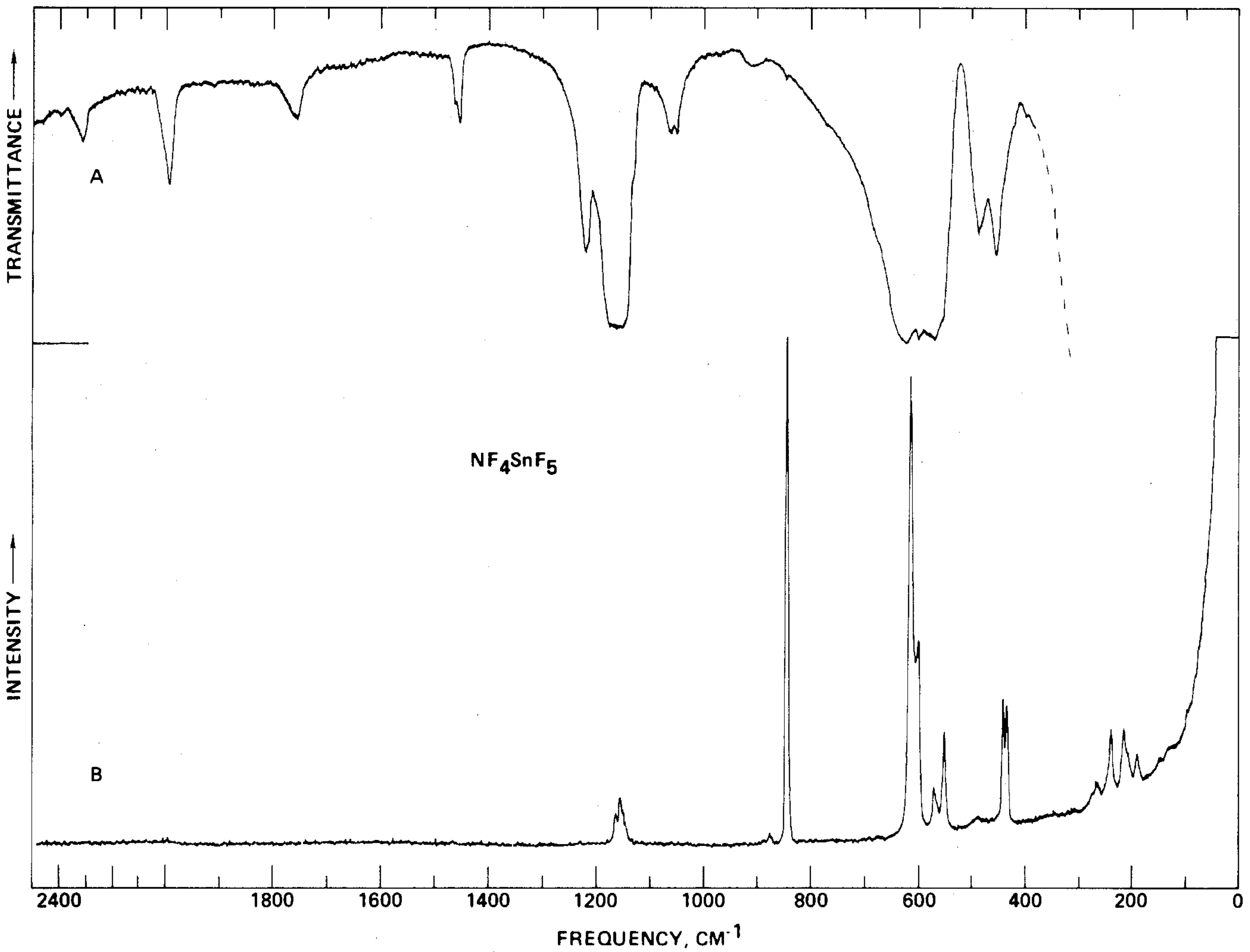

Figure 4. Vibrational spectra of solid NF_4SnF_5, recorded under the same conditions as those of Figure 3.

$(NF_4)_2SnF_6$. Reliable indexing of the pattern was not possible owing to the large number of observed lines, but it somewhat resembles that previously observed[2] for NF_4GeF_5.

