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Condensed Phases of Difluoramine and Its Alkali-Metal Fluoride Adducts

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Infrared and Raman spectra of HNF_2 and DNF_2 in the liquid and the solid phases show that the compounds are associated through hydrogen bridges between the nitrogen atoms. Raman spectra of the KF, RbF, and CsF adducts and infrared spectra of the RbF adduct of difluoramine are interpreted in terms of strongly hydrogen-bridged $[F\cdots HNF_2]^-$ anions. For the CsF and RbF adducts evidence was obtained for the existence of a distinct second modification of the $[F\cdots HNF_2]^-$ anion with a significantly stronger hydrogen bridge. The reactions of $KF\cdot HNF_2$ with TeF_5OF, OF_2, $FONO_2$, and $FOClO_3$ were studied and resulted in the fluorination of HNF_2 to HF and N_2F_4.

Introduction

Although HNF_2 (difluoramine or fluorimide) has been known[1,2] since 1959, the literature on this interesting compound is sparse. This lack of data may be attributed to the fact that HNF_2 is a vicious explosive.[3-5] While studying alkali-metal fluoride catalyzed[5-7] reactions of HNF_2 with various inorganic hypofluorites, we became interested also in the nature of the $MF\cdot HNF_2$ adducts (M = K, Rb, Cs). The existence of these adducts was reported[6] in 1965, and it was shown that $KF\cdot HNF_2$, $RbF\cdot HNF_2$, and $CsF\cdot HNF_2$ are stable up to about −90, −72, and −64 °C, respectively. Whereas $KF\cdot HNF_2$ and $RbF\cdot HNF_2$ undergo smooth dissociation on warm-up, $CsF\cdot HNF_2$ invariably explodes before reaching room temperature.[6] The nature of these adducts has previously been studied by low-temperature infrared spectroscopy, and it was postulated that $CsF\cdot HNF_2$ possesses a structure different from those of the other $MF\cdot HNF_2$ adducts.[8] However, the experimental evidence in support of either structure was not convincing due to strong interference from water and impurity bands. In order to obtain more reliable data on these interesting adducts, we have recorded their low-temperature Raman and infrared spectra. Since for difluoramine only gas-phase[9] and partial, low-resolution, solid-phase[10] infrared spectra had previously been reported, it became also necessary to record its infrared and Raman spectra in the condensed phases. This allowed a better distinction between $MF\cdot HNF_2$ bands and those due to associated HNF_2 and provided some insight into the nature of the association of HNF_2 in the condensed phases.

Experimental Section

Caution! Difluoramine is highly explosive,[10,11] and protective shielding and clothing should be used during handling operations. The compound was always condensed at −142 °C, and the use of a −196 °C bath for condensing HNF_2 should be avoided.[3] Furthermore, the $CsF\cdot HNF_2$ adduct invariably explodes before reaching 0 °C.[6] The hypofluorites $FOClO_3$,[11] $FONO_2$,[11] and TeF_5OF[12] are also shock sensitive and must be handled with the same precautions.

Materials and Apparatus. Difluoramine was handled in either a glass or all Teflon–FEP and Teflon–PFA vacuum line to avoid metal fluoride catalyzed HF elimination. Other voltaile materials were handled in a stainless-steel vacuum line equipped with Teflon–FEP U-traps, 316 stainless-steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. Nonvolatile materials were handled in the dry N_2 atmosphere of a glovebox.

Difluoramine was prepared by hydrolysis of difluorourea using a literature method.[3] For the synthesis of DNF_2, a previously reported method involving H–D exchange between HNF_2 and a large excess of D_2O[9] produced only a low yield of DNF_2, and the sample still contained 14% of HNF_2. Essentially pure DNF_2 was obtained in high yield by the method used for the preparation of HNF_2,[3] with NH_2CONH_2, H_2O, and H_2SO_4 substituted by their deuteriated analogues. The alkali metal fluorides were dried by fusion in a platinum crucible, followed by immediate transfer of the hot clinkers to the dry N_2 atmosphere of a glovebox. The RbF crystal (Semi-Elements Inc.) used for the low-temperature infrared study of the $RbF\cdot HNF_2$ adduct was freshly cleaved with a razor blade in the drybox and mounted in a dry N_2 atmosphere into the tip of the helium refrigerator. Small amounts of moisture absorbed onto the surface of the RbF crystal were completely removed by pumping on the crystal in the infrared beam for 24 h at 10^{-6} Torr. Literature methods were used for the syntheses of $FONO_2$,[13] TeF_5OF,[14] and $FOClO_3$.[15] OF_2 (Allied Chemical) was purified by fractional condensation at −210 °C prior to its use. The alkali-metal fluoride–difluoramine adducts were generally prepared by condensing an excess of HNF_2 onto the alkali-metal fluoride at −142 °C, warming the mixture to −78 °C for several hours, and then removing the excess of HNF_2 in a dynamic vacuum at −64, −78, and −95 °C for $CsF\cdot HNF_2$, $RbF\cdot HNF_2$, and $KF\cdot HNF_2$, respectively. The composition of the resulting adducts generally approached at 1:1 mole ratio.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. The spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The low-temperature infrared spectra were obtained at various temperatures with an Air Products Model DE 202S helium refrigerator equipped with internal RbF and external CsI windows. The Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. Sealed, 3-mm-o.d. quartz tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. For neat HNF_2 the tip of the tube was drawn out to a smaller diameter to minimize the sample size. A previously described[16] device was used for recording the low-temperature spectra.

