zirconium core levels measured by XPS are slightly (0.3 eV) but consistently more tightly bound in ZrBr, contrary to expectations based on electronegativity. Again, the additional electrostatic interaction discussed above, related changes with the metallic bands, or both may be responsible.

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Registry No. ZrBr, 31483-18-8; ZrCl, 14989-34-5; HfCl, 25516-75-0; $ZrCl_4$, 10026-11-6; Zr, 7440-67-7.

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Hydrogen Bonding. 8. Preparation, Properties, and Low-Temperature Infrared Structural Analysis of Ammonium and Alkylammonium Trihydrogen Tetrafluorides and Tetramethylammonium Dihydrogen Trifluoride[1,2]

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Trialkylammonium trihydrogen tetrafluorides are extremely stable species in which the cation is hydrogen bonded to the central fluoride of a C_{3v} $H_3F_4^-$ anion; these zwitterionic liquid complexes resist loss of hydrogen fluoride even at elevated temperatures and can be distilled intact. Ammonium and methyl- and dimethylammonium ions form similar complexes with additional hydrogen bonding from extra cation hydrogens to terminal fluorines in the anion. The structure of these compounds accounts for the unusual stability order of acid fluoride complexes of hydrogen-bond donor cations relative to alkali metal cations; in each series the highest complex species stable at room temperature is one in which the central fluoride is coordinatively saturated with four hydrogen bonds. The broad, diffuse room-temperature infrared spectra of these complexes are completely resolved at 12 K and show in addition to bands of the cationic and anionic species an intense set of bands in the 2900–2300-cm^{-1} region. These anomalous bands are combination bands formed by intramolecular coupling of the H–F and F–F stretching frequencies. The low-temperature infrared spectrum of the C_{2v} $H_2F_3^-$ anion in tetramethylammonium dihydrogen trifluoride shows similar combination bands, which shift on deuterium substitution.

Introduction

The literature poses an interesting question concerning the relative stability of complex acid fluoride anions: with simple cations such as sodium,[4,5] potassium,[6-8] rubidium,[9,10] and cesium[10,11] the order of anion stability is $H_4F_5^- < H_3F_4^- < H_2F_3^- < HF_2^-$; however, with the hydrogen-bond donor cations hydronium[12] and ammonium[13-15] the observed order is $H_3F_4^- < HF_2^-$, and no compounds containing either $H_4F_5^-$ or $H_2F_3^-$ anions are found.

The alkali metal series, as represented by the potassium ion salts, has been described well; the crystal structures of potassium hydrogen difluoride,[16] dihydrogen trifluoride,[17] and tetrahydrogen pentafluoride[18] show the anions in these salts to be of $D_{\infty h}$, C_{2v}, and T_d symmetries, respectively, when packing modifications are neglected, and we have recently determined[2,19] that the $H_3F_4^-$ anion in potassium trihydrogen tetrafluoride has C_{3v} symmetry through correlation of anion structures with low-temperature infrared spectra for potassium dihydrogen trifluoride, trihydrogen tetrafluoride, and tetrahydrogen pentafluoride. Thus the HF_2^-, $H_2F_3^-$, $H_3F_4^-$, and $H_4F_5^-$ ions in potassium ion salts are formed by successive hydrogen bonding of one, two, three, and four hydrogen fluorides to a central fluoride ion. The structures of the four anions are shown in Figure 1, and the formulas and melting points of the complex acid fluorides of the alkali metals, with the exception of lithium which only forms a hydrogen difluoride, are listed in Table I.

Table I. Stoichiometries and Melting Points of Alkali Metal Complex Acid Fluorides

Cation	Mp, °C				Ref
	HF_2^-	$H_2F_3^-$	$H_3F_4^-$	$H_4F_5^-$	
Na^+	~270 dec	*a*	61.6*b*	38.8	4, 5
K^+	239	71.7	65.8	72	7
Rb^+	205	61.5	51	30*c*	9
Cs^+	176	50.2	32.6	*d*	11

[a] Not available. [b] Incongruent. [c] RbF·7HF (mp −77.3 °C, incongruent) also found. [d] CsF·6HF (mp −42.3°) also found.

The stoichiometries of the complex acid fluorides of hydronium and ammonium ions have been established by detailed thermochemical studies. Cady and Hildebrand[12] studied the freezing point diagram of the water–hydrogen fluoride system and showed that the only compounds to form were $H_3O^+F^-$ (mp −35.5 °C), $H_3O^+HF_2^-$ (mp −75.6 °C), and $H_3O^+H_3F_4^-$ (mp −100.4 °C). There was no indication of $H_2F_3^-$ or $H_4F_5^-$ species. Westrum and co-workers[13,14] carried out a calorimetric study of the ammonia–hydrogen fluoride system with similar results; the only compounds that exist in this system are $NH_4^+F^-$ (decomposes), $NH_4^+HF_2^-$ (mp 126.2 °C), and

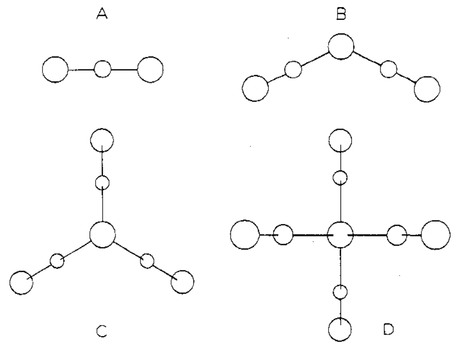

Figure 1. Schematic structures of complex hydrogen fluoride anions, free from packing distortions: (A) $D_{\infty h}$ HF_2^-; (B) C_{2v} $H_2F_3^-$; (C) C_{3v} $H_3F_4^-$; (D) T_d $H_4F_5^-$.

$NH_4^+H_3F_4^-$ (mp 23.2 °C). These results were confirmed by a phase study of the ammonia–hydrogen fluoride–water system by Buettner and Jache;[15] the above compounds were the only ones observed, and no hydrated species were isolated. There is no structural or spectroscopic information available on hydronium or ammonium trihydrogen tetrafluorides.

This paper reports the results of a study of the preparation and infrared spectral properties of ammonium and methyl-, dimethyl-, trimethyl-, and triethylammonium trihydrogen tetrafluorides and of tetramethylammonium dihydrogen trifluoride. Our objectives in this work were to elucidate the structures of the ammonium-type trihydrogen tetrafluorides through low-temperature infrared spectroscopy, to investigate the unusual physical and spectroscopic properties of these compounds as a function of cation structure, and to determine why the $H_3F_4^-$ species are the highest hydrogen fluoride adducts found with hydrogen-bond donor cations.

