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Perfluoroammonium and Alkali-Metal Salts of the Heptafluoroxenon(VI) and Octafluoroxenon(VI) Anions

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The NF_4XeF_7 salt was prepared from XeF_6 and NF_4HF_2 and was converted to $(NF_4)_2XeF_8$ by selective laser photolysis. These new salts and the known $CsXeF_7$ and Cs_2XeF_8 were characterized, and their vibrational spectra are reported. Evidence is presented for the existence of a stable $NaXeF_7$ salt. The presence of different phases in solid XeF_6 was confirmed by Raman spectroscopy.

Introduction

Perfluoroammonium salts are the major ingredient in solid-propellant NF_3–F_2 gas generator compositions for chemical lasers.[1] For these applications, the active fluorine content should be high, and the evolved gases should contain, besides F_2 and NF_3, only inert gases to avoid deactivation of the laser. Removal of undesired gases such as the parent Lewis acids of the salts' anions can be accomplished by the addition of a suitable alkali-metal fluoride which forms a nonvolatile clinker with the Lewis acids.[2] However, the additional weight of the clinkering agents lowers the effective fluorine yields of these compositions and renders them less desirable. This problem might be circumvented by the use of NF_4^+ salts containing noble-gas fluoride anions which, on decomposition, would yield additional fluorine values and inert noble-gas diluent as the only byproduct. In this paper we report the successful synthesis of the first known examples of NF_4^+ salts containing noble-gas fluoride anions and the characterization of the XeF_7^- and XeF_8^{2-} anions.

Experimental Section

Caution! Hydrolysis of XeF_6 and of its NF_4^+ salts produces highly sensitive xenon oxides and results in violent explosions. These compounds must therefore be handled with the necessary safety precautions and in the complete absence of moisture.

Materials and Apparatus. The apparatus, handling procedures, analytical methods, and spectroscopic techniques used in this study have previously been described.[3] Literature methods were used for the preparation of $XeFe_6$,[4] $CsXeF_7$, Cs_2XeF_8,[5] and the NF_4HF_2 solution in anhydrous HF.[6] Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox.

Preparation of NF_4XeF_7. Dry CsF (15.54 mmol) and NF_4SbF_6 (15.65 mmol) were loaded in the drybox into half of a prepassivated Teflon U metathesis apparatus. Dry HF (9 mL of liquid) was added on the vacuum line, and the mixture was stirred with a Teflon-coated magnetic stirring bar for 45 min at 25 °C. After the apparatus was cooled to −78 °C, it was inverted and the NF_4HF_2 solution was filtered into the other half of the apparatus. Most of the HF solvent was pumped off during warm-up from −78 °C toward room temperature until the first signs of NF_4HF_2 decomposition became noticeable. At this point the solution was cooled to −196 °C and XeF_6 (17.87 mmol) was added. The mixture was warmed to 25 °C and stirred for 12 h. Although most of the XeF_6 dissolved in the liquid phase, there was some evidence for undissolved XeF_6. Material volatile at 25 °C was removed under a static vacuum and separated by fractional condensation through traps kept at −64 and −196 °C. Immediately, a white copious precipitate formed in the reactor but disappeared after about 10 min, resulting in a clear colorless solution. As soon as the first signs of NF_4HF_2 decomposition were noted, removal of volatiles was stopped and the reactor was cooled to −196 °C. The HF collected in the −196 °C trap was discarded, but the XeF_6 collected in the −64 °C trap was recycled into the reactor, resulting in a yellow solution at room temperature. This mixture was stirred at 25 °C for several hours, followed by removal of the material volatile at 25 °C under a dynamic vacuum. The volatiles were separated by fractional condensation through traps kept at −210, −126, and −64 °C and consisted of NF_3 (~0.3 mmol), HF (~11 mmol), and XeF_6, respectively. The reactor was taken to the drybox, and the solid products were weighed. The yellow filtrate residue (5.149 g; weight calculated for 15.54 mmol of NF_4XeF_7 5.506 g, corresponding to a yield of 93.5%) consisted of NF_4XeF_7, and the white filter cake (5.78 g; weight calculated for 15.54 mmol of $CsSbF_6$ 5.72 g) consisted of $CsSbF_6$. The composition of these solids was confirmed by vibrational and ^{19}F NMR spectroscopy, pyrolysis, and analysis of the pyrolysis residue for NF_4^+, Cs^+, and SbF_6^-. On the basis of these results, the reaction product had the following composition (wt %): NF_4XeF_7 (98.01), NF_4SbF_6 (0.88), and $CsSbF_6$ (1.11).