TeF_5OF–$KF\cdot HNF_2$ System. A passivated (with ClF_3), 0.5-in.-o.d. Teflon–FEP ampule equipped with a Teflon–PFA valve (Galtek Corp.) was loaded in the drybox with finely powdered, dry KF (2.0 g). On the glass vacuum line, HNF_2 (3.2 mmol) was added to the ampule at −142 °C, and the mixture was kept at −78 °C for 1 h. On the steel–Teflon vacuum line, TeF_5OF (1.57 mmol) was added at −196 °C. The ampule was slowly warmed to −78 °C for 87 h by means of a CO_2–liquid-N_2 slush bath and then to −64 °C for 1 h. The material volatile at −64 °C was fractionated through a series of traps kept at −78, −95, −126, and −196 °C and consisted of N_2F_4 (1.55 mmol) and traces of TeF_6, TeF_5OTeF_5, and FNO. Then the ampule was allowed to warm to 25 °C, and the volatile material was fractionated through traps kept at −78, −126, and −196 °C. It consisted of N_2F_4 (0.05 mmol), TeF_5OH (0.35 mmol), and traces of TeF_6, HF, and TeF_5OTeF_5. The vibrational spectra of the white solid residue showed the presence of HF_2^- and TeF_5O^-.

OF_2–$KF\cdot HNF_2$ System. The $KF\cdot HNF_2$ adduct was prepared as described above from KF (7.3 mmol) and HNF_2 (4.2 mmol), and OF_2 (2.95 mmol) was added at −196 °C. After slow warm-up to −78 °C no noticeable reaction had occurred. Repeating the reaction at −22 °C for 1 h resulted in a 73% consumption of the OF_2 and the formation of N_2F_4 (1.0 mmol) as the main product.

$FOClO_3$–$KF\cdot HNF_2$ System. A mixture of $FOClO_3$ (5.65 mmol) and $KF\cdot HNF_2$ (KF 69 mmol, HNF_2 7.44 mmol), when warmed slowly from

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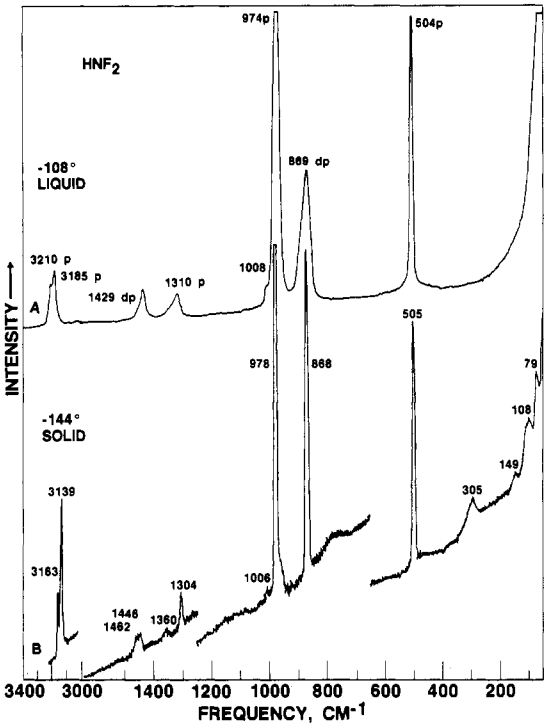

Figure 1. Raman spectra of liquid and solid HNF_2.

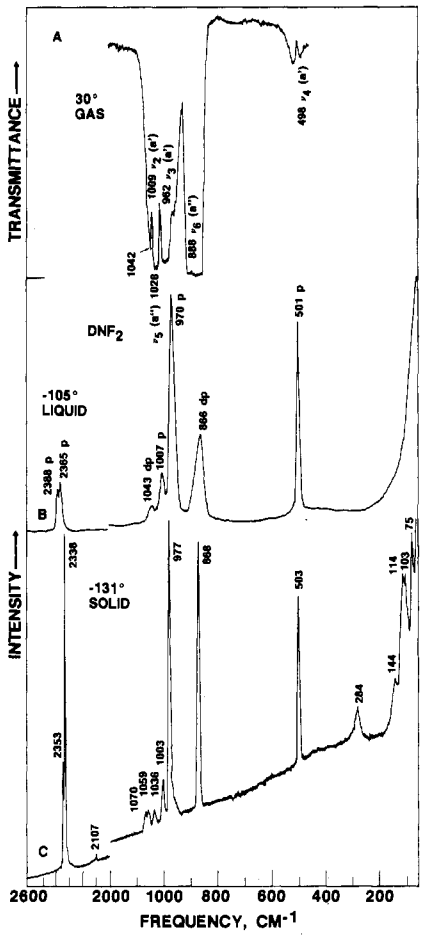

Figure 2. Vibrational spectra of DNF_2: trace A, infrared spectrum of the gas at 270 Torr in a 5-cm path length cell; traces B and C, Raman spectra of liquid and solid DNF_2, respectively.

−196 to −78 °C resulted in an explosion.