Preparation and Properties of the Complex Acid Fluorides

The removal of excess hydrogen fluoride from a solution of trimethylammonium fluoride in hydrogen fluoride, either in vacuo or by sweeping with dry nitrogen, proceeds rapidly and smoothly without any observable change in rate or vapor pressure halt until an amine to hydrogen fluoride ratio of 1:4 is reached. The trimethylammonium trihydrogen tetrafluoride so obtained is a mobile, water-white, apparently nonhygroscopic liquid which freezes into white prisms over a 1 °C range at −51 °C. The vapor pressure of hydrogen fluoride over this liquid is negligible, and we have found it impossible to remove any further hydrogen fluoride. The composition of the trihydrogen tetrafluoride is not changed by storing in a vacuum desiccator over barium oxide nor by heating at 80 °C at 0.01 Torr for 12 h; if the sample is heated above 80 °C, the liquid simply distills intact into cooler portions of the cell. This is in sharp contrast to the behavior of potassium trihydrogen tetrafluoride, which is easily converted to the dihydrogen trifluoride by pumping at 0.01 Torr and 25 °C for 2 h.[19]

Rapid removal of hydrogen fluoride from solutions of ammonium, methyl- and dimethylammonium, and triethylammonium fluorides also ceases abruptly at the 1:4 amine to hydrogen fluoride ratio. Triethylammonium trihydrogen tetrafluoride is similar in its properties to the trimethylammonium compound. It appears to be no less stable, but it is significantly more volatile. Samples of the triethylammonium compound lose weight steadily if stored in vacuo at 25 °C. This loss of weight does not, however, result from lowering the hydrogen fluoride content of the sample; the material that remains has an analysis unchanged from that of the original trihydrogen tetrafluoride. Thus the material that evaporates has the stoichiometry of the 1:4 complex.

Dimethylammonium, methylammonium, and ammonium trihydrogen tetrafluorides show decreasing stability in that order. It is possible to lower the hydrogen fluoride content of the dimethylammonium compound somewhat by heating in vacuo, but this process is accompanied by loss of amine and no stoichiometric lower acid fluorides are produced. Extended pumping on methylammonium trihydrogen tetrafluoride reduces the amine to hydrogen fluoride ratio to about 1:1.5 and yields a slush whose infrared spectrum suggests a hydrogen difluoride dissolved in excess hydrogen fluoride. Again, we have not been successful in removing the last of the excess hydrogen fluoride from this material. Ammonium trihydrogen tetrafluoride, on the other hand, loses hydrogen fluoride with relative ease, either under vacuum or on storage in the glovebox, to give the crystalline hydrogen difluoride. This behavior is predicted by the thermochemical data of Westrum,[13] from which we calculate a vapor pressure of 3.23 Torr of hydrogen fluoride over ammonium trihydrogen tetrafluoride at 25 °C. The ammonium compound is noticeably hygroscopic.

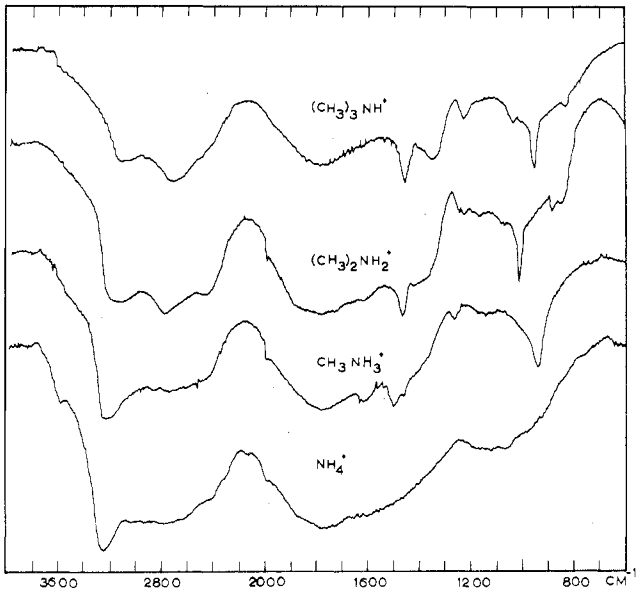

Figure 2. Infrared spectra of ammonium and alkylammonium trihydrogen tetrafluorides at 300 K (liquid films on AgCl).

The infrared spectra of ammonium and methyl-, dimethyl-, and trimethylammonium trihydrogen tetrafluorides are shown in Figure 2; the spectrum of triethylammonium trihydrogen tetrafluoride is identical with that of the trimethyl compound with the exception of cation bands. The spectra shown are of liquid films; however, the spectra of the corresponding solids are essentially identical. The bands become slightly narrower and more intense on cooling but there is no discontinuity in this process in the vicinity of the freezing point, and the spectra at 100 K are nearly superimposable on those taken at 300 K.

The spectra of the ammonium-type trihydrogen tetrafluorides are quite different in appearance from that of potassium trihydrogen tetrafluoride.[2,19] The potassium salt at 300 K shows a broad F–H stretching band (ν_s(FHF)) centered at 1750 cm^{-1}, a structured F–H–F bending band (δ(FHF)) between 1200 and 800 cm^{-1}, and a strong F–F stretching band (ν_s(FF)) at 450 cm^{-1}. The ammonium complexes show absorption in these three regions as expected; however, the ν_s(FHF) and δ(FHF) bands are broader and more diffuse, and the ν_s(FF) bands (not shown in Figure 2) are of much lower intensity. In addition, there is a new absorption above 3000 cm^{-1} and a second new, very broad band envelope between 3000 and 2200 cm^{-1}. The band above 3000 cm^{-1} increases in both frequency and intensity in the order $(CH_3)_3NH^+ < (CH_3)_2NH_2^+ < CH_3NH_3^+ < NH_4^+$. We assign this band to N–H vibrations, as the frequency shifts in the same manner as in the corresponding chlorides, and the intensity increases

Table II. Low-Temperature Infrared Spectra of the $H_3F_4^-$ Anion in Potassium, Methylammonium, and Trimethylammonium Trihydrogen Tetrafluorides[a,b]

Vibration	Assignment[c]	$K^+H_3F_4^-$ [d]	$CH_3NH_3^+H_3F_4^-$	$(CH_3)_3NH^+H_3F_4^-$
ν_{comb}[e]	Combination		2670 (vs)	2680 (vs)
ν_{comb}[f]	Combination		2440 (vs)	2180 (m)
ν_6(e)	Unsym HF str	1750 (b, s)[h]	1905 (s)[g]	1810 (m)[g]
ν_1(a$_1$)	Sym HF str		1808 (vs)	1710 (s)
ν_7(e)	Unsym HF bend (*z*)	1200 (w), 1165 (m)	1100 (vs)	1071 (m), 1056 (s)
ν_2(a$_1$)	Sym HF bend (*z*)	1105 (s)	1055 (s)	1015 (s)
ν_8(e)	Unsym HF bend (*xy*)	1050 (m), 1035 (s)	975 (s), 955 (s)	950 (vs), 928 (sh)
ν_5(a$_2$)	Sym HF bend (*xy*)	1000 (m)	939 (s)	909 (m)
ν_3(a$_1$), ν_9(e)[i]	FF str	480 (sh), 450 (vs)	432 (s)	470 (m)
ν_4(a$_1$), ν_{10}(e)	FFF def	*j*	*j*	*j*

