Amine-Poly(Hydrogen Fluoride) Solid Complexes: New Studies of Formation, Crystal Structures, and $H_{n-1}F_n^-$ Ion Diversity**

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Dedicated to Professor Gerhard Hägele on the occasion of his 60th birthday

Abstract: After earlier work in this laboratory on phase relations and crystal structures in the quasibinary system of hydrogen fluoride and pyridine, six low-melting adducts with trimethyl- and triethylamine in lieu of pyridine have now been identified and their structures determined at $-150\,^{\circ}$C: $Me_3N \cdot 3HF$ (m.p. $0\,^{\circ}$C, orthorhombic, $Pnma$, $Z=4$), $Et_3N \cdot 3HF$ (m.p. $-27\,^{\circ}$C, orthorhombic, $Pbca$, $Z=8$), $Me_3N \cdot 4HF$ (m.p. $-53\,^{\circ}$C, triclinic, $P\bar{1}$, $Z=4$), $Et_3N \cdot 4HF$ (m.p.

$-87\,^{\circ}$C, monoclinic, $P2_1$, $Z=2$), $Me_3N \cdot 5HF$ (m.p. $-93\,^{\circ}$C (decomp), triclinic, $P\bar{1}$, $Z=2$) and $Me_3N \cdot 7HF$ (m.p. $-88\,^{\circ}$C, hexagonal, $P6_3$, $Z=2$). Structure analysis was also performed on a further pyridine adduct: $Py \cdot 6HF$ (m.p. $-95\,^{\circ}$C (decomp), triclinic, $P\bar{1}$, $Z=2$).

Keywords: fluorine · hydrogen bonds · ion pairs · protonation · solid-state structures

With the base protonated and the hydrogen fluoride content correspondingly deprived of one proton, all structures are ionic. They are described with respect to the $F-H\cdots F$ and $N-H\cdots F$ hydrogen bonding and the various $H_{n-1}F_n^-$ complex ions present. These ions and others of the same kind observed in crystal structures are surveyed with regard to homology (size) and isomerism.

Introduction

Solutions of pyridine and also of small trialkylamines, mainly triethylamine, in a large molar excess of hydrogen fluoride (typically 1:9 and 1:3, respectively) have already been described and are in wide use as convenient reagents for a variety of preparative fluorination reactions.[1] The present study is focused on the binary systems themselves, more precisely on the adducts or complexes that can be crystallized from them on cooling, as a function of composition. In an earlier investigation in this laboratory, as many as eight different low-melting adducts were identified by phase analysis in the hydrogen fluoride and pyridine system, and four of them were characterized by their crystal structures.[2, 3] In the following, these methods are applied to hydrogen

fluoride adducts of trimethylamine and triethylamine,[4] and the structure of another pyridine adduct is also reported.

Results and Discussion

The melting diagram obtained for the system of trimethylamine and hydrogen fluoride (Figure 1) proves the existence of four solid adducts $Me_3N \cdot nHF$ ($n = 3, 4, 5$, and 7) with melting points at $0, -53, -93$, and $-88\,^{\circ}$C, respectively. (A phase transition at $-104\,^{\circ}$C of the adduct $n = 5$ was indicated by the difference thermal analysis (DTA), but was not confirmed by the X-ray powder work.) Phase analysis in the
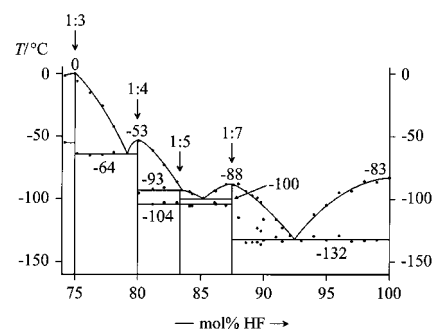
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Figure 1. Melting diagram of the system Me_3N/HF in the range 75–100 mol% HF, with measuring points obtained by DTA.