$FONO_2$–KF·HNF_2 System. A mixture of $FONO_2$ (0.92 mmol) and KF·HNF_2 (KF 172 mmol, HNF_2 1.22 mmol), when warmed slowly from −142 to −78 °C and then to +25 °C during fractionation of the volatile material, produced N_2F_4 (0.5 mmol) with NO_2, FNO_2, and some O_2 as the major volatile byproducts.

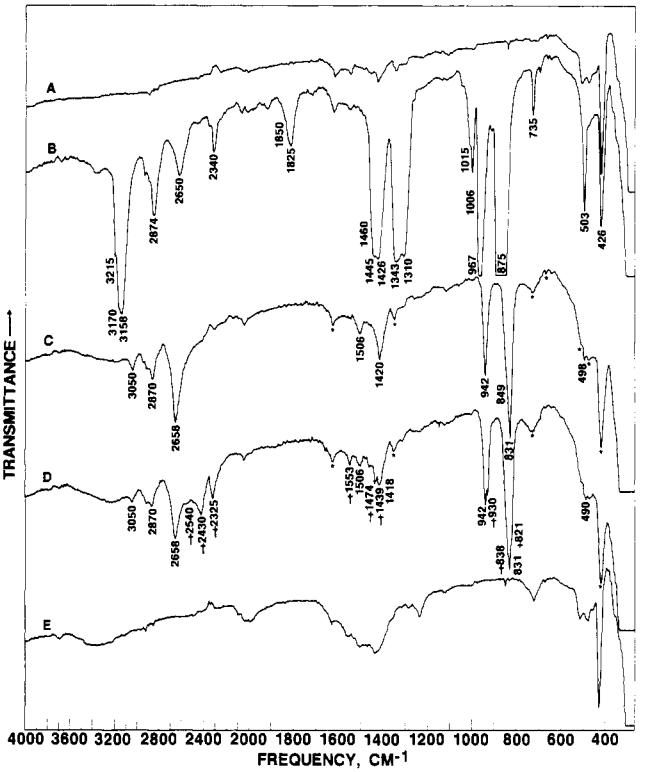

Figure 3. Infrared spectra of solid HNF_2 and of the RbF·HNF_2 adduct at −220 °C: trace A, background of the RbF window; trace B, solid HNF_2; trace C, RbF·HNF_2 adduct generated by cycling the deposit of trace B through −110 °C, with the bands marked by an asterisk due to cell background; trace D, spectrum produced by cycling deposit of trace C through −105 °C, with the new set of bands marked by a dagger ascribed to the second, more strongly hydrogen-bridged species; trace E, cell background after cycling through 25 °C with pumping.

Results and Discussion

Vibrational Spectra of Difluoramine. Infrared spectra were recorded for gaseous HNF_2 and DNF_2 and solid HNF_2. Raman spectra were measured for the liquid and solid phases of HNF_2 and DNF_2. The spectra are given in Figures 1–3, and the observed frequencies and their assignments are summarized in Table I.

The infrared spectrum of gaseous HNF_2 was in excellent agreement with previous results by Lide and co-workers[9] and requires no further comment. These authors also reported four fundamental vibrations for gaseous DNF_2, which were measured on a partially deuteriated sample. In our study, for a completely deuteriated sample, a fifth fundamental, $\nu_4(a')$, was observed at 498 cm^{-1}. Furthermore, we prefer to assign the center of the $\nu_5(a'')$ band to 1028 cm^{-1} and not to the maximum at 1042 cm^{-1}, which, we believe, represents the maximum of the R branch of ν_5 (see trace A of Figure 2). This preference is based on the reasonable assumption of similar band contours for ν_5 in HNF_2 and DNF_2. Similarly, the band center of $\nu_3(a')$ of DNF_2 is preferably assigned to 962 cm^{-1} instead of the previously proposed[9] value of 972 cm^{-1}. The 962-cm^{-1} value is also supported by the observation of the $(\nu_3 + \nu_6)(a'')$ combination band at 1849 cm^{-1} (calculated for 962 + 888 = 1850 cm^{-1}). It is also noteworthy that our revised frequency values for DNF_2 result in a better match with those obtained by Pulay and co-workers by ab initio calculations from the HNF_2 values.[17]

The liquid-phase frequencies are almost identical with the gas-phase values (see Table I), indicating only weak association for liquid difluoramine. The only remarkable feature is the