Results and Discussion

The XeF_7^- and XeF_8^{2-} anions are thermally quite stable[5] and, therefore, were a logical choice for the synthesis of the corresponding NF_4^+ salts. Although the syntheses of $MXeF_7$ (M = Cs, Rb, NO_2)[5,7] and M_2XeF_8 (M = Cs, Rb, K, Na, NO)[5,8] salts have been reported, these salts have not been well characterized, except for a crystal structure determination of

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(1) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1977**, *16*, 937.
(2) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1977**, *16*, 849.
(3) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1982**, *21*, 2091.
(4) Malm, J. G.; Schreiner, F.; Osborne, D. W. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 97.
(5) Peacock, R. D.; Selig, H.; Sheft, I. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2561.
(6) Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1980**, *19*, 1494.
(7) Holloway, J. H.; Selig, H.; El-Gad, U. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3624.
(8) Moody, G. J.; Selig, H. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 319.

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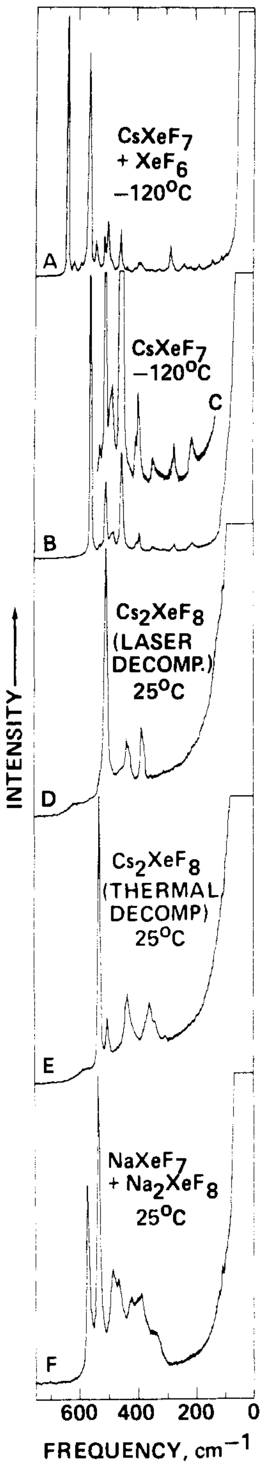

Figure 1. Raman spectra of $CsXeF_7$ containing excess XeF_6 (trace A), $CsXeF_7$ recorded at two different sensitivity levels (traces B and C), Cs_2XeF_8 generated by decomposition of $CsXeF_7$ at 25 °C in the 4880-Å laser beam (trace D), Cs_2XeF_8 generated by vacuum pyrolysis of $CsXeF_7$ at 160 °C (trace E), and a mixture of $NaXeF_7$ and Na_2XeF_8 (trace F).

$(NO)_2XeF_8$.[9] Therefore, a better characterization of the XeF_7^- and the XeF_8^{2-} anion was necessary to allow proper identification of their NF_4^+ salts.

Synthesis and Characterization of $CsXeF_7$, Cs_2XeF_8, and XeF_6. In agreement with a previous report[5] it was found that CsF reacts with XeF_6 at 60 °C to form $CsXeF_7$. However, the following observations deviate from the previous report.[5]

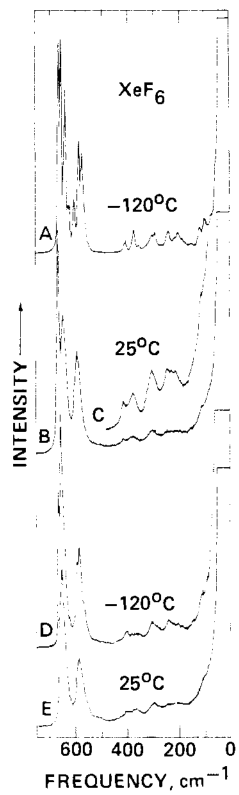

Figure 2. Raman spectra of XeF_6 recorded at −120 and 25 °C and at different sensitivity levels. The differences between traces A–C and D, E are attributed to different phases (see text).