Table 1. Summary of crystallographic data and some numbers related to the structure determinations.

	$Me_3N \cdot 3HF$	$Et_3N \cdot 3HF$	$Me_3N \cdot 4HF$	$Et_3N \cdot 4HF$	$Me_3N \cdot 5HF$	$Py \cdot 6HF$	$Me_3N \cdot 7HF$
m.p. [°C]	0	− 27	− 53	− 87	− 93 (decomp)	− 95 (decomp)	− 88
T [°C]	−150	−150	−150	−150	−150	−150	−150
crystal system	orthorhombic	orthorhombic	triclinic	monoclinic	triclinic	triclinic	hexagonal
space group; Z	$Pnma$; 4	$Pbca$; 8	$P\bar{1}$; 4	$P2_1$; 2	$P\bar{1}$; 2	$P\bar{1}$; 2	$P6_3$; 2
a [Å]	10.479(4)	11.896(7)	7.622(2)	6.182(4)	6.559(4)	7.542(6)	9.951(8)
b [Å]	9.726(4)	12.704(8)	9.321(8)	11.859(7)	6.804(4)	7.568(6)	
c [Å]	6.375(3)	12.950(9)	10.70(1)	6.965(3)	10.002(8)	8.945(6)	5.968(4)
α [°]			102.57(6)		83.23(6)	76.78(6)	
β [°]			92.03(5)	93.18(5)	72.09(5)	67.38(5)	
γ [°]			91.09(5)		88.16(5)	86.24(6)	
V [Å³]	649.7(5)	1957(2)	741(1)	509.8(5)	421.8(5)	458.7(6)	511.8(7)
ρ_{calcd} [g cm⁻³]	1.218	1.094	1.247	1.180	1.253	1.442	1.292
μ Mo$_{K\alpha}$ [mm⁻¹]	0.13	0.10	0.14	0.12	0.15	0.17	0.17
2θ range [°]	$3 \le 2\theta \le 60$	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 55$	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 60$	$3 \le 2\theta \le 60$
unique data: obsd.[a]; all	849; 999	1317; 1766	2163; 2595	1169; 1228	1235; 1476	2284; 2679	436; 545
reflections for refinement	998	1762	2562	1228	1471	2665	539
variables in last cycle	63	154	249	176	138	153	57
weighting:[b] m; n	0.059; 0.067	0.116; 3.956	0.174; 0.850	0.063; 0.030	0.086; 0.339	0.065; 0.129	0.039; 0.082
R(F) (obsd.); $wR(F^2)$	0.036; 0.100	0.082; 0.251	0.077; 0.291	0.032; 0.089	0.060; 0.185	0.043; 0.126	0.039; 0.105
$\Delta\rho$: min.; max. [e Å⁻³]	− 0.16; +0.48	− 0.29; +0.95	− 0.33; +0.65	− 0.20; +0.22	− 0.31; +0.59	− 0.31; +0.28	− 0.23; +0.14

[a] $|F_o| > 4\sigma_F$. [b] $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$ with $P = (F_o^2 + 2F_c^2)/3$

system with triethylamine was severely hampered by vitrification, and only two crystalline adducts $Et_3N \cdot nHF$ ($n = 3$ and 4), with melting points at − 27 and − 87 °C, could be found.

Single crystals were obtained for all these adducts and for the pyridine adduct $Py \cdot 6HF$, which melts incongruently at − 95 °C,[2] and their structures were determined. The crystallographic data are listed in Table 1 in the order of increasing molar HF content. With the base protonated and the hydrogen fluoride content deprotonated, all the adducts were found to be ionic. Strong hydrogen bonds F−H···F are effective within the $H_{n-1}F_n^-$ ions and weaker N−H···F between these and the NH⁺ ions.