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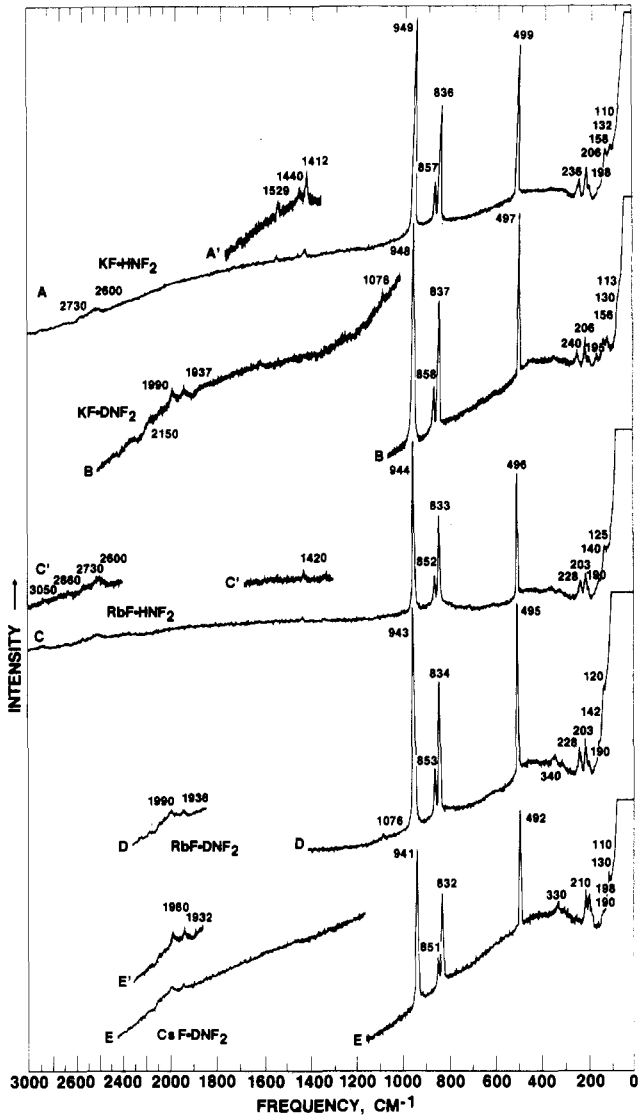


Figure 4. Raman spectra of $KF \cdot HNF_2$ (traces A, A'), $KF \cdot DNF_2$ (trace B), $RbF \cdot HNF_2$ (traces C and C'), $RbF \cdot DNF_2$ (trace D), and $CsF \cdot DNF_2$ (traces E and E'), all recorded at −140 °C. Traces A', C', and E' were recorded at a higher sensitivity setting.

splitting of the NH and the ND stretching mode, $\nu_1(a')$, into two components. These splittings and their relative Raman intensities and polarization ratios are similar for both HNF_2 and DNF_2 and do not permit their attribution to combination bands in Fermi resonance with ν_1. Similar splittings have been observed for the symmetric stretching modes of liquid NH_3 and ND_3[18] and solid HOF[19] and have been attributed to aggregates.[19,20] Therefore, this explanation is also preferred for difluoramine.

For solid difluoramine the previously reported infrared spectrum had been recorded with only low precision in the NaCl region[10] and deviates significantly from that given in Figure 3. Compared to the liquid-phase values, the NH stretching frequency of solid HNF_2 decreased by about 40 cm^{-1} and the NH deformation frequencies increased by about 23 cm^{-1}. Furthermore, all these modes are split into two components each, and bands due to libration and lattice modes appear below 310 cm^{-1}. All these features suggest an increased degree of association. Since the N–H modes are shifted and split relative to the gas phase, and those of the NF_2 group are not, the association must involve intermolecular N–H···N and not N–H···F bridges. This surprising result is discussed elsewhere in more detail.[21] The fact that in HNF_2

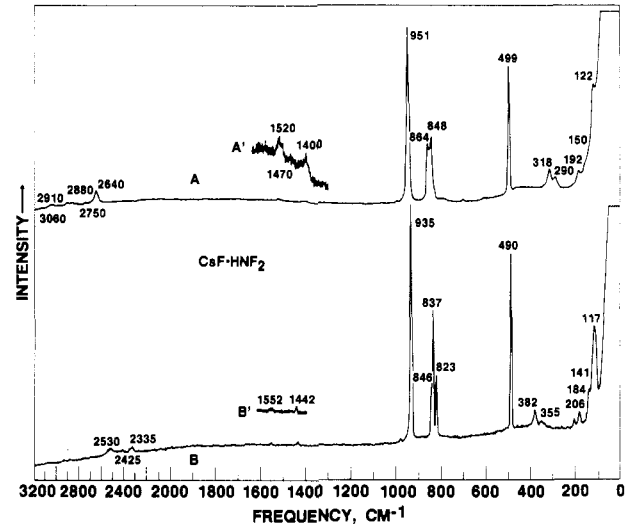
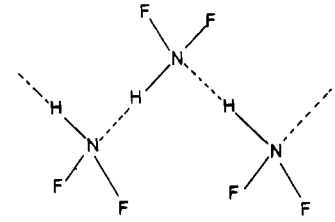


Figure 5. Raman spectra of the two modifications of $CsF \cdot HNF_2$ at −140 °C. Traces A and A' show the spectrum of the more weakly hydrogen-bridged adduct at two different sensitivity levels, respectively, and traces B and B' show those of the stronger hydrogen-bridged adduct.

the nitrogen is a better electron donor than fluorine is in accord with the previous report by Craig that the weak $HNF_2 \cdot BF_3$ and $HNF_2 \cdot BCl_3$ donor–acceptor adducts contain B–N and not B–F bridges.[10] By analogy with the known structure of solid HF,[21] a zigzag chain structure, such as



is most likely for $(HNF_2)_n$, but without additional structural support a more detailed interpretation of the vibrational data appears unwarranted.