(i) It was not necessary to carefully add the XeF_6 in small increments to the CsF. No evidence for decomposition or explosions was noted, as long as the CsF was carefully dried. (ii) We could not obtain complete conversion of CsF to $CsXeF_7$. Even with a 13-fold excess of XeF_6 and 3-week reaction time at 60 °C, followed by 1 week at ambient temperature, the XeF_6 uptake by the CsF was less than expected for a 1:1 stoichiometry. When the removal of the excess of XeF_6 from the sapphire reactor was stopped at a weight corresponding approximately to a 1:1 adduct, the Raman spectrum of the product showed, in addition to $CsXeF_7$, the presence of either free or very weakly associated XeF_6, and the product evolved XeF_6 on standing. Even after removal of additional XeF_6 (weight corresponding to the composition of $CsXeF_7{\cdot}0.19CsF$) the Raman spectrum still showed the presence of free XeF_6 (see trace A of Figure 1). A pumping time of about 8 h at ambient temperature was required to obtain a constant weight and to completely remove free XeF_6 (see trace B of Figure 1). At this point the composition of the product had dropped to $CsXeF_7{\cdot}0.89CsF$. (iii) The Cs_2XeF_8 salt, prepared by vacuum pyrolysis of $CsXeF_7$ at 160 °C, was white and not cream colored.

Since xenon fluorides are excellent Raman scatterers, Raman spectroscopy was used to distinguish XeF_6, XeF_7^-, and XeF_8^{2-} from each other. Previous work on similar MF_6, MF_7^-, MF_8^{2-} (M = Mo, W, Re)[10] systems has shown that the addition of F^- to a MF_6 molecule or MF_7^- anion increases the polarity of the M–F bonds and therefore progressively lowers the frequencies of the MF_n stretching modes. Since XeF_7^- salts are yellow, they strongly absorbed the blue 4880-Å exciting line of our laser. To avoid decomposition of the samples in the laser beam, we recorded the Raman spectra of XeF_7^- salts at low temperature. Although the Raman spectrum of solid

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(9) Peterson, S. W.; Holloway, J. H.; Coyle, B. A.; Williams, J. M. *Science (Washington, D.C.)* **1971**, *173*, 1238.

(10) Beuter, A.; Kuhlmann, W.; Sawodny, W. *J. Fluorine Chem.* **1975**, *6*, 367 and references cited therein.

Table I. Raman Spectra of Solid XeF_6[a]

A		B	
25 °C	−120 °C	25 °C	−120 °C
656 (10)	658 (10)	652 sh	658 (5)
	649 (9.7)	646 (10)	649 (10)
636 (6)	633 (7.1)		
	620 (1)		620 sh
	613 (1)		613 sh
	597 (2)		589 sh
582 (4.2)	576 (5.0)	579 (4.1)	579 (4.3)
	564 (4.5)		564 sh
404 (0.1)	396 (0.4)	398 (0.3)	396 (0.2)
365 (0.2)	365 (1.0)	362 (0.4)	365 (0+) br
	346 (0+)		
294 (0.3)	296 (0.4)	291 (0.6)	296 (0.4) br
	284 (0.5)		
236	232 (0.4)	235-180 (0+) br	235-180 (0.4) br
220 (0.2)	205 sh		
204	195 (0.3)		
	179 sh		
	142 (0+)		140 (0+)
105 (0+)	110 (0.2)		107 (0+)
	93 (0.3)		86 (0+)
	64 sh		

[a] The observed differences in the A and B type spectra are attributed to the presence of more than one phase in different ratios. Observed frequencies are given in cm^{-1}, with relative intensities in parentheses (uncorrected Raman intensities).