Abstract in German: *Nach einer früheren Arbeit in diesem Institut über Phasenbeziehungen und Kristallstrukturen im quasibinären System von Fluorwasserstoff und Pyridin wurden nun sechs tiefschmelzende Addukte mit Trimethyl- und Triethylamin an Stelle von Pyridin identifiziert und ihre Strukturen bei −150 °C bestimmt: $Me_3N \cdot 3HF$ (Schmp. 0 °C, orthorhombisch, Pnma, Z = 4), $Et_3N \cdot 3HF$ (Schmp. −27 °C, orthorhombisch, Pbca, Z = 8), $Me_3N \cdot 4HF$ (Schmp. −53 °C, triklin, P$\bar{1}$, Z = 4), $Et_3N \cdot 4HF$ (Schmp. −87 °C, monoklin, P2_1, Z = 2), $Me_3N \cdot 5HF$ (Schmp. −93 °C (Zers.), triklin, P$\bar{1}$, Z = 2) und $Me_3N \cdot 7HF$ (Schmp. −88 °C, hexagonal, P6_3, Z = 2). Auch an einem weiteren Pyridinaddukt wurde eine Strukturanalyse durchgeführt: $Py \cdot 6HF$ (Schmp. −95 °C (Zers.), triklin, P$\bar{1}$, Z = 2). Da die Base protoniert und der Fluorwasserstoffanteil entsprechend deprotoniert ist, liegen ausschließlich ionische Strukturen vor. Ihre Beschreibung erfolgt anhand der auftretenden Wasserstoffbrücken F−H···F sowie N−H···F sowie komplexen Anionen $H_{n-1}F_n^-$. Letztere und solche aus weiteren Kristallstrukturen werden nach Homologie (Größe) und Isomerie geordnet in einem Überblick zusammengestellt.*

In the following, the structures will be dealt with in three groups, $n = 3$ (two complexes), $n = 4$ (two complexes), and $n = 5 - 7$ (three complexes). Drawings with 25% ellipsoids for the non-hydrogen atoms and geometric data for the hydrogen bonds are in Figures 2 – 4 and Tables 2 – 4, respectively. The hydrogen atom positions are not corrected for the systematic error of the X-ray method. To emphasize the complex anions in the drawings, ellipsoid equatorial lines are shown only for the F atoms and atomic labeling is omitted in the whole C−H range.

In $Me_3N \cdot 3HF$ and $Et_3N \cdot 3HF$, the N−H···F hydrogen bond is donated to the central fluoride of an $H_2F_3^-$ or $[F(HF)_2]^-$ ion and binds this and the cation in a discrete ion pair (Figure 2 and Table 2). For the Me_3N complex, the pair is located on the mirror plane of the space group.

In the structures of the two remaining groups, the hydrogen bonding between the cations and larger anions involves only terminal F atoms of the latter. At the same time, the hydrogen bonds are not of the unidirectional type, but bi- or trifurcated instead. This leads to higher connectivities than those of ion pairs.

In $Me_3N \cdot 4HF$ and $Et_3N \cdot 4HF$, the anions $H_3F_4^-$ are virtually planar and in the branched-chain form $[F(HF)_3]^-$.
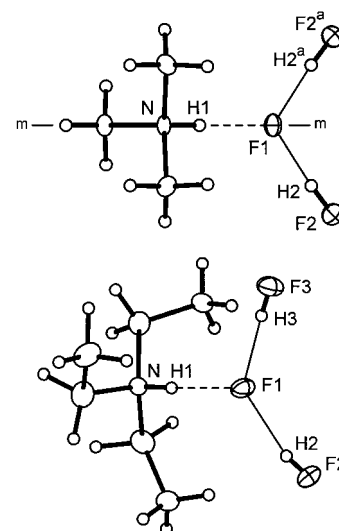

Figure 2. The ion pairs in the crystal structures of $Me_3N \cdot 3HF$ (top, on the mirror plane of the space group) and $Et_3N \cdot 3HF$ (bottom). Symmetry code as in Table 2.

Table 2. Me$_3$N · 3HF and Et$_3$N · 3HF: Selected interatomic distances [Å] and angles [°].