[a] Values are reported in wavenumbers, cm^{-1}. [b] Abbreviations used: weak, w; medium, m; strong, s; very, v; broad, b; shoulder, sh. [c] See Discussion. [d] From ref 19. [e] Combination of $\nu_1(a_1) + 2\nu_s$(FF); see footnote *i*. [f] Combination of $\nu_6(e) + \nu_s$(FF); see footnote *i*. [g] Structured peak; identification of two components of ν_6(e) complicated by overtones of δ(FHF) region. [h] Cannot distinguish ν_6(e) and ν_1(a$_1$) in broad peak. [i] Cannot separate ν_3(a$_1$) and ν_9(e) in ν_s(FF) region. [j] Out of range of these experiments.

Table III. Low-Temperature Infrared Spectra of the $H_2F_3^-$ Anion in Potassium and Tetramethylammonium Dihydrogen Trifluorides[a,b]

Vibration	Assignment[c]	$K^+H_2F_3^-$ [c]	$(CH_3)_4N^+H_2F_3^-$
ν_{comb}[d]	Combination		2675 (s)
ν_{comb}[e]	Combination	2350 (w)[f]	2330 (m)
ν_1(a$_1$), ν_6(b$_1$)[g]	HF str	1800 (b, s)	1800 (b, s)
ν_9(b$_2$)	Sym HF bend (*y*)	1115 (s)	1155 (s)
ν_5(a$_2$)	Unsym HF bend (*y*)	1080 (w)[h]	*i*
ν_2(a$_1$)	Sym HF bend (*xz*)	1035 (s)	1090–1073 (s)[j]
ν_7(b$_1$)	Unsym HF bend (*xz*)	1007–1000 (s)[j]	1057–1045 (s)[j]
ν_3(a$_1$), ν_8(b$_1$)[k]	FF str	490 (sh), 460 (vs)	472 (s), 440 (vs)
ν_4(a$_1$)	Sym FFF def	*l*	*l*

[a] Footnote *a*, Table I. [b] Footnote *b*, Table I. [c] From ref 19. [d] Combination of ν_s(FHF) with $2\nu_s$(FF); see footnotes *g* and *k*. [e] Combination of ν_s(FHF) and ν_s(FF); see footnotes *g* and *k*. [f] From ref 33. [g] Cannot distinguish between ν_1(a$_1$) and ν_6(b$_1$) in ν_s(FHF). [h] Allowed under C_1 crystal symmetry. [i] Inactive. [j] Slightly cleaved doublet. [k] Cannot assign which peak is ν_3(a$_1$) and which is ν_8(b$_1$) in ν_s(FF) region. [l] Out of range of these experiments.

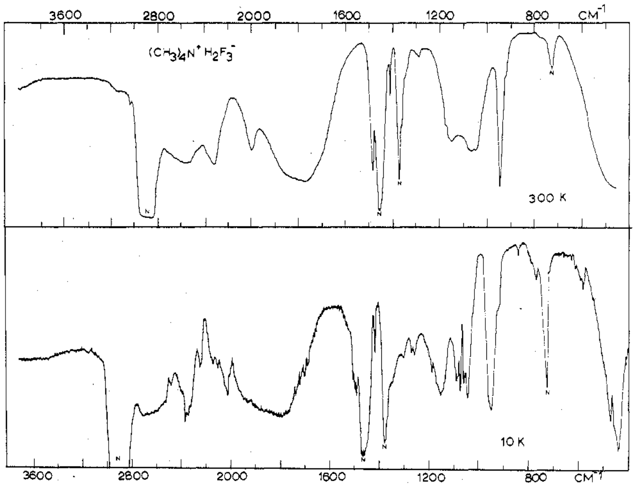

Figure 3. Infrared spectra of tetramethylammonium dihydrogen trifluoride at 300 and 10 K (peaks marked N are Nujol). Note: upper and lower spectra have different frequency scales.

with the number of protons on the cation. The bands between 3000 and 2200 cm^{-1} cannot be accounted for as either cation or anion fundamental vibrations, and we have assigned the absorptions in this region to combination bands.

Tetramethylammonium dihydrogen trifluoride, prepared by evaporation of excess solvent from a solution of tetramethylammonium fluoride monohydrate in hydrogen fluoride, is a crystalline, nonhygroscopic white solid with no detectable vapor pressure of hydrogen fluoride at 25 °C. The infrared spectrum (Figure 3) of the $H_2F_3^-$ anion in this salt in the 2200–400-cm^{-1} region bears a close resemblance to that of potassium dihydrogen trifluoride;[19] however, there are additional strong combination bands in the 3000–2200-cm^{-1} region that are weak and difficult to observe in the potassium salt. These bands, centered at 2670 and 2330 cm^{-1}, shift to 1935 and 1725 cm^{-1} in tetramethylammonium dideuterium trifluoride for ν_H/ν_D ratios of 1.38 and 1.35, respectively. Also, the appearance of the cation methyl C–H stretching bands in the deuterated salt clearly shows the presence of cation C–H to anion hydrogen bonding of the type we have previously identified[20] in a wide variety of tetramethylammonium ion salts.

Tetramethylammonium dihydrogen trifluoride has been previously prepared by O'Malley et al., who reported a single infrared band at 1220 cm^{-1} in a KBr pellet.[21] This is not a band of the $H_2F_3^-$ salt and is undoubtedly due to potassium hydrogen difluoride which forms rapidly even when Nujol mulls of higher acid fluorides contact KBr plates; it is the principal species present when such acid fluorides are compressed into a KBr disk.

The infrared spectrum of tetramethylammonium dihydrogen trifluoride at 10 K is shown in Figure 3, and the spectra of methyl- and trimethylammonium trihydrogen tetrafluorides at 12 K are shown in Figure 4. Infrared spectral values and assignments for these compounds are listed in Tables II and III. The broad bands present at room temperature for these species are resolved at low temperatures into a plethora of individual absorptions. The low-temperature spectra will be considered in detail in the Discussion.