XeF_6 has previously been recorded at 40 °C,[11] its low-temperature spectrum was required to allow its comparison with those of XeF_7^- and XeF_8^{2-}. The spectrum observed for XeF_6 at −120 °C (trace A of Figure 2) shows splittings for most of the bands observed in the room-temperature spectrum (trace B of Figure 2). The latter agrees well with that previously reported.[11] However, depending on temperature cycling and exposure time to the laser beam, a second type of spectrum could reversibly be generated from the same sample and was recorded at both −120 °C (trace D of Figure 2) and 25 °C (trace E of Figure 2). Since XeF_6 is known to exist in at least four different crystalline modifications,[12] the different spectra are attributed to the presence of more than one XeF_6 phase. The observed frequencies are summarized in Table I.

As expected from the previously known MF_6, MF_7^-, MF_8^{2-} series spectra,[10] the strongest Raman line in the spectra of XeF_6 and XeF_7^- and XeF_8^{2-} shows a frequency decrease with increasing negative charge (see Figure 1). For Cs_2XeF_8, two different spectra were observed, depending on its method of preparation. When the sample was prepared by laser photolysis at ambient temperature (XeF_7^- is yellow and strongly absorbs the blue 4880-Å line of the Ar ion laser, whereas XeF_8^{2-} is white and does not decompose in the laser beam), the spectrum shown by trace D of Figure 1 was observed. When the Cs_2XeF_8 sample was prepared by vacuum pyrolysis of $CsXeF_7$ at 160 °C,[5] the spectrum shown by trace E of Figure 1 was obtained. The general appearance of the spectra is quite similar, but some of the bands exhibit significant frequency shifts (see Table II). These shifts might be caused by solid-state effects.

On the Existence of $NaXeF_7$. On the basis of a previous report[5], only CsF and RbF form 1:1 adducts with XeF_6, while for NaF only a 2:1 adduct can be isolated. However, the experimental evidence given by the same authors[5] (combining ratios of NaF:XeF_6 were as low as 1.73) suggested that $NaXeF_7$ might exist in addition to Na_2XeF_8. This was now verified by Raman spectroscopy. As can be seen from Table II and trace F of Figure 1, the product obtained by reacting Xe with a large excess of F_2 and NaF at 250 °C, followed by removal of all material volatile at 55 °C in vacuo,[4] clearly contains XeF_7^- in addition to XeF_8^{2-}. Consequently, NaF can form a 1:1 adduct with XeF_6 that is stable up to at least 55 °C. Since KF generally forms more stable adducts than NaF, it appears safe to predict that $KXeF_7$ should also exist. The difficulty in obtaining 1:1 combining ratios for MF (M = Na or K) with XeF_6 might therefore be attributed to difficulties in achieving a high conversion of the starting materials and not to the nonexistence of the 1:1 adducts.

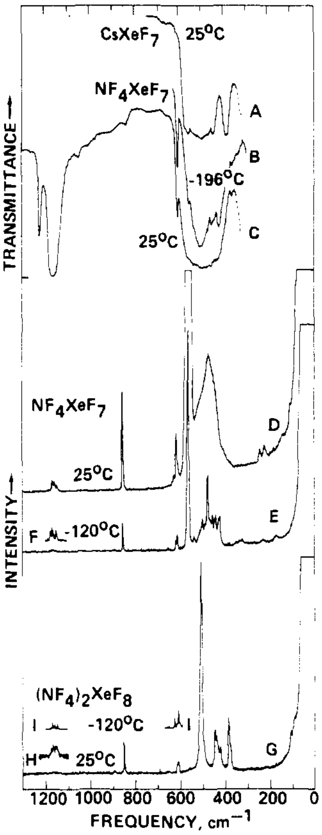

Figure 3. Infrared spectra of $CsXeF_7$ recorded at 25 °C between AgCl windows (trace A) and of NF_4XeF_7 recorded at −196 °C between CsI windows (trace B) and 25 °C between AgCl windows (trace C) and Raman spectra of NF_4XeF_7 and $(NF_4)_2XeF_8$ recorded at different temperatures and sensitivities (traces D–I). The broken lines in the infrared spectra indicate absorption due to the AgCl windows.