Me$_3$N · 3HF				
H bonds:	d(D···A)	d(D–H)	d(H···A)	angles at H
F2–H2···F1	2.371(1)	0.80(2)	1.57(2)	174(2)
N–H1···F1	2.669(1)	0.88(2)	1.79(2)	179(2)
angles at F1:				
F2···F1···F2[a]	97.9(1)			
F2···F1···N	130.8(1)			
Et$_3$N · 3HF				
H bonds:	d(D···A)	d(D–H)	d(H···A)	angles at H
F2–H2···F1	2.351(4)	0.65(6)	1.71(6)	166(6)
F3–H3···F1	2.351(4)	0.70(6)	1.65(6)	176(6)
N–H1···F1	2.687(4)	0.83(4)	1.86(4)	175(4)
angles at F1:				
F2···F1···F3	119.7(1)			
F2···F1···N	126.7(1)			
F3···F1···N	113.6(1)			

[a] $x, -y+1/2, z$.

Table 3. Me$_3$N · 4HF and Et$_3$N · 4HF: Selected interatomic distances [Å] and angles [°].

Me$_3$N · 4HF				
H bonds:	d(D···A)	d(D–H)	d(H···A)	angles at H
F2–H2···F1	2.368(4)	0.84(7)	1.53(7)	175(7)
F3–H3···F1	2.370(3)	0.93(5)	1.47(5)	163(5)
F4–H4···F1	2.373(3)	0.91(6)	1.47(6)	173(5)
F6–H6···F5	2.392(4)	0.82(7)	1.58(7)	175(7)
F7–H7···F5	2.373(4)	0.80(7)	1.58(8)	173(7)
F8–H8···F5	2.386(4)	0.9(1)	1.5(1)	174(10)
N1–H1···F2	2.812(5)	0.89(5)	2.22(5)	124(4)
N1–H1···F3[a]	2.921(5)	0.89(5)	2.29(5)	128(4)
N1–H1···F4[b]	2.984(4)	0.89(5)	2.41(5)	123(3)
N2–H5···F6	2.910(5)	0.88(4)	2.22(4)	135(3)
N2–H5···F3[a]	2.989(4)	0.88(4)	2.38(4)	127(3)
N2–H5···F4[b]	3.123(5)	0.88(4)	2.56(4)	123(3)
angles at F1 and F5:				
F2···F1···F3	106.4(1)			
F2···F1···F4	110.2(1)			
F3···F1···F4	143.2(1)			
F6···F5···F7	103.6(1)			
F6···F5···F8	125.2(2)			
F7···F5···F8	130.2(2)			
Et$_3$N · 4HF				
H bonds:	d(D···A)	d(D–H)	d(H···A)	angles at H
F2–H2···F1	2.365(2)	0.87(4)	1.50(4)	175(3)
F3–H3···F1	2.366(2)	0.77(4)	1.62(4)	167(4)
F4–H4···F1	2.406(2)	0.77(4)	1.64(5)	174(4)
N–H1···F2	2.893(2)	0.89(3)	2.10(3)	148(2)
N–H1···F3[c]	2.951(3)	0.89(3)	2.36(3)	124(2)
angles at F1:				
F2···F1···F3	122.6(1)			
F2···F1···F4	113.6(1)			
F3···F1···F4	113.4(1)			

[a] $-x, -y+1, -z$. [b] $-x+1, -y+1, -z$. [c] $x-1, y, z$.