Vibrational Spectra and Structure of the $MF \cdot HNF_2$ Adducts. Adducts of both HNF_2 and DNF_2 with KF, RbF, and CsF were prepared as previously described.[6] When an excess of HNF_2 was used in the syntheses, followed by removal of unreacted HNF_2 at low temperature, the combining ratios approximated 1:1. Low-temperature Raman spectra were measured for all these adducts (Figures 4 and 5). Low-temperature infrared spectra were recorded only for $RbF \cdot HNF_2$ (Figure 3) due to the limited availability of the corresponding alkali-metal fluoride windows and the treacherous explosiveness of the $CsF \cdot HNF_2$ adduct on warm-up to ambient temperature, which caused severe damage to the cryostats.

The Raman spectra of $MF \cdot HNF_2$ (M = K and Rb) and $MF \cdot DNF_2$ (M = K, Rb, and Cs) were completely analogous (see Figure 3 and Table II), suggesting essentially identical structures for these adducts. Compared to the spectra of free HNF_2 (see above), the frequency of the N–H stretching mode has decreased by about 600 cm^{-1} and consists of numerous broad bands. The two N–H deformation frequencies have increased by about 100 cm^{-1} and are also split, whereas the three NF_2 modes exhibit only relatively small frequency decreases with $\nu_{as}(NF_2)$ also being split. These observations are thoroughly consistent with an adduct involving a strong hydrogen bridge between HNF_2 and the fluoride anion

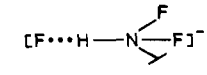


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Table I. Vibrational Spectra of HNF_2 and DNF_2 in the Gas, Liquid, and Solid Phases

		obsd freq, cm^{-1} (rel intens[a])							
		HNF_2				DNF_2			
				solid					
assignt	approx descripn of mode	gas IR	liquid Raman	IR	Raman	gas IR	liquid Raman	solid Raman	gas calcd[b]
C_s		3193 vw	3210 (0.8) p	3215 w	3163 (0.8)	[2333][c]	2388 (1) p	2353 (3.2)	2340
$\nu_1(a')$	ν(NH)		3185 (1.7) p	3170 sh	3139 (2.0)		2365 (2.2) p	2338 (10)	
				3158 s					
$2\nu_5(a')$				2874 mw				2107 (0+)	
$\nu_2 + \nu_5(a'')$		2730 vw							
$2\nu_2(a')$				2650 mw					
$\nu_5 + \nu_6(a')$				2340 w					
$\nu_2 + \nu_6(a'')$						1897 vw			
$\nu_3 + \nu_6(a'')$		1850 mw		1850 sh		1849 mw			
$\nu_2 + \nu_4(a')$				1825 mw					
				1460 sh	1462 (0.3)			1070 (0.6)	
$\nu_5(a'')$	$\delta_{as}(F_2NH)$	1424 s	1429 (0.9) dp	1445 s	1446 (0.3)	1028 s	1043 (0.8) dp	1059 (0.6)	1034
				1426 s					
				1343 s	1360 (0.1)			1036 (0.5)	
$\nu_2(a')$	$\delta_s(F_2NH)$	1307 s	1310 (0.7) p			1009 s	1007 (2) p		1007
				1310 s	1304 (0.5)			1003 (1.2)	
$2\nu_4(a')$			1008 sh	1006 m	1110 (0+)				
$\nu_3(a')$	$\nu_s(NF_2)$	972 ms	974 (10) p	967 s	978 (10)	962 ms	970 (10) p	977 (10)	961
$\nu_6(a'')$	$\nu_{as}(NF_2)$	888 vs	869 (4.0) dp	875 vs	868 (7.3)	888 vs	866 (3.6) dp	868 (8.3)	888
				735 mw					
$\nu_4(a')$	$\delta_s(NF_2)$	500 mw	504 (8.2) p	503 m	505 (5.4)	498 mw	501 (8.4) p	503 (5.2)	498
					305 (0.7)			284 (1.0)	
					149 (0.3)			144 (1)	
								114 (3)	
					108 (0.7)			103 (3)	
					79 (0.4)			75 (2)	

[a] Uncorrected Raman intensities (peak heights). [b] Data from ref 17, calculated by ab initio methods from HNF_2 values. [c] Estimated value from ref 9; not observed in this study because of its low intensity.

Table II. Vibrational Spectra of the Alkali-Metal Fluoride–Difluoramine Adducts[a]