On the Structure of XeF_7^- and XeF_8^{2-}. From a crystal structure determination of $(NO)_2XeF_8$,[9] the XeF_8^{2-} anion is known to possess a square-antiprismatic structure. The observed Raman spectra of Cs_2XeF_8 are in excellent agreement with such a structure of symmetry D_{4d}. Three Raman-active stretching modes should be observed, one each in species A_1, E_2, and E_3. Of these, the A_1 mode is assigned to the most intense and single band at about 510–530 cm^{-1}, while the two doubly degenerate E modes are assigned to the two doublets at about 430 and 370 cm^{-1} (see Table II). The observed frequencies agree well with those reported for TaF_8^{3-} (622, 426, and 377 cm^{-1}),[10] which is also known from X-ray data[13] to be a square antiprism. The fact that XeF_8^{2-} has a square-antiprismatic structure suggests that the free valence electron pair on xenon is sterically inactive. This is analogous to the observations previously made for BrF_6^-, which due to its smaller central atom can accommodate only a maximum of six ligands, thus forcing the free valence electron pair on bromine to become sterically inactive.[14]

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(11) Gasner, E. L.; Claassen, H. H. *Inorg. Chem.* **1967**, *6*, 1937.
(12) Sladky, F. *MTP Int. Rev. Sci., Inorg. Chem., Ser. One* **1972**, *3*, 14.
(13) Hoard, J. L.; Martin, W. J.; Smith, M. E.; Whitney, J. F. *J. Am. Chem. Soc.* **1954**, *76*, 3820.

Table II. Vibrational Spectra of $MXeF_7$ and M_2XeF_8 Salts ($M = NF_4$, Cs, and Na)

Assignment (point group)	obsd freq, cm^{-1}, and rel intens[a]												Assignment (point group)
	$NaXeF_7 + Na_2XeF_8$	Cs_2XeF_8			$(NF_4)_2XeF_8$		NF_4XeF_7				$CsXeF_7$		
		Thermal	Thermal	Photolytic									
XeF_8^{2-} (D_{4d})[b]	Ra	Ir	Ra		Ra		Ra		Ir		Ra	Ir	NF_4 (T_d)[c]
	25°C	25°C	25°C	25°C	-120°C	25°C	-120°C	25°C	-196°C	25°C	-120°C	25°C	
									1215w	1222mw			$2\nu_4(A_1+E+F_2)$
					1160(0.3)	1158(0.1)	1163(0.1)	1159(0.1)					
					1150(0.2)		1154(0.1)	1149(0.1)	1149vs	1160vs			$\nu_3(F_2)$
						1145(0.1)							
					1138(0.3)		1138(0.1)	1137(0.1)					
					841(2.4)	841(1.6)	842(1.3)	841(2.2)					$\nu_1(A_1)$
					616(0.5)	609sh	610(0.4)	610sh	610sh	610sh			
					602(1)	602(0.6)	603(0.8)	603(1)	604mw	605mw			$\nu_4(F_2)$
							559						
	572(6.2)						(10)	558(10)	556mw	560sh	552(10)	560m	
							554						
							529(0.3)				521(0.1)		
							505sh		500vs	500vs,br		500vs,br	
$\nu(A_1)$	525(10)	522vw	522(10)	500(10)	502(10)	500(10)							
			492(1.2)										
							494(1)	495sh			500(2.2)		
							483(0+)		481vw				
	475(3)						471(3.3)	464(3)			476(0.5)		
	456(1)						459sh		455m			450m	
					440(0.5)	440(1.8)	447(1)	440sh					$\nu_2(E)$
							439(0+)						
							434(1)				445(3.4)		
			426(2)	430(1.8)	432(3)	433(1.5)							
$\nu(E_2$ or $E_3)$	415(1)												
			418sh	422sh	426(2)	416(1)							
$\nu(E_1)$		425vs,vbr											
							422sh		424m	425sh	396(0.2)	392s	
	378(2)						415(1)				386(0.5)		
			351(1.5)	378(2.1)	381(2.1)	380(2.5)							
$\nu(E_2$ or $E_3)$	345(1)												
			335sh	370sh	377sh	374(2)							
							320(0.2)				340(0.1)		
								233(0.2)			266(0.3)		
							222(0.2)						
								212(0.2)			206(0.2)		
							163(0.2)	130(0.1)					

[a] Uncorrected Raman intensities. [b] Tentative assignments. [c] Observed splittings into degenerate components are caused by solid-state effects.