With two independent cations and anions each in general positions, the structure of the Me$_3$N complex is the most complicated of this study. The cations each donate three hydrogen bonds, that is, of the type N–H($\cdots$F)$_3$, to terminal F atoms of three anions. For one set of cations and anions, this produces a one-dimensional (1D) double chain or ribbon (Figure 3, the remaining ions are omitted for clarity, but see Table 3). In the Et$_3$N complex, the ions form a 1D single chain through bifurcated N–H($\cdots$F)$_2$ bonds (see also Figure 3 and Table 3). The results for the Me$_3$N complex confirm the melting point and particular isomer assignment of the anion
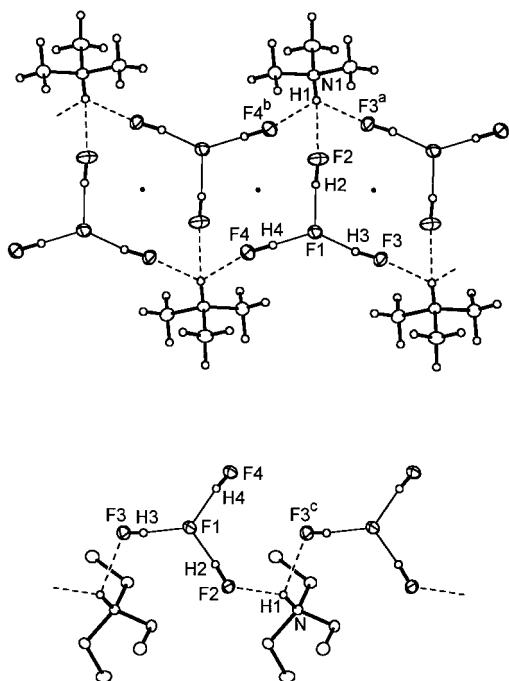
from a low-temperature IR study,[5] but disprove the proposal of an ion pair with a straight N–H$\cdots$F hydrogen bond to the central fluoride.

In the complexes with $n = 5–7$ (Figure 4 and Table 4), the H$_{n-1}$F$_n^-$ anions are either new isomers (Me$_3$N · 5HF and Py · 6HF) that are the same size as some of those observed previously in other crystal structures (see below), or of a new size (Me$_3$N · 7HF). With one inner hydrogen bond particularly short (F$\cdots$F distance 2.273 Å) and virtually centered, the H$_4$F$_5^-$ ion of Me$_3$N · 5HF contains a specific FHF$^-$ subunit at its core so that the formula can be written as [(FH)(FHF)(HF)$_2$]$^-$. The remaining anions ($n = 6$ and 7) have the structures [(FH)F{(HF)(HF)}$_2$]$^-$ and [F{(HF)(HF)}$_3$]$^-$, respectively. These can be derived from the [F(HF)$_3$]$^-$ type above, by attaching—at noticeably larger F$\cdots$F distances—an additional HF molecule each to two or three of its terminal F atoms.

The hydrogen bonding between the cations and anions in each complex of this group is trifurcated, leading to a 1D ribbon in Me$_3$N · 5HF, a dimer of the formula unit around an inversion center of the space group in Py · 6HF, and a 2D layer in Me$_3$N · 7HF. In the last complex, the cation is located on the genuine threefold rotation axis and the anion on the 6$_3$ screw axis (also point symmetry 3) of the space group. In this way, the conspicuous cyclic gap in the hydrogen-bonded layer is filled by the cation that sticks out from one of the next