NMR Spectra. The ^{19}F NMR spectra were recorded for both $(NF_4)_2SnF_6$ and NF_4SnF_5 in BrF_5 solution. In spite of its higher melting point (−60.5 °C) and lower solubilities, this solvent was preferred over HF, because it was found difficult[2] to suppress rapid fluoride exchange between HF and the anions. In BrF_5 solution, no such problems were encountered. Well-resolved spectra were observed for both the NF_4^+ cation and the corresponding anions, in addition to the sharp quintet (ϕ −272) and doublet (ϕ −136) with J_{FF} = 74.7 Hz characteristic for BrF_5.[2,17] For both the $(NF_4)_2SnF_6$ and the NF_4SnF_5 solution a triplet of equal intensity with ϕ −220, J_{NF} = 229.6 Hz, and a line width at half-height of about 5 Hz was observed which is characteristic for tetrahedral NF_4^+.[2,15,18] The $(NF_4)_2SnF_6$ solution showed in addition to these resonances a narrow singlet at ϕ 149 with the appropriate $^{117/119}Sn$ satellites (average J_{SnF} = 1549 Hz). These values are in good agreement with those previously reported[14,19] for octahedral SnF_6^{2-} in different solvents. This assignment was further confirmed by recording the spectrum of Cs_2SnF_6 in BrF_5 solution.

Two resonances were observed for SnF_5^- of NF_4SnF_5 at ϕ 145.4 and 162.4, respectively, with an area ratio of 1:4. At −20 °C the resonances consisted of broad lines, but at lower temperatures the ϕ 162.4 signal showed splittings. These splittings exhibited a pronounced temperature dependence (see Figure 2). The observed spectrum can be interpreted by comparison with the data previously reported[14] by Dean for $(SnF_5)_n^{n-}$ in SO_2 solution. For this ion, Dean observed a singlet at 140.4 ppm and two approximately 1:2:1 triplets at 154.2 and 158.1 ppm, respectively, with area ratios of 1:2:2. The lower field triplet was broader than the higher field triplet and the coupling constant was 58 Hz. These data unambiguously showed[14] that $(SnF_5)_n^{n-}$ must have a polymeric structure consisting of cis-fluorine-bridged SnF_6 octahedrons. Our data for $(SnF_5)_n^{n-}$ in NF_4SnF_5 are quite similar with the only exception that the difference in chemical shift between the two triplets has decreased and decreases further with decreasing temperature. Thus the resonance at 164.2 ppm (area 4) can be interpreted as an A_2B_2 system strongly distorted by second-order effects.[20] The singlet at 145.4 ppm (area 1) must then be due to the bridging fluorines. The 4:1 area ratio results from the fact that only the two bridging fluorines are shared by two octahedrons. As found by Dean, the coupling between the axial and the terminal equatorial fluorines is much larger (about 40–60 Hz) than that between the terminal and the bridging fluorines. Furthermore, the lower field half of the 162.4-ppm resonance shows a greater line width than the upper half, indicating weak, but differing, coupling between the bridging and the two types of terminal fluorines.

Our observations for NF_4SnF_5 are in excellent agreement with the data of Dean[14] and demonstrate the polymeric cis-fluorine-bridged nature of SnF_5^-. However, we are less confident than Dean that, in $(SnF_5)_n^{n-}$, *n* equals 2. Higher values of *n* can certainly not be excluded and *n* might vary within and from sample to sample, as indicated by varying

Table II. Vibrational Spectra of Solid $(NF_4)_2SnF_6$ Compared to Those of Cs_2SnF_6

Obsd freq, cm^{-1}, and rel intens[a]				Assignments (point group)	
$(NF_4)_2SnF_6$		Cs_2SnF_6			
IR	Raman	IR	Raman	NF_4^+ (T_d)	SnF_6^{2-} (O_h)
2310 vw				$2\nu_3$ $(A_1 + E + F_2)$	
2005 vw				$\nu_1 + \nu_3$ (F_2)	
1764 vw				$\nu_3 + \nu_4$ $(A_1 + E + F_2)$	
1463 vw				$\nu_1 + \nu_4$ (F_2)	
1224 mw				$2\nu_4$ $(A_1 + E + F_2)$	
1160 vs	1158 (1.5)			ν_3 (F_2)	
1132 vw, sh					$\nu_1 + \nu_3$ (F_{1u})
1059 vw				$\nu_2 + \nu_4$ $(F_1 + F_2)$	
1026 vw					$\nu_2 + \nu_3$ $(F_{1u} + F_{2u})$
	881 (0.1)			$2\nu_2$ $(A_1 + A_2 + E)$	
854 vvw	853 (10)			ν_1 (A_1)	
613 mw	613 (5.0)			} $\nu_4 (F_2)$	
605 mw	607 (1.5)				
	579 (8.3)		573 (10)		ν_1 (A_{1g})
550 vs		555 vs			ν_3 (F_{1u})
	470 (0+) br		460 (1.2)		ν_2 (E_g)
	449 (3.1)			} ν_2 (E)	
	442 (2.9)				
	251 (3.3)		249 (4.5)		ν_5 (F_{2g})
	84 (0.3)			Lattice vib	