For XeF_7^- no structural data are available and several structural models must be considered. The free valence electron pair on xenon could be sterically either active or inactive. If it is active, one would expect a structure derived from a square antiprism with one of the positions being occupied by the free pair. Such a structure would be of low symmetry and result in 18 mutually nonexclusive infrared and Raman bands. If the free pair is sterically inactive, two models are most likely. One model is a pentagonal bipyramid of symmetry D_{5h}, as observed for MF_7 (M = I, Re), ZrF_7^{3-}, and certain $CsMF_7$ (M = W, Mo, Re) salts.[10] In this case, five infrared- and five Raman-active bands are expected, which should be mutually exclusive.[15] The other model is a monocapped trigonal prism of symmtry C_{2v}, as in MF_7^{2-} (M = Nb, Ta),[13] for which 18 Raman and 15 mutually nonexclusive infrared bands are expected. The spectra observed for $CsXeF_7$ (Table II, trace B of Figure 1, and trace A of Figure 3) show at least 10 Raman bands, most of which are also observed in the infrared spectrum. Therefore, a model of symmetry D_{5h} appears unlikely. However, a distinction between the two remaining models (pseudo square antiprism and monocapped trigonal prism) is not possible on the basis of the available data.

Synthesis and Properties of NF_4XeF_7 and $(NF_4)_2XeF_8$. The NF_4XeF_7 salt, the first example of an NF_4^+ salt containing a noble-gas fluoride anion, was prepared by repeatedly treating a highly concentrated solution of NF_4HF_2 in anhydrous HF with an excess of XeF_6 in order to shift the equilibrium

$$NF_4HF_2 + XeF_6 \rightleftarrows NF_4XeF_7 + HF \qquad (1)$$

to the right-hand side. The displaced HF was removed together with unreacted XeF_6. The XeF_6 was separated from the HF by fractional condensation and was recycled. In this manner, NF_4XeF_7 was prepared in 94% yield and 98% purity. The yield is based on NF_4SbF_6 used in the NF_4HF_2 preparation step[6]

$$NF_4SbF_6 + CsHF_2 \rightarrow NF_4HF_2 + CsSbF_6\downarrow \qquad (2)$$

and is less than quantitative due to hang-up of some mother liquor on the $CsSbF_6$ filter cake. The 2% impurities consisted of $CsSbF_6$ and NF_4SbF_6 and are typical[3,16] for metathetical reactions involving NF_4HF_2.

The NF_4XeF_7 salt is a light yellow solid. It is stable at ambient temperature and starts to slowly decompose at about 75 °C. Under a dynamic vacuum, the decomposition rates at 75 and 100 °C were found to be 1.6%/h and 28%/h, respectively. The decomposition mode

$$NF_4XeF_7 \rightarrow NF_3 + F_2 + XeF_6 \qquad (3)$$

was established by mass balance and the observed decomposition products. Since the NF_4XeF_7 salt violently explodes on contact with water and therefore could not be analyzed by standard hydrolytic methods,[17] an exhaustive vacuum pyrolysis at 120 °C, followed by an analysis of the solid residue, was used to assay the compound.