Figure 3. The 1D connectivities, each parallel to [100], in the crystal structures of Me$_3$N · 4HF (top; with inversion centers of the space group) and Et$_3$N · 4HF (bottom). For the Me$_3$N compound, only one of its two independent kinds of cations and anions is shown. Alkyl H atoms are omitted for clarity in the Et$_3$N compound. Symmetry codes as in Table 3.
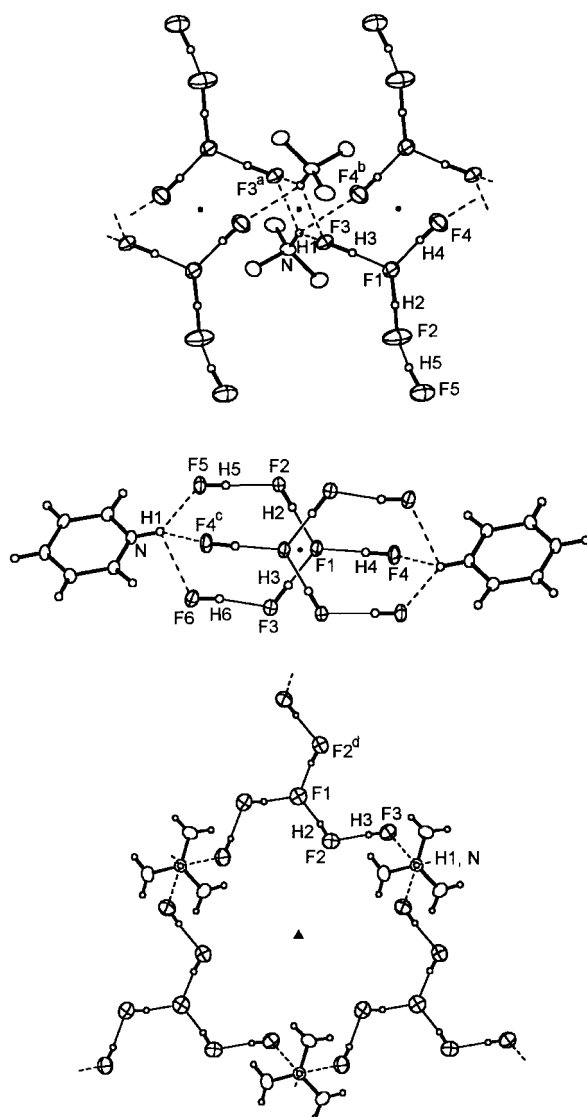
Figure 4. The 1D ribbon (top; along [100]; alkyl H atoms omitted), cyclic dimer of the formula unit (center) and 2D layer (bottom; parallel to (001)) in the crystal structures of Me₃N·5HF, Py·6HF, and Me₃N·7HF, respectively. Symmetry codes as in Table 4.

layers along the polar *c*-axis direction, while the anions of subsequent layers are arranged with their central fluorides on top of each other.

Besides the hydrogen bonds F–H···F and N–H···F considered in the structures so far, much weaker ones of the unconventional type C–H···F can also be recognized. This holds particularly when a terminal F atom of an anion is not approached by an N–H hydrogen-bond donor function of a cation. Thus, H···F and overall C···F distances to such F atoms have lower limits as small as 2.31 and 3.21 Å, respectively, and the angles at the H atoms involved go up to 163°. However, with the numerous C–H functions and F atoms (also of other types) present, larger distances follow more or less continuously, and discrimination between still significant C–H···F hydrogen bonding and mere packing contacts gets rather speculative very quickly, regardless of the pertinent angles.

Table 4. Me₃N·5HF, Py·6HF and Me₃N·7HF: Selected interatomic distances [Å] and angles [°].