	obsd freq, cm^{-1} (rel intens[b])								
assignt for $[F\cdots H\text{–}NF_2]^-$[c]	KF·HNF_2 Raman	KF·DNF_2 Raman	RbF·HNF_2 Raman	RbF·HNF_2 IR(I)	RbF·HNF_2 IR(II)	RbF·DNF_2 Raman	CsF·HNF_2 Raman (I)	CsF·HNF_2 Raman (II)	CsF·DNF_2 Raman
		2160 (0.3)	3050 (0.1)	3050 mw		2160 (0+)	3060 (0.2)		
		2080 (0.1)				2085 (0+)	2910 (0.2)		2080 (0+)
ν(N–H)(I)		2040 (0+)	2860 (0.1)	2870 m		2035 (0+)	2880 (0.2)		2035 (0+)
	2730 (0.1)	1990 (0.6)	2730 (0.1)			1990 (0.5)	2750 (0.1)		1980 (0.3)
	2600 (0.3)	1937 (0.5)	2600 (0.3)	2658 s		1936 (0.2)	2640 (0.6)		1932 (0.2)
					2540 sh			2530 (0.3)	
ν(N–H)(II)					2430 m			2425 (0.1)	
					2325 m			2335 (0.2)	
$\delta_{as}(HNF_2)$(II)					1553 mw			1552 (0.1)	
$\delta_{as}(HNF_2)$(I)	1529 (0.2)			1506 mw			1520 (0.1)		
$\delta_s(HNF_2)$(II)					1474 w				
					1439 m			1442 (0.1)	
	1440 (0.1)						1470 (0+)		
$\delta_s(HNF_2)$(I)	1412 (0.4)	1076 (0.4)	1420 (0.2)	1420 mw		1076 (0.2)	1400 (0.1)		
$\nu_s(NF_2)$(I)	949 (10)	948 (10)	944 (10)	942 s		943 (10)	951 (10)		941 (10)
$\nu_s(NF_2)$(II)					930 s			935 (10)	
$\nu_{as}(NF_2)$(I)	857 (1.7)	858 (1.7)	852 (1.7)	849 sh		853 (2)	864 (3)		851 (1.5)
	836 (5.5)	837 (5.5)	833 (5.5)	831 vs		834 (5.7)	848 (3.5)		832 (5.5)
								846 sh	
$\nu_{as}(NF_2)$(II)					838 vs			837 (5.2)	
					821 sh			823 (2.5)	
$\delta_s(NF_2)$(I)	499 (7.1)	497 (7.2)	496 (7.2)	498 mw		495 (7.5)	499 (7.1)		492 (7.5)
$\delta_s(NF_2)$(II)					490 mw			490 (7)	
			350 (0.1)	330 vs		340 (0.3)	318 (1.0)	382 (0.7)	330 (0.5)
							290 (0.5)	355 (0.2)	
	236 (0.8)	240 (0.6)	228 (0.6)			228 (1)	192 (0.3)	206 (0.3)	210 (2)
	206 (1.5)	206 (1)	203 (1.2)			203 (1.4)	150 sh	184 (0.5)	198 (2)
librations I and II and lattice modes	198 sh	195 sh	190 sh			190 (0.4)		141 (0.2)	190 sh
	158 sh	156 (0.3)	140 sh			142 sh			
	132 (1)	130 (1)	125 (1)			120 sh	122 (1)	117 (3)	130 sh
	110 (1)	113 (1)							110 (1)
		60 sh							

[a] I and II refer to the two modifications (see text for explanation). All Raman spectra were recorded at −140 °C; infrared spectra, at −220 °C. [b] Uncorrected Raman intensities (peak heights). [c] For the MF·DNF_2 adducts, assignments involving the N–D group have been listed in the N–H rows.

similar to those previously reported for $CsF \cdot HONO_2$[23] and $KF \cdot (CH_2COOH)_2$.[24] The minor frequency decrease of the NF_2 vibrations can be explained by the electron-density release from F^- to HNF_2, which increases the partial negative charges on the two fluorines of the NF_2 group, causing an increase of the $NH^{\delta+}-F^{\delta-}$ bond polarity and a decrease of the N–F force constants.

The Raman spectra of the corresponding DNF_2 adducts are completely analogous and show the expected N–H:N–D frequency ratio of about 1.35–1.40. In addition to these major effects, all the spectra exhibit some more subtle features. For example, the NF_2 modes show a frequency decrease of about 10 cm^{-1} on going from $KF \cdot HNF_2$ to $CsF \cdot HNF_2$. This can be ascribed to the higher negative charge on F^- in CsF, relative to that in KF.

In addition to the internal modes of the HNF_2 subunit in the $[F \cdots H-NF_2]^-$ anion, we would also expect librational modes due to the F···H–N bridge, i.e. one F···H stretch and two F···H–N deformation modes. Furthermore, bands due to the interaction between the alkali-metal cations and the fluoride anions should be observable. All these modes should occur at relatively low frequencies and indeed numerous bands below 350 cm^{-1} were observed. By analogy with the N–H modes, the F···H modes are probably broad and of low Raman intensity and therefore difficult to observe in the Raman spectra. In the infrared spectra of $RbF \cdot HNF_2$ (traces C and D of Figure 3) there is clear evidence for a strong absorption at about 330 cm^{-1}, and this could be one of the F··H libration modes. The sharper features observed in the 240–190-cm^{-1} region of the Raman spectra do not exhibit the large deuterium isotopic shifts expected for the F··H–N bridge modes and therefore are probably due to modes involving mainly fluoride ion motions in the lattice.

The Raman spectra of $CsF \cdot HNF_2$ showed the following interesting additional features. Two different sets of bands were observed, which exhibited similar overall patterns but pronounced frequency shifts from each other, as shown by traces A and B of Figure 5. The spectrum depicted as trace A is very similar, although not quite analogous, to those of all the adducts given in Figure 4. The spectrum of trace B shows very pronounced frequency shifts (decrease of ν(NH) by about 300 cm^{-1}, increase of the N–H deformations by about 40 cm^{-1}, decrease of the NF_2 modes by about 10–30 cm^{-1}, and increase of the librational frequencies) relative to trace A. These shifts are best attributed to a hydrogen-bonded $[F \cdots HNF_2]^-$ adduct, which is very similar to that discussed above for the other adducts but contains a significantly stronger hydrogen bridge. No evidence was observed for the existence of adducts showing frequencies intermediate between those of traces A and B, thus suggesting the presence of two distinct structures and not a progressive variation of the hydrogen-bond strength.