The ionic nature of solid NF_4XeF_7 was established by vibrational spectroscopy (see Table II and Figure 3, traces B–F), which showed the bands characteristic for tetrahedral NF_4^+ [18] and XeF_7^- (see above). When solid NF_4XeF_7 was dissolved in anhydrous HF, ^{19}F NMR and Raman spectra of the resulting solution showed XeF_6 and NF_4^+ as the principal species, suggesting that, in a large excess of HF, equilibrium 1 is shifted all the way to the left-hand side. In BrF_5 solution at −40 °C, the ^{19}F NMR spectra originally showed the presence of NF_4^+ (triplet of equal intensity at 221 ppm below external $CFCl_3$

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(14) Bougon, R.; Charpin, P.; Soriano, J. *C. R. Hebd. Seances Acad. Sci. Paris, Ser. C* **1971**, *272*, 565.
(15) Ferraro, J. R. In "Low Frequency Vibrations of Inorganic and Coordination Compounds"; Plenum Press: New York, 1971; pp 112–114.
(16) Wilson, W. W.; Christe, K. O. *J. Fluorine Chem.* **1982**, *19*, 253.
(17) Rushworth, R.; Schack, C. J.; Wilson, W. W.; Christe, K. O. *Anal. Chem.* **1981**, *53*, 845.
(18) Christe, K. O. *Spectrochim. Acta, Part A* **1980**, *36A*, 921.

with J_{NF} = 232 Hz),[16] which was slowly replaced by the signal of NF_3 (triplet of equal intensity at 145 ppm below $CFCl_3$ with J_{NF} = 290 Hz),[19] suggesting again solvolysis of NF_4XeF_7, followed by decomposition of the unstable NF_4BrF_6 intermediate:

$$NF_4XeF_7 + BrF_5 \rightleftarrows [NF_4BrF_6] + XeF_6 \quad (4)$$

$$[NF_4BrF_6] \rightarrow NF_3 + F_2 + BrF_5 \quad (5)$$

When a sample of NF_4XeF_7 was exposed at room temperature for prolonged time to blue 4880-Å laser light, photolytic decomposition of NF_4XeF_7 occurred, resulting in $(NF_4)_2XeF_8$ formation:

$$2NF_4XeF_7 \xrightarrow{h\nu\ (4880\ \text{Å})} (NF_4)_2XeF_8 + XeF_6 \quad (6)$$

Attempts were unsuccessful to duplicate this reaction by carefully controlled thermal decomposition of NF_4XeF_7. The only products obtained were NF_3, F_2, XeF_6, and unreacted NF_4XeF_7. The selective decomposition of NF_4XeF_7 and stability of $(NF_4)_2XeF_8$ in the laser beam can be explained by the different color of the two compounds. The yellow NF_4XeF_7 strongly absorbs the blue 4880-Å light, whereas the white $(NF_4)_2XeF_8$ does not. Since the output of the available laser was just 75 mW, only very small amounts of $(NF_4)_2XeF_8$ could be produced in this manner, and identification of the product was limited to Raman spectroscopy. As can be seen from traces G–I of Figure 3 and Table II, the spectra clearly show the presence of the NF_4^+[18] and XeF_8^{2-} ions (see above). The observed splittings are due to lifting of the degeneracies for the E and F modes in the solid state.[18]

Conclusion. The present study further demonstrates the unique ability of the NF_4^+ cation to form a host of stable salts. The successful synthesis of NF_4XeF_7 and $(NF_4)_2XeF_8$ provided the first known examples not only of NF_4^+ salts containing noble-gas fluoride anions but also of an NF_4^+ salt containing an octafluoro anion. These salts are very powerful oxidizers and on thermal decomposition generate NF_3, F_2, and only inert gases. The formation of $(NF_4)_2XeF_8$ is an interesting example of a selective laser-induced reaction. The XeF_7^- and XeF_8^{2-} anions were characterized by vibrational spectroscopy. Raman spectroscopic evidence was obtained for the existence of a stable $NaXeF_7$ salt, and the presence of different phases in solid XeF_6 was confirmed.

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Registry No. $(NF_4)(XeF_7)$, 82963-12-0; CsF, 13400-13-0; $(NF_4)SbF_6$, 16871-76-4; $Cs(XeF_7)$, 19033-04-6; $Cs_2(XeF_8)$, 17501-71-2; XeF_6, 13693-09-9; $Na(XeF_7)$, 82963-13-1; Xe, 7440-63-3; F_2, 7782-41-4; NaF, 7681-49-4; $(NF_4)_2XeF_8$, 82963-15-3; $Na_2(XeF_8)$, 17501-70-1.