Experimental Section

Matheson hydrogen fluoride was drawn from a cylinder whose content had been reduced to approximately 50% of its original value in previous work; no compounds prepared from this hydrogen fluoride have ever shown any water in their infrared spectra. Eastman Kodak White Label methyl-, dimethyl-, trimethyl-, and triethylammonium chlorides were recrystallized from ethanol and dried at 56 °C and 0.01 Torr over P_2O_5 for 24 h. Alfa ammonium hydrogen difluoride was dried in a similar manner. Tetramethylammonium fluoride monohydrate was prepared as reported previously.[22] All manipulations

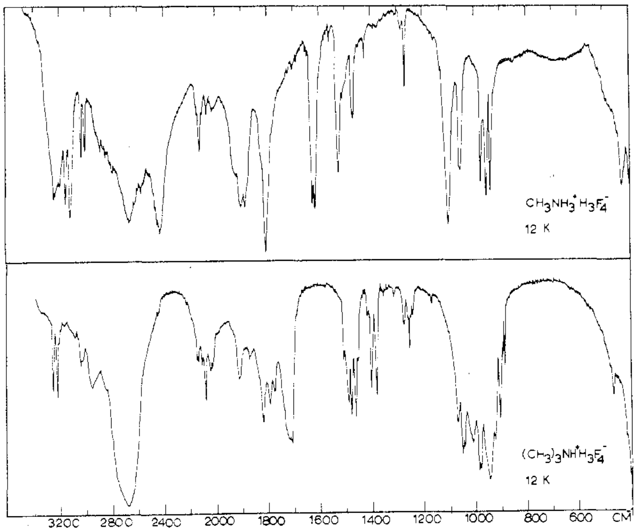

Figure 4. Infrared spectra of alkylammonium trihydrogen tetrafluorides at 12 K.

including the preparation of spectral samples were carried out in a glovebox under dry nitrogen.

The compositions of the complex acid fluoride salts were established by tracking to the desired weight by repeated weighings during preparation and confirmed by titration with sodium hydroxide solution.

Infrared spectra were recorded on Beckman IR-33 and IR-12 spectrophotometers, as either liquid films or Nujol mulls on silver chloride plates. An evacuated cell holder cooled by a two-stage helium refrigerator and fitted with potassium bromide windows was used for low-temperature spectra.

Complex Acid Fluoride Salts. A. Trimethylammonium Trihydrogen Tetrafluoride. A weighed sample of trimethylammonium chloride was placed in a tared polyethylene bottle, which in turn was attached to a Monel gas-handling system via a threaded fitting arranged so that the bottle could be removed from the system under nitrogen at any time and capped for weighing. The system was designed to pass either hydrogen fluoride or dry nitrogen through the bottle. Hydrogen fluoride was passed over the salt, which deliquesced immediately; then a few extra milliliters of hydrogen fluoride was condensed with the aid of an ice bath. Nitrogen was then passed through the cell at 25 °C until the evolution of hydrogen fluoride vapor abruptly ceased. This process was repeated twice more; during the latter stages of the final evaporation the weight of the cell was continually monitored. The final product was a water-white liquid with a reproducible freezing point of −50.5 to −51.5 °C and a composition of $(CH_3)_3N \cdot 4.02HF$. The absence of chloride ion was confirmed by a negative silver nitrate test.

The weight of a sample of this material could not be reduced by storing overnight in a vacuum desiccator over barium oxide or by heating in vacuo at 80–90 °C for 12 h, nor was the infrared spectrum of the material altered by these treatments. A portion was placed in a horizontal polyethylene tube and heated in vacuo at 100 °C; liquid condensed in the cooler portion of the tube. This liquid had an infrared spectrum identical with that of the trimethylammonium trihydrogen tetrafluoride starting sample.

B. Triethylammonium Trihydrogen Tetrafluoride. This compound was prepared by the method of section A from triethylammonium chloride; the water-white, mobile liquid had a composition of $(C_2H_5)_3N \cdot 4.01HF$.

A sample of triethylammonium trihydrogen tetrafluoride was pumped in vacuo at 25 °C until the weight loss of the sample corresponded to the loss of 1 mol of hydrogen fluoride. The infrared spectrum of the liquid that remained was unchanged, and titration showed a composition of $(C_2H_5)_3N \cdot 3.96HF$.

C. Other Trihydrogen Tetrafluorides. Ammonium and methyl- and dimethylammonium trihydrogen tetrafluorides were prepared by the method of section A from ammonium hydrogen difluoride and methyl- and dimethylammonium chlorides, respectively. The compositions of the three liquids corresponded to $NH_3 \cdot 4.03HF$ (mp 23 °C), $CH_3NH_2 \cdot 4.03HF$ (mp −72 °C), and $(CH_3)_2NH \cdot 3.98HF$ (mp −46 °C).

D. Tetramethylammonium Dihydrogen Trifluoride. A sample of tetramethylammonium fluoride monohydrate[22] was placed in a copper cell attached to a Monel vacuum system. Excess hydrogen fluoride was condensed on the monohydrate with the aid of an ice bath and then removed in vacuo; when the vapor pressure of the sample was no longer detectable, it was left to pump overnight at 25 °C and 0.01 Torr. This gave a white, crystalline solid. Anal. Calcd for $C_4H_{14}NF_3$: HF, 30.05. Found: HF, 30.08.

E. Tetramethylammonium Dideuterium Trifluoride. A sample of tetramethylammonium dihydrogen trifluoride was dissolved in 99.7% D_2O and the solvent was removed in vacuo. This process was repeated twice more; on the last dehydration the weight of the sample was followed until it matched the starting sample weight. The infrared spectrum of this material did not show any bands attributable to HF or H_2O.

Discussion

Any spectral–structural correlation discussion is of necessity cyclic; the spectrum is best considered in terms of the model structure, and the structure proposed is best understood in light of the spectral interpretations. For the ammonium-type trihydrogen tetrafluorides we will first examine the low-temperature spectra and then correlate the spectral information with model structures.

Infrared Spectra of Methyl- and Trimethylammonium Trihydrogen Tetrafluorides. A. General Data. The low-temperature infrared spectra of methyl- and trimethylammonium trihydrogen tetrafluorides are shown in Figure 4, and the band frequencies and assignments of the $H_3F_4^-$ anion in ammonium and potassium trihydrogen tetrafluoride salts are listed in Table II. We have made two specific assumptions in deriving the assignments in Table II. First, in each set of similar motions containing a singly degenerate and a doubly degenerate mode–for example, the $\nu_8(e)$ and $\nu_5(a_2)$ FHF bending bands–the doubly degenerate vibration is assigned to the absorption or pair of absorptions under conditions of lowered symmetry that lie to higher energy. This is based on the structural appearance or splitting of these peaks. Second, in the δ(FHF) region the vibrations in the σ_v planes are assumed to lie at higher energy than those out of these planes.[19] These assumptions preclude a definitive assignment of the vibrational bands, which awaits normal-coordinate analysis, single-crystal spectra, and Raman studies. This preliminary assignment, however, is convenient and should not affect our structural conclusions, which do not depend on assignment of bands within the ν_s(FHF), δ(FHF), and ν_s(FF) regions.

In addition to the peaks listed in Table II the low-temperature spectrum of trimethylammonium trihydrogen tetrafluoride shows a number of small peaks between 2160 and 1780 cm^{-1}. These are attributed to the first overtones of the FHF deformation bands between 1070 and 890 cm^{-1}. Similarly, weak bands between 2120 and 1890 cm^{-1} in the 12-K spectrum of methylammonium trihydrogen tetrafluoride are assigned to the first overtones of the FHF deformations between 1100 and 935 cm^{-1}.

B. The N–H and C–H Stretching Bands. The N–H stretching band of trimethylammonium trihydrogen tetrafluoride at 300 K (Figure 2) shows the width and intensity characteristic of hydrogen-bonded N–H. By comparison, the N–H stretch of trimethylammonium tetraphenylborate, in which hydrogen bonding would be minimal, appears as a sharp singlet at 3120 cm^{-1}, with a bandwidth of only 50 cm^{-1}. The N–H···F hydrogen bond in the acid fluoride complex (3160 cm^{-1}) is much weaker than the hydrogen bonds in trimethylammonium chloride (2600 cm^{-1}), bromide (2680 cm^{-1}), or iodide (2730 cm^{-1}).

At 12 K the N–H band of trimethylammonium trihydrogen tetrafluoride narrows (bandwidth 80 cm^{-1}) and splits into a sharp doublet at 3260 and 3230 cm^{-1} (Figure 4). In contrast, the N–H stretching region of methylammonium trihydrogen tetrafluoride shows two types of absorptions at 12 K (Figure 4), a sharp doublet at 3159 and 3120 cm^{-1} and a broad peak at 3250 cm^{-1}. These data indicate a lower than threefold symmetry for the methylammonium cation in the acid fluoride adduct due to different hydrogen-bonding roles of the three N–H bonds in the adduct.

In trimethylammonium trihydrogen tetrafluoride the cation N–H is apparently hydrogen bonded to the central fluoride of the C_{3v} $H_3F_4^-$ anion producing a dipolar zwitterionic compound in which the N–H···F stretch is susceptible[23] to correlation group splitting[24] due to coupling of the dipolar oscillators within the unit cell. Such correlation group splitting could double the infrared-active band. The sharp N–H doublet stretch in methylammonium trihydrogen tetrafluoride is assigned to a similar hydrogen bond, and the second, broad N–H peak of this compound would then be due to weaker, secondary hydrogen bonding to terminal fluorines of $H_3F_4^-$. The number of such secondary hydrogen bonds is expected to increase as the number of protons on the nitrogen increases. Figure 2 clearly demonstrates this trend for the ammonium trihydrogen tetrafluoride salts; i.e., the intensity increases for the N–H band as the number of N–H hydrogens increases.[25]

The symmetric and antisymmetric methyl C–H stretches of methylammonium trihydrogen tetrafluoride appear as two sharp singlets at 3025 and 3000 cm^{-1} at 12 K (Figure 4). In the 12-K spectrum of the trimethylammonium compound, however, the C–H stretches appear as broad peaks at 3050 and 2960 cm^{-1}, with bandwidths of 50 and 110 cm^{-1}, respectively. These broad absorptions are characteristic of cation C–H to anion hydrogen bonding.[20,26]

In methylammonium trihydrogen tetrafluoride a strong N–H bending band is found in the 12-K spectrum (Figure 4) as a doublet at 1645 and 1615 cm^{-1}.

C. The ν_s(FHF) Region. In potassium complex acid fluorides[19] the ν_s(FHF) regions are broad ($\sim$400 cm^{-1}), strong, unresolved absorptions even at 10 K. Salthouse and Waddington[27] have ascribed this type of line broadening to the coupling of extended arrays of F–H–F stretching oscillators throughout the bulk crystal. Wilkinson et al. found that combined absorbance and reflectance also contribute to these broad bands.[28] Unlike potassium trihydrogen tetrafluoride,[19] the ν_s(FHF) region of the ammonium-type trihydrogen tetrafluorides is split into sharp peaks at 12 K.

The ν_s(FHF) absorptions of a C_{3v} $H_3F_4^-$ species consist of $\nu_1(a_1)$ and ν_6(e); under a symmetry environment lower than C_{3v} the degeneracy of the E vibration would be lifted. The spectrum of methylammonium trihydrogen tetrafluoride shows two strong absorptions in the ν_s(FHF) region at 12 K: a broad structured peak centered at 1905 cm^{-1} and an extremely intense, much narrower band at 1808 cm^{-1}. At this time we assign the structured peak at 1905 cm^{-1} to ν_6(e) and the intense peak at 1808 cm^{-1} to $\nu_1(a_1)$. The atom motions in these two vibrations are formally analogous to the antisymmetric ν_3(e) and symmetric $\nu_1(a_1)$ stretching bands of ammonia.[29] In the spectrum of ammonia, $\nu_1(a_1)$, with its greater dipole moment change,[30] is much more intense than ν_3(e) and lies at lower energy.

The intensities of the δ(FHF) overtones relative to the ν_s(FHF) absorptions are greater for trimethylammonium trihydrogen tetrafluoride than for the methylammonium complex; consequently, it is more difficult to separate these bands into their vibrational components. There is a strong peak at 1710 cm^{-1} which we assign to $\nu_1(a_1)$ and a second, broad, less intense peak—significantly overlapped by bending overtones—centered at 1810 cm^{-1}, which is assigned to ν_6(e). The two stretching frequencies are shifted to lower energy ($\sim$100 cm^{-1}) in trimethylammonium trihydrogen tetrafluoride relative to methylammonium trihydrogen tetrafluoride; thus the hydrogen bonds are weaker in the latter salt.

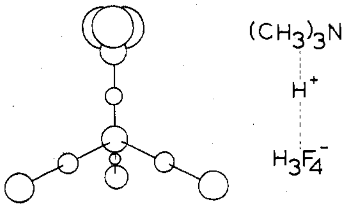

Figure 5. Schematic structure of proposed model for trimethylammonium trihydrogen tetrafluoride.

D. The δ(FHF) Region. The δ(FHF) region of a C_{3v} $H_3F_4^-$ species would show two vibrations in the σ_v planes, $\nu_2(a_1)$ and ν_7(e), and two vibrations perpendicular to these planes, $\nu_5(a_2)$ and ν_8(e). In potassium trihydrogen tetrafluoride the degeneracies of the E vibrations are lifted and six bending bands are observed.[2,19]

The overall band pattern in the δ(FHF) region of methylammonium trihydrogen tetrafluoride is very similar to that of the potassium salt, though displaced about 100 cm^{-1} to lower energy. In the 12-K spectrum of the methylammonium salt ν_7(e) is not split, as is the case with potassium trihydrogen tetrafluoride, but appears as a broad, very intense single band at 1100 cm^{-1}. However, the splitting of ν_8(e) into two bands at 975 and 955 cm^{-1} can be seen. The two singlet absorptions $\nu_2(a_1)$ at 1055 cm^{-1} and $\nu_5(a_2)$ at 939 cm^{-1} are also clearly resolved in this spectrum.

The δ(FHF) region of trimethylammonium trihydrogen tetrafluoride is not as well resolved and shows a broad, intense band between 1150 and 900 cm^{-1} with a number of sharp peaks developing from it (Figure 4). The unusual appearance of this band is not a function of the physical state of the material, as it remains unchanged by repeated annealing of the sample. When a cation absorption at 991–984 cm^{-1} is subtracted from the δ(FHF) region of trimethylammonium trihydrogen tetrafluoride, a six-band system remains which again, except for the overlap of the peak bases, is extremely similar in pattern and energy span to the δ(FHF) region of potassium trihydrogen tetrafluoride. Again there is a 100-cm^{-1} shift to lower energy in comparison with the potassium salt.

The similarity in band pattern and total energy span of the δ(FHF) regions of potassium, methylammonium, and trimethylammonium trihydrogen tetrafluorides demonstrates that the $H_3F_4^-$ moiety in the ammonium compounds retains its essential C_{3v} symmetry, with three hydrogen fluorides hydrogen bonded to a central fluoride ion. As discussed in detail elsewhere,[19] a chain-type anion F–H–F–H–F–H–F, regardless of the geometry chosen, would not be expected to show a similar spectrum in the bending region.

E. The ν_s(FF) Region. There are broad, low-lying bands in the neighborhood of 450 cm^{-1} in the room-temperature spectra of the alkylammonium trihydrogen tetrafluorides arising from F–F stretching vibrations. These bands are much less intense than the strong absorption of potassium trihydrogen tetrafluoride at 450 cm^{-1}; however, at 12 K they sharpen sufficiently to be observed at 470 and 432 cm^{-1} in the trimethylammonium and methylammonium compounds, respectively. As in the case of the potassium salt,[19] the absorption in this region cannot be separated into its $\nu_3(a_1)$ and ν_9(e) components.

Structures of the Ammonium-Type Trihydrogen Tetrafluorides. The structure proposed for trimethylammonium trihydrogen tetrafluoride (Figure 5) consists of a trimethylammonium cation hydrogen bonded to the central fluoride ion of a C_{3v} trihydrogen tetrafluoride anion. The trigonal symmetry of the anion is conserved in this model as required by the infrared spectrum of the $H_3F_4^-$ moiety. Unlike potassium trihydrogen tetrafluoride, where, by analogy with the potassium dihydrogen trifluoride[17] and tetrahydrogen pentafluoride[18] of known crystal structure, trihydrogen tetrafluoride ions interact with a number of potassium counterions in an extended ionic lattice, the cation–anion pairs in trimethylammonium trihydrogen tetrafluoride interact with each other on a one-to-one basis to form internally neutralized, tightly bound zwitterionic molecular complexes. This internalization of Coulombic attraction decreases extended interactions and results in the complex being a distillable liquid at room temperature rather than an ionic solid. There is intermolecular interaction, however, at least at 12 K, by means of C–H···F hydrogen bonds between cation methyl hydrogens and terminal fluorines of the $H_3F_4^-$ portion of adjacent molecules. The structure of triethylammonium trihydrogen tetrafluoride is expected to be similar; however, steric factors would decrease both dipolar and C–H···F hydrogen-bonding intermolecular interactions and account for higher volatility.

In methylammonium trihydrogen tetrafluoride the cation is bound by a similar combination of N–H···F hydrogen bonding and Coulombic attraction to the central flouride of a trigonal $H_3F_4^-$ anion. In this molecular complex C–H···F hydrogen bonding does not occur, and the primary intermolecular interaction is from hydrogen bonding by excess protons on nitrogen to terminal fluorines in other molecules. Increased capacity for such intermolecular hydrogen bonding might be expected to raise the melting points of the complexes; however, the observed melting points for trimethyl- (−51 °C), dimethyl- (−46 °C), and methylammonium (−72 °C) and ammonium (23 °C) trihydrogen tetrafluorides demonstrate that entropic effects on the fusion of these compounds can outweigh enthalpic effects.

The frequency of the central N–H···F hydrogen bond in these complexes shows that the hydrogen bond itself is weak. This is not unexpected; a fourth hydrogen fluoride is relatively loosely bound to the weak acceptor $H_3F_4^-$ anion, as demonstrated by the vapor pressure of hydrogen fluoride (~8 Torr) over potassium tetrahydrogen pentafluoride at 25 °C,[19] and the trimethylammonium ion is a much weaker hydrogen-bond donor than hydrogen fluoride. The cation and anion in these ammonium complexes are, however, tightly bound together; the trimethylammonium complex is not noticeably separated into its constituents at 80 °C, while hydrogen fluoride is readily removed from potassium tetrahydrogen pentafluoride at 25 °C. The primary force of attraction between the cationic and anionic moieties in these complexes is the Coulombic attraction between the proximate positive and negative centers of the molecular zwitterions.

Low-Temperature Infrared Spectrum and Structure of Tetramethylammonium Dihydrogen Trifluoride. The infrared spectrum of the tetramethylammonium ion in tetramethylammonium dihydrogen trifluoride (Figure 3) shows a sharp singlet for the symmetric methyl deformation band at 1411 cm^{-1}, a very weak methyl rocking band at 1290 cm^{-1}, incipient doublet character in the N–C breathing mode at 945 cm^{-1}, and no methyl rotation band in the 1500–1450-cm^{-1} region. This is in excellent accord with the spectrum expected for a tetragonal D_{4h}^{7} crystal lattice containing undistorted T_d tetramethylammonium cations.[31] The nature of the C–H stretching region in tetramethylammonium dideuterium trifluoride demonstrates that C–H···F hydrogen bonding is present in this salt.

The vibrations in the δ(FHF) region of a C_{2v} $H_2F_3^-$ ion consist of $A_1 + A_2 + B_1 + B_2$ (Table II). In potassium dihydrogen trifluoride,[19] where the C_1 crystal symmetry makes the A_2 vibration allowed, four bands are observed in the bending region. In the infrared spectrum of tetramethylammonium dihydrogen trifluoride only three bands are observed; the spectrum is identical in appearance with that of the potassium salt with the exception of the band assigned to $\nu_5(a_2)$ in the potassium dihydrogen trifluoride spectrum, which is completely missing in the tetramethylammonium ion case. The spectrum of the cation in tetramethylammonium dihydrogen trifluoride is identical with that of the perchlorate salt.[20] In the perchlorate the anion lies at a C_{4v} site in a D_{4h} unit cell.[32] If the C_{2v} $H_2F_3^-$ ion occupies a similar site, the $\nu_5(a_2)$ out-of-plane bending band, symmetry forbidden under C_{2v}, would remain infrared inactive. The absence of this band, coupled with the overall appearance of the cation spectrum of tetramethylammonium dihydrogen trifluoride, leads to the prediction that this salt has a D_{4h}^{7} lattice isomorphous with that of the perchlorate. The observed doubling of the in-plane vibrations (Figure 3) suggests that two anion types differing in internal angle will be present in this salt, as is the case in potassium dihydrogen trifluoride.[17,19]

The ν_s(FHF) and ν_s(FF) absorptions of the anion in tetramethylammonium dihydrogen trifluoride are also similar to the corresponding bands in the spectrum of the potassium salt (Table II), although both regions develop more structure on cooling. The primary difference in the spectra of these two compounds lies in the region above 2000 cm^{-1}, where, in addition to a group of small bending overtone bands centered around 2200 cm^{-1}, the tetramethylammonium ion salt shows two strong, broad absorptions at 2675 and 2330 cm^{-1}. These bands show the expected isotope shift in tetramethylammonium dideuterium trifluoride and are thus anion bands. Potassium dihydrogen trifluoride shows a weak band at 2350 cm^{-1} in this region, which can only be observed in a film formed by cooling a melted sample.[33] The nature of these absorptions will be discussed in the next section.

The Anomalous Bands between 3000 and 2200 cm^{-1} in the Infrared Spectra of Alkylammonium Complex Acid Fluorides. The strong absorptions in the 3000–2200-cm^{-1} regions of the infrared spectra of methyl- and trimethylammonium trihydrogen tetrafluorides are not hydrogen-bonded N–H···F vibrations. This conclusion is based on three observations. First, the position of the bands in the methylammonium salt relative to that of the N–H···Cl stretching mode of methylammonium chloride (3100 cm^{-1}) would give a shift to lower energy of about 600 cm^{-1} and require that the acid fluoride anion be a much stronger hydrogen-bond acceptor than the chloride ion. This remarkable acceptor strength of the acid fluoride complex is contrary to expectation and experience; however, if it did exist, we would expect a commensurate shift for the trimethylammonium species relative to the frequency of the N–H···Cl stretch in trimethylammonium chloride (2600 cm^{-1}) and expect to see strong bands in the vicinity of 2000 cm^{-1}. In fact, the principal anomalous band of the trimethylammonium complex spectrum lies at 2680 cm^{-1}. Second, the anomalous bands show marked exaltation on cooling, which is not observed with strong N–H···X hydrogen bonds of this type. The hydrogen-bonded N–H stretching bands of trimethylammonium chloride become slightly narrower on cooling from 300 to 10 K but show a negligible increase in intensity. Finally, tetramethylammonium dihydrogen trifluoride, in which there are no ammonium protons, shows a very similar set of absorptions; the resemblance to the methylammonium trihydrogen tetrafluoride spectrum is particularly striking. These bands in tetramethylammonium dihydrogen trifluoride are associated with the $H_2F_3^-$ moiety (see above). We therefore assign the anomalous bands of the alkylammonium acid fluorides to H–F stretching vibrations.

These bands cannot be fundamentals; there are already sufficient bands in the characteristic spectral regions to account for all of the fundamental vibrations of the complex fluoride anions in the alkylammonium ion salts (Tables II and III). The occurrence of supernumerary strong absorptions in the

A–H stretching region of compounds with strong hydrogen bonds is common and has been the subject of extensive investigations, particularly in the areas of OHO and NHN hydrogen bonds.[34] At various times and in various systems these extra bands have been accounted for by Fermi resonance with torsional vibrations,[35,36] proton double-minimum potentials,[37] proton tunneling,[38] anharmonicity-induced borrowing by bending overtones,[39] and combination bands of the A–H···B stretch with the A···B "hydrogen bond" stretch.[40] Although some explanations are satisfactory in individual cases, no one explanation is able to account for all cases.[41]

We assign the anomalous bands in the complex acid fluorides to combination bands of F–H–F stretches with F···F stretches. The appearance of bands of this type occurs with increasing enhancement in the series $K^+HF_2^- < K^+H_2F_3^- < (CH_3)_4N^+H_2F_3^- < CH_3NH_3^+H_3F_4^- < (CH_3)_3NH^+H_3F_4^-$; apparently the same phenomenon operates throughout the series. In potassium hydrogen difluoride the relative positions of fundamentals and overtones rule out Fermi resonance as an explanation of this phenomenon and since detailed thermochemical[42] and spectroscopic[43,44] studies have shown that the HF_2^- ion in potassium hydrogen difluoride has a single proton potential minimum, explanations based on double minima are also invalid for this salt. Fermi resonance is also an unsatisfactory explanation for the existence of two sets of strong stretching peaks grouped around 2600 and 1800 cm^{-1} in the infrared spectra of the alkylammonium complex acid fluorides. Instead of a transmission window between the peaks, we actually observe the bending overtones in this region. We may also eliminate a double-minimum effect, since all of the peaks increase in intensity on cooling; if the two sets of peaks arose from a double minimum, those at lower energy should decrease in intensity at low temperature.[45,46] On the other hand, these bands can be satisfactorily accounted for as combination bands.

Newman and Badger[47] first assigned the bands in the 1800–5000-cm^{-1} region of the low-temperature spectrum of potassium hydrogen difluoride to the progression $\nu_3 + n\nu_1$, where ν_3 is the antisymmetric F–H–F stretch at 1425 cm^{-1} and ν_1 the symmetric F···F stretch at 600 cm^{-1}. This assignment has been recently confirmed by a detailed single-crystal polarized infrared and Raman study by Wilkinson et al.[28] Hadzi et al.[33] have also assigned a weak band at 2350 cm^{-1} in potassium dihydrogen trifluoride to an unspecified combination. The combination bands of the alkylammonium complex acid fluorides and the summations that we assign to them are listed in Tables II and III. The observed frequencies for the combination bands do not match exactly with summations of the parent bands; however, the deviations from calculated values are all within the range shown by the combination bands of potassium hydrogen difluoride.[28]

The intensity enhancement of the complex acid fluoride combination bands as the cation is varied from potassium through tetramethylammonium to methyl- and trimethylammonium ion logically arises from increased anharmonicity in the proton motion potential functions.[48] This anharmonicity results from the unsymmetrical heterohydrogen bonding and electrostatic environment around the central fluoride ion and increases in the order shown as a function of the increased strengths of cation-to-anion hydrogen bonds and increased proximity of the cation positive charge.

Stabilities of Complex Acid Fluorides. The observed differences between the stability orders of alkali metal cation and hydrogen-bond donor cation complex acid fluorides outlined in the Introduction raise two separate questions. The first, why $H_4F_5^-$ salts are observed with the alkali metals and not with donor cations, has been answered by this study. In each case the first stable species to separate from solution in liquid hydrogen fluoride is one in which a fluoride ion is coordinated to four other molecules. In the case of the alkali metal salts there are four hydrogen fluorides hydrogen bonded to the central fluoride, and with the ammonium cations three hydrogen fluorides and one ammonium ion satisfy the acceptor capacity of the fluoride ion. The N–H···F hydrogen bond in the latter compounds is not strong; however, the interaction is greatly enhanced by Coulombic interaction between cation nitrogen and fluoride, and the ammonium ion thus competes successfully with hydrogen fluoride for the fourth position.

The second question, why $H_2F_3^-$ salts of donor cations are never observed, cannot be answered at this time. It is an important question, as it bears directly on the remarkable tenacity with which the alkylammonium trihydrogen tetrafluorides retain hydrogen fluoride relative to potassium trihydrogen tetrafluoride.

For a complex formation of the type

$$HF(g) + R^+H_2F_3^- = R^+H_3F_4^-$$

the free energy change is given by the expression $\Delta G° = \Delta G°(L) + \Delta G°(H)$, where $\Delta G°(H)$ is the free energy change for the formation of the hydrogen bond in the complex and $\Delta G°(L)$ is, in the case of crystalline salts, the differential lattice energy, i.e., the change in free energy when the lattice is expanded to form the higher complex.[49] If both complexes are liquids, a qualitative picture of $\Delta G°(L)$ is more difficult; however, it would still represent the free energy change for interactions other than hydrogen-bond formation.

The hydrogen bonds between hydrogen fluoride and central fluoride in the ammonium trihydrogen tetrafluoride complexes are weaker[50] than in the potassium ion case as expected from the lowered acceptor capacity of the central fluoride ion from interaction with the cation; thus $\Delta G°(H)$ would be less negative for the ammonium compounds. However, since these compounds have much lower vapor pressures, $\Delta G°$ is more negative than with the potassium salt; therefore, $\Delta G°(L)$ must be significantly less positive for the ammonium complexes. Whether this is an intrinsic stability difference between the structures of the dihydrogen trifluorides and trihydrogen tetrafluorides involved or is a function of the liquid state cannot be answered at this time.

We are continuing a program directed toward the synthesis and study of the lower complex acid fluorides of donor cations with the particular object of finding systems in which all complexes will be crystalline solids, to attempt to answer the unresolved questions concerning the stability order of these materials.

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Registry No. $NH_4^+H_3F_4^-$, 12371-50-5; $CH_3NH_3^+H_3F_4^-$, 62562-71-4; $(CH_3)_2NH_2^+H_3F_4^-$, 62562-70-3; $(CH_3)_3NH^+H_3F_4^-$, 62562-69-0; $(C_2H_5)_3NH^+H_3F_4^-$, 62562-68-9; $(CH_3)_4N^+H_2F_3^-$, 62562-67-8.

Supplementary Material Available: Complete listing of frequency values in the 12-K infrared spectra of methyl- and trimethylammonium trihydrogen tetrafluorides (2 pages). Ordering information is given on any current masthead page.

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Fluorinated Four-Membered Sila or Stanna Heterocycles with Nitrogen and Elements of Group 4, 5, or 6

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The dilithium salts $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$ and $(CH_3)_2Sn[NLiC(CF_3)_2CH_3]_2$ are ready precursors to cyclic compounds. They can be reacted with $(CH_3)_2SiCl_2$, $(CH_3)_2SnCl_2$, $(CH_3)_2GeCl_2$, $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2ZrCl_2$, $(C_6H_5)_2PbCl_2$, $C_2H_5PCl_2$, and $SeCl_4$ to form the corresponding four-membered heterocycles and the spiro compound.

The current literature reflects the increasing interest in cyclodisilazanes and cyclodistannazanes[1–4] as well as in the mixed four-membered heterocycles[4,5] and spiro compounds with silicon on tin or phosphorus and nitrogen.[4–9] However, with the exception of cyclodisilazanes with pentafluorophenyl groups bonded to the nitrogen members of the rings,[10,11] the nitrogen substituents on these compounds are typically hydrogenated.

We now have been able to prepare a variety of four-membered heterocycles with nitrogen and silicon or tin and germanium or titanium or phosphorus or zirconium or lead as well as a spiro compound which contains selenium. The substituents on nitrogen are fluorinated alkyl groups. The compounds $(CH_3)_2M[NLiC(CF_3)_2CH_3]_2$ (M = Si, Sn) are useful nucleophiles in the preparation of these new cyclic molecules.

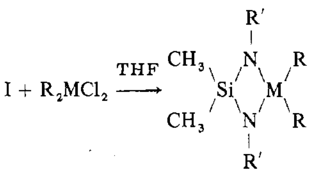
Discussion

Polar addition of methyllithium to the >C=N– bond of the hexafluoroisopropylidenimino group in $(CH_3)_2M[N{=}C(CF_3)_2]_2$ (M = Si, Sn) gives rise to a dilithium salt which is useful in the preparation of heterocycles.

$$(CH_3)_2M[N{=}C(CF_3)_2]_2 + 2CH_3Li \xrightarrow{Et_2O} (CH_3)_2M[NLiC(CF_3)_2CH_3]_2{}^{12}$$

I, M = Si
II, M = Sn

These dilithium salts are soluble in tetrahydrofuran. While it is possible to prepare a cyclodisilazane by reacting I with dimethyl(dichloro)silane, the analogous cyclodistannazane did not result when II was reacted with dimethyl(dichloro)stannane. However, several mixed four-membered heterocycles were synthesized in this manner:



M = Si,[12] Sn,[12] Ge, P, Ti, Zr, Pb; R = CH_3 except R = C_5H_5 when M = Ti, Zr, R = C_2H_5 when M = P, and R = C_6H_5 when M = Pb; R′ = $C(CF_3)_2CH_3$