	d(D···A)	d(D–H)	d(H···A)	angles at H
Me₃N·5HF				
H bonds:				
F2–H2···F1	2.273(4)	1.13(9)	1.16(9)	168(8)
F3–H3···F1	2.367(3)	0.98(4)	1.40(4)	174(4)
F4–H4···F1	2.410(3)	0.88(7)	1.54(7)	170(6)
F5–H5···F2	2.424(4)	1.07(7)	1.37(7)	169(6)
N–H1···F3	2.890(3)	0.84(3)	2.27(3)	131(2)
N–H1···F3[a]	2.933(4)	0.84(3)	2.31(3)	132(2)
N–H1···F4[b]	2.950(4)	0.84(3)	2.41(3)	123(2)
angles at F1 and F2:				
F2···F1···F3	116.3(1)			
F2···F1···F4	130.7(1)			
F3···F1···F4	111.8(1)			
F1···F2···F5	130.3(1)			
Py·6HF				
H bonds:	d(D···A)	d(D–H)	d(H···A)	angles at H
F2–H2···F1	2.337(2)	0.83(3)	1.51(3)	178(3)
F3–H3···F1	2.357(2)	0.89(3)	1.47(3)	175(2)
F4–H4···F1	2.419(2)	0.89(3)	1.53(3)	175(3)
F5–H5···F2	2.470(2)	0.80(3)	1.67(3)	175(3)
F6–H6···F3	2.497(2)	0.86(3)	1.64(3)	171(3)
N–H1···F4[c]	2.820(2)	0.92(2)	2.11(2)	134(2)
N–H1···F5	2.865(3)	0.92(2)	2.20(2)	129(2)
N–H1···F6	2.929(3)	0.92(2)	2.63(2)	100(1)
angles at F1, F2 and F3:				
F2···F1···F3	112.5(1)			
F2···F1···F4	123.8(1)			
F3···F1···F4	123.5(1)			
F1···F2···F5	118.0(1)			
F1···F3···F6	118.5(1)			
Me₃N·7HF				
H bonds:	d(D···A)	d(D–H)	d(H···A)	angles at H
F2–H2···F1	2.322(3)	0.84(5)	1.49(5)	173(6)
F3–H3···F2	2.466(3)	0.84(4)	1.63(4)	174(5)
N–H1···F3	2.944(4)	0.93(6)	2.28(4)	128(1)
angles at F1 and F2:				
F2···F1···F2[d]	119.3(1)			
F1···F2···F3	117.9(1)			

[a] −x+1, −y+1, −z+1. [b] −x, −y+1, −z+1. [c] −x, −y+1, −z. [d] −y, x−y, z.

In Table 5, the poly(hydrogen fluoride) anions of this study are brought together for an overview along with those reported for other crystal structures, most of which have been determined in this laboratory.

Experiments and Calculations

Table 5. Compounds characterized by crystal structure analysis (#: this work) that contain $H_{n-1}F_n^-$ ions with $n \geq 3$. Isomeric forms are listed separately side by side.

$n = 3$:	**[F(HF)$_2$]**$^-$
	$KF \cdot 2 HF^{[6]}$, $KF \cdot 2.5 HF^{[7]}$, $Me_4NF \cdot 2 HF^{[8]}$
	$[(C_{10}H_{12}Se_4)_2]F \cdot 2 HF^{[9]}$
	$Me_3N \cdot 3 HF^{[\#]}$, $Et_3N \cdot 3 HF^{[\#]}$, $Py \cdot 3 HF^{[2]}$

$n = 4$:	**[F(HF)$_3$]**$^-$ **[(FH)F(HF)(HF)]**$^-$
	$KF \cdot 3 HF^{[7]}$, $NOF \cdot 3 HF^{[10]}$ $KF \cdot 2.5 HF^{[7]}$
	$Me_4NF \cdot 3 HF^{[8]}$ $H_2O \cdot 4 HF^{[14]}$
	$3 IF_5 \cdot CsF \cdot 3 HF^{[11]}$
	$K_3BiCl_6 \cdot 2 KCl \cdot KF \cdot 3 HF^{[12]}$
	$NH_3 \cdot 4 HF^{[13]}$, $Me_3N \cdot 4 HF^{[\#]}$
	$Et_3N \cdot 4 HF^{[\#]}$, $Py \cdot 4 HF^{[2]}$

$n = 5$:	**[F(HF)$_4$]**$^-$ **[(FH)(FHF)(HF)$_2$]**$^-$
	$KF \cdot 4 HF^{[15]}$, $NOF \cdot 4 HF^{[10]}$ $Me_3N \cdot 5 HF^{[\#]}$
	$NH_3 \cdot 5 HF^{[13]}$

$n = 6$:	**[(FH)$_2$(FHF)(HF)$_2$]**$^-$ **[(FH)F{(HF)(HF)}$_2$]**$^-$
	$Me_4NF \cdot 5 HF^{[8]}$ $Py \cdot 6 HF^{[\#]}$

$n = 7$:	**[F{(HF)(HF)}$_3$]**$^-$
	$Me_3N \cdot 7 HF^{[\#]}$

$n = 8$:