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[19] Dungan, C. H.; Van Wazer, J. R. In "Compilation of Reported ^{19}F NMR Chemical Shifts"; Wiley: New York, 1970.

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Synthesis of 2-Aryl Derivatives of Pentaborane(9)

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A series of 2-aryl derivatives of B_5H_9 have been prepared via aluminum chloride catalyzed electrophilic substitution by $2\text{-}ClB_5H_8$ on various alkylbenzenes. Analyses of ^1H NMR spectra suggest that the site of attack of the B_5H_8 moiety is controlled by steric interactions.

Introduction

During the early 1960s, a heavy emphasis was placed on the preparation of alkyl derivatives of the boron hydrides. Much of the impetus for this research came from the demand for suitable borane-based fuels for various aviation and rocket programs.[1] In several of the early syntheses of alkylboranes, simple heating of olefins in the presence of boranes produced varying yields of 2-substituted pentaborane(9) derivatives (eq 1).[2] Subsequent investigations with B_5H_9 disclosed that

$$C_2H_4 + B_5H_9 \xrightarrow{150\ °C} 2\text{-}EtB_5H_8 \quad (1)$$

Friedel–Crafts-catalyzed electrophilic attack by olefins and alkyl halides produced only 1-alkylpentaborane derivatives (eq 2 and 3).[3] The corresponding 2-alkylpentaborane derivatives were then prepared from the 1-substituted isomers in nearly quantitative yield by thermal or Lewis-base-catalyzed isomerization.

$$RCl + B_5H_9 \xrightarrow{AlCl_3} 1\text{-}RB_5H_8 + HCl \quad (2)$$

$$C_2H_4 + B_5H_9 \xrightarrow{AlCl_3} 1\text{-}EtB_5H_8 \quad (3)$$

A series of 1- and 2-arylpentaborane(9) derivatives is conspicuously absent from the organopentaborane(9) derivatives prepared in previous studies. This absence can be rationalized on the basis of the low Friedel–Crafts activity of the aryl halides.[4] It is clear that an alternate synthetic route is necessary to produce arylpentaboranes. The recent observation that 2-halopentaboranes can function as electrophiles under Friedel–Crafts catalysis conditions[5] suggested a new pathway for the formation of one of the arylpentaborane isomers.

We report the synthesis of a series of $2\text{-}ArB_5H_8$ derivatives by an $AlCl_3$-catalyzed reaction of $2\text{-}ClB_5H_8$ with various aromatic hydrocarbons. These compounds have been characterized by mass spectroscopy and ^{11}B, ^{13}C and ^1H NMR spectroscopy.

Experimental Section

Inert-atmosphere manipulations were performed in dry-nitrogen-filled glovebags and on standard high-vacuum lines.[6] All aromatic reagents used were dried over $LiAlH_4$. Benzene and *m*-xylene (Aldrich

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[1] Butler, E. M.; Fein, M. M. U.S. Patent 3 130 019, 1964. Hughes, R. L.; Smith, I. C.; Lawless, E. W.; "Production of the Boranes and Related Research"; Holtzmann, R. T., Ed.; Academic Press: New York, 1967.

[2] Ryschkewitsch, G. E.; Mezey, E. J.; Altwicker, E. L.; Sisler, H. H.; Garrett, A. B. *Inorg. Chem.* **1963**, *2*, 893–895.

[3] Ryschkewitsch, G. E.; Harris, S. W.; Mezey, E. J.; Sisler, H. H.; Weilmuenster, E. A.; Garrett, A. B. *Inorg. Chem.* **1963**, *2*, 890–893.

[4] Olah, G. A. "Friedel-Crafts Chemistry"; Wiley: New York, 1973; p 65.

[5] Gaines, D. F.; Jorgenson, M. W.; Kulzick, M. J. *J. Chem. Soc., Chem. Commun.* **1979**, 380–381.

[6] Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

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