[a] Uncorrected Raman intensities

Table III. Vibrational Spectra of Solid NF_4SnF_5 Compared to Those of NF_4GeF_5

Obsd freq, cm^{-1}, and rel intens[a]				Assignments[c] (point group)	
NF_4SnF_5		NF_4GeF_5[b]			
IR	Raman	IR	Raman	NF_4^+ (T_d)	$(MF_5)_4^{4-}$
		2380 vw		} $2\nu_3$ $(A_1 + E + F_2)$	
2320 w		2320 w			
2000 w		2010 w		$\nu_1 + \nu_3$ (F_2)	
1760 w		1766 w		$\nu_3 + \nu_4$ $(A_1 + E + F_2)$	
1464 vw		1465 w		} $\nu_1 + \nu_4$ (F_2)	
1456 w		1456 vw			
1222 mw		1221 mw		$2\nu_4$ $(A_1 + E + F_2)$	
	1168 (0.4)		1168 (0.8)	} ν_3 (F_2)	
1165 vs	1159 (0.8)	1160 vs	1159 (0.8)		
	1150 sh		1149 (0.9)		
1134 w, sh					
1061 w		1055 w		} $\nu_2 + \nu_4$ $(F_1 + F_2)$	
1048 w					
	881 (0.2)		881 (0+)	$2\nu_2$ $(A_1 + A_2 + E)$	
850 vw	851 (10)		848 (10)	ν_1 (A_1)	
635 vs		701 vs			$\nu_{as}(MF_2)_{ax}$ (ν_{22}) + $\nu_{as}(MF_2)_{eq}$ (ν_{25})
		690 sh	689 (1.0)		$\nu_{as}(MF_2)_{ax}$ (ν_{17}) + $\nu_{sym}(MF_2)_{eq}$ (ν_7)
	622 (9.2)	673 mw	672 (4.9)		$\nu_{sym}(MF_2)_{eq}$ (ν_1)
		613 m	615 (0.8)	} ν_4 (F_2)	
605 mw	606 (3.3)	604 m	604 (3.2)		
		593 m	594 (2.6)		
575 vs		630 vs			$\nu_{as}(MF_2)_{eq}$ (ν_{26})
	574 (0.5)				$\nu_{as}(MF_2)_{eq}$ (ν_{13})
559 w, sh	558 (2.0)		578 (1.6)		$\nu_{sym}(MF_2)_{ax}$ (ν_2)
490 m	490 (0+)		490 (0+)		$\nu_{sym}(MFM)_{bridge}$ (ν_9)
458 m		474 mw			$\nu_{as}(MFM)_{bridge}$ (ν_{28})
	448 (2.5)		440 (2.6)	} ν_2 (E)	
	440 (2.3)		431 (2.2)		
		386 m			
		373 w	373 (0+) br		} Def modes
			343 (0+) br		
		335 m			
	272 (0.6)		321 (0.8)		
	247 (1.4)		281 (1.0)		
	222 (1.1)		249 (0.6)		
	197 (0.6)		212 (0.4)		
	154 (0+)				
	135 (0.2)		152 (0.4)		

[a] Uncorrected Raman intensities. [b] Data from ref 2. [c] Assignments for $(MF_5)_4^{4-}$ were made by analogy with the data of ref 25.

solubilities observed for different samples during this study. Attempts were unsuccessful to observe the spectrum of a 1:1 mole ratio mixture of Cs_2SnF_6 and SnF_4 in BrF_5 solution owing to its low solubility. Only a signal due to SnF_6^{2-} was observed.

Vibrational Spectra. The infrared and Raman spectra of $(NF_4)_2SnF_6$ and NF_4SnF_5 were recorded and are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are listed in Tables II and III. Comparison with the known spectra[1,2] of other NF_4^+ salts clearly demonstrates the presence of tetrahedral NF_4^+ cations, and the bands due to NF_4^+ can be easily assigned. The observation of small splittings for the degenerate modes of NF_4^+ and the observation of the ideally infrared-inactive $\nu_1(A_1)$ mode as a very weak band in the infrared spectra indicate that the site symmetry of NF_4^+ in these solids is lower than T_d. This is not surprising in view of the above given x-ray powder data and has previously been also observed[1,2] for other NF_4^+ salts.