In the case of HF addition to the fluoride anion, each free valence electron pair of the fluoride can form a hydrogen bridge, resulting in the $[F(\cdot\cdot HF)_\eta]^-$ polyanions where η can range from 1 to 4.[25-28] The interpretation of the second, more strongly hydrogen-bridged $F \cdots HNF_2$ type adduct in terms of an analogous $[F(\cdots HNF_2)_\eta]^-$ anion can be ruled out because the observed frequency changes (decrease of the N–H and NF_2 stretching modes) are opposite to those predicted for these polyanions.

Further evidence for the existence of a second, distinct, more strongly hydrogen-bonded adduct was obtained from the low-temperature infrared spectra of $RbF \cdot HNF_2$ (see below). This demonstrates that the occurrence of a second, more strongly bridged HNF_2 adduct is not limited to CsF but also occurs for RbF.

For the low-temperature infrared spectra of $RbF \cdot HNF_2$, difluoramine was condensed at −220 °C onto an RbF single-crystal window. After the spectrum of the solid HNF_2 deposit was recorded (Figure 3, trace B), the temperature of the RbF window was warmed briefly to −110 °C in a static vacuum. Volatile material was pumped off quickly at −110 °C, and the window was cooled back again to −220 °C. The infrared spectrum of the resulting product (Figure 3, trace C) showed the absence of any unreacted HNF_2 and corresponded well to the low-temperature Raman spectra of the $MF \cdot HNF_2$ adducts shown in Figure 4. When the temperature of the infrared sample was briefly cycled through −105 °C and cooled down again to −220 °C, additional bands were observed, which are marked in trace D of Figure 3 by a dagger. The frequencies of these bands are almost identical with those of the major Raman bands of the more strongly hydrogen-bonded modification of the $CsF \cdot HNF_2$ adduct shown in trace B of Figure 5 and were assigned accordingly (see Table II). Cycling of the $RbF \cdot HNF_2$ sample from −220 °C through ambient temperature in a dynamic vacuum resulted in the disappearance of the bands attributed to these $RbF \cdot HNF_2$ adducts.

Comparison of the results from this work with those from a previous low-temperature infrared study[6] show only fair to poor agreement. This disagreement can be attributed to the poor quality of the previously reported data, which is no surprise in view of the great experimental difficulties encountered. Although the existence of two different types of compounds, one a hydrogen-bonded $MF \cdots HNF_2$ compound and the other an $MNF_2 \cdot HF$ adduct, had been postulated, this conclusion was based more on the then known reaction chemistry of the adducts than on the spectroscopic data. The $MNF_2 \cdot HF$ structure had been proposed to account for the fact that only $CsF \cdot HNF_2$ exhibited a propensity to explode on warming toward room temperature. The present study demonstrates that the $KF \cdot HNF_2$, $RbF \cdot HNF_2$, and $CsF \cdot HNF_2$ adducts exhibit the same structural features involving a strong hydrogen bridge between the HNF_2 and the fluoride anion of the alkali-metal fluoride, and that the existence of a second, distinct modification which differs from the first one only in the strength of its hydrogen bridge is not unique for CsF. Although this second modification appears to form more readily with CsF, it was also observed for RbF and therefore might not necessarily be the main reason for the explosive nature of $CsF \cdot HNF_2$. Other factors, such as the higher affinity of CsF for HF, might be significant contributors. No evidence was obtained in this study for the presence of a distinct NF_2^- anion, which should exhibit vibrational spectra very different from those observed.[29]

Reaction Chemistry of $MF \cdot HNF_2$ Adducts. Since $MF \cdot HNF_2$ adducts are known to react with perfluoroalkyl hypofluorites according to

$$R_fOF + MF \cdot HNF_2 \rightarrow R_fONF_2 + MHF_2$$

the analogous reactions were studied for several hypofluorites for which the corresponding $-ONF_2$ derivatives are still unknown. The hypofluorites studied included TeF_5OF, $FOClO_3$, and $FONO_2$. In the case of TeF_5OF the observed reaction products are best explained by the oxidation of HNF_2 by TeF_5OF

$$TeF_5OF + 2KF \cdot HNF_2 \xrightarrow{-64\ °C} TeF_4O + 2KF + 2HF + N_2F_4$$

followed by the competing reactions

$$TeF_4O + HF \rightarrow TeF_5OH$$

$$TeF_4O + KF \rightarrow KTeF_5O$$

$$HF + KF \rightarrow KHF_2$$

The reaction of OF_2 with $KF \cdot HNF_2$ required a considerably higher temperature and even at −22 °C was still incomplete after 1 h.

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(29) **Note Added in Proof.** Since submission of this paper, warm-up of $RbF \cdot HNF_2$ has also resulted in some instances in explosions.

Again the main reaction was the oxidation of HNF_2 to N_2F_4.

$$2OF_2 + 4KF{\cdot}HNF_2 \rightarrow 2N_2F_4 + 4KHF_2 + O_2$$

In the case of $FOClO_3$ and $KF{\cdot}HNF_2$, the mixture exploded when warmed from −196 toward −78 °C. For $FONO_2$, the reaction could be sufficiently controlled, but again N_2F_4 was formed in almost quantitative yield with NO_2, O_2, and FNO_2 as the major byproducts. It thus appears that with hypofluorites, which are powerful oxidizers, fluorination of HNF_2 to N_2F_4 and HF is favored over $XONF_2$ formation.