The assignments for the anion bands in $(NF_4)_2SnF_6$ are also straightforward. The vibrational spectra of octahedral SnF_6^{2-} are well-known[19,21–24] and establish the presence of SnF_6^{2-} in $(NF_4)_2SnF_6$ (see Table II).

The anion spectrum in NF_4SnF_5 shows a pattern very similar to that of the anion in NF_4GeF_5. Furthermore, the general appearance of these anion spectra closely resembles the spectrum previously reported[25] for solid TaF_5. The structure of the latter has been established by x-ray diffraction data[26] as a cis-fluorine-bridged tetramer. Consequently, the observed vibrational spectra indicate a value of 4 for *n* in these $(MF_5)_n^{n-}$ polyanions. A thorough vibrational analysis has been carried out[25] for tetrameric NbF_5 and TaF_5 by Beattie and co-workers. Using their data, we have made tentative assignments for the stretching modes of SnF_5^- and GeF_5^- based on tetrameric anions, which are given in Table III. The assumption of a low degree of polymerization, such as a cyclic tetramer, for the anions in these NF_4MF_5 salts is not unreasonable in view of their appreciable solubility in solvents, such as HF or BrF_5. However, a crystal structure determination is desirable to confirm the above conclusions.

Summary

The successful syntheses of NF_4SnF_5 and $(NF_4)_2SnF_6$ demonstrate the possibility of preparing NF_4^+ salts derived from nonvolatile and unreactive polymeric Lewis acids. Such salts are important for solid propellant NF_3–F_2 gas generators for chemical HF–DF lasers, because they do not require the addition of a clinker-forming reagent. The synthesis of NF_4SnF_5 was achieved by depolymerizing SnF_4 in anhydrous HF and displacing BF_4^- from NF_4BF_4 as BF_3 gas. For the synthesis of $(NF_4)_2SnF_6$ a metathetical process was required. Both NF_4^+ salts were characterized by material balance, elemental analysis, infrared, Raman, and ^{19}F NMR spectroscopy, x-ray powder diffraction data, and DSC. Whereas $(NF_4)_2SnF_6$ contains monomeric SnF_6^{2-} anions, NF_4SnF_5 contains polymeric, cis-fluorine-bridged, hexacoordinated anions. The vibrational spectra indicate that in solid NF_4SnF_5 the anion is probably present as a cyclic tetramer.

Acknowledgment. We are grateful to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

Registry No. $(NF_4)_2SnF_6$, 61587-66-4; $(NF_4)_4(SnF_5)_4$, 61587-68-6; NF_4SnF_5, 61587-75-5; Cs_2SnF_6, 16919-25-8; SnF_4, 7783-62-2.

Supplementary Material Available: Tables IV and V, showing x-ray powder data (2 pages). Ordering information is given on any current masthead page.

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Molecular Photoelectron Spectroscopic Investigation of Some Caged Phosphorus Compounds and Related Acyclic Species

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Received May 28, 1976 AIC60700M

He I molecular photoelectron (PE) spectra have been obtained for the caged compounds $P[N(CH_3)CH_2]_3CCH_3$ (**1**), $P[N(CH_3)N(CH_3)]_3P$ (**4**), $CH_3C(OCH_2)_3CCH_3$ (**5**), $CH_3C(OCH_2)_3P$ (**6**), $P(OCH_2)_3CCH_3$ (**8**), and $P(OCH_2)_3P$ (**9**) and the related acyclic species $[(CH_3)_2N]_3PF_2$ (**2**), $[(CH_3)_2N]_3P$ (**3**), $(C_2H_5)_3P$ (**7**), and $(CH_3O)_3P$ (**10**). Some He II PE spectra are also reported. The interpretation of the PE spectrum of **1** fully supports our earlier interpretation of the PE spectrum of **2**. Likewise, the various lone-pair interactions in **4**, **5**, **6**, **8**, and **9** are consistent with the available structural data. However, it is not possible to interpret the PE spectra of **3** and **10** unequivocally because the ground-state structures of these molecules have not been established. The phosphorus lone-pair ionization energies of the caged phosphorus compounds are appreciably different from those of their acyclic analogues. Possible origins of these differences are discussed.

One of the more exciting developments in the field of phosphorus chemistry has been the application of molecular photoelectron spectroscopy (PES) to questions of conformation and bonding.[2,3] The stereochemical information in the PES