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Registry No. D_2, 7782-39-0; HNF_2, 10405-27-3; KF, 7789-23-3; RbF, 13446-74-7; CsF, 13400-13-0; TeF_5OF, 83314-21-0; OF_2, 7783-41-7; $FONO_2$, 7789-26-6; $FOClO_3$, 10049-03-3; HF, 7664-39-3; N_2F_4, 10036-47-2.

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Kinetics of the Consecutive Binding of Bipyridyl Ligands and of Phenanthroline Ligands to Copper(II)

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By the application of temperature-jump relaxation techniques, the kinetics of the consecutive binding of bipyridyl ligands (bpy) and of phenanthroline ligands (phen) to Cu(II) have been studied, $CuL_{i-1}^{2+} + L \rightleftarrows CuL_i^{2+}$ (i = 2, 3; L = bpy, phen). At 25 °C and ionic strength 0.5 M, the following forward rate constants have been obtained: for bpy, $k_2 = 1.5 \times 10^9$ M^{-1} s^{-1} and $k_3 = 8.6 \times 10^8$ M^{-1} s^{-1}; for phen, $k_2 = 6.9 \times 10^8$ M^{-1} s^{-1} and $k_3 = 1.8 \times 10^9$ M^{-1} s^{-1}. These rate constants are appreciably larger than those for formation of the 1:1 complexes, which were determined earlier, $k_1 = (4-5) \times 10^7$ and 6.4×10^7 M^{-1} s^{-1}, respectively. The rate enhancement in the formation of the bis and tris complexes is attributed to stacking interactions between the coordinated and the incoming ligands. Several kinetic features of these reactions are discussed.

Introduction

Complex formation processes involving Cu(II) are usually very fast, with second-order rate constants not far below the diffusion-controlled limit.[2,3] The rapidity of these reactions not only requires the application of specialized techniques for their investigation but also impedes the elucidation of mechanistic details. Several experimental studies have indicated that substitution processes at hexacoordinated Cu(II) are best described to proceed by a dissociative mechanism,[3-5] like those of various other divalent metal ions. On the other hand, associative mechanisms for Cu(II) have also been suggested.[6,7]

The high rates of substitution at $Cu(H_2O)_6^{2+}$ reflect the weak binding of the H_2O ligands in the axial positions of the distorted octahedron.[8] The observation that many multidentate ligands, too, react very fast with Cu^{2+} is obviously due to a rapid inversion of the Jahn-Teller distortion.[3,8] It has been reported that for $Cu(H_2O)_6^{2+}$ this inversion occurs with a rate of 6×10^{10} s^{-1}.[9]

A subject of wide interest is the effects of ligands already coordinated to metal ions on the kinetics of further ligand binding.[2] A variety of factors may be of importance in this context: steric and electronic effects, inhibited Jahn-Teller inversion, and specific interactions between the ligands already bound and the incoming ligand. In this paper we report on the kinetics of the consecutive binding of 2,2'-bipyridyl (bpy) and of 1,10-phenanthroline (phen) to Cu(II) to form the corresponding bis and tris complexes, $CuL_{i-1}^{2+} + L \rightleftharpoons CuL_i^{2+}$ (i = 2, 3). The rates of formation of the 1:1 complex species have been previously determined.[10,11]

Table I. Values of log K_{stab} for Complexes of bpy and phen (25 °C; I = 0.5 M)

		log K			
		bpy	ref	phen	ref
$H^+ + L = HL^+$	K_H	4.54	14	5.03	17
$Cu^{2+} + L = CuL^{2+}$	K_1	8.70[a]	10	9.20	17
$CuL^{2+} + L = CuL_2^{2+}$	K_2	5.78	15	6.70	17
		5.70[b]		6.69[b]	
$CuL_2^{2+} + L = CuL_3^{2+}$	K_3	3.25[c]	16	5.20	17

[a] I = 0.3 M. [b] This work; see text. [c] I = 1.0 M.

Experimental Section

Materials. Stock solutions of $CuCl_2$, KCl, bpy, and phen were prepared from "reagent grade" chemicals (Merck) without further purification. In order to solubilize bpy and phen, equivalent amounts of HCl were added. The ligand solutions were kept in the dark to avoid any possible photodecomposition. The pH of the reactant solutions was brought to the desired value (±0.01) by the dropwise addition of 1 M KOH or HCl (Baker Chemicals). The ionic strength (I) was adjusted to 0.5 M by using KCl. The chloride medium was chosen because of the UV absorption of NO_3^- and the solubility problems encountered in the presence of ClO_4^-.

Methods. pH measurements were carried out by means of a Radiometer PHM 52 digital pH meter equipped with a Metrohm EA 125 combined electrode. The calibration procedure for converting pH values to H^+ concentrations was described elsewhere.[4] The kinetics of the complex formation reactions were studied by applying the temperature-jump relaxation technique with spectrophotometric detection.[12] The instrument used was either a conventional apparatus[12] with a lower limit of the accessible time range of 2 μs or a cable T-jump apparatus[13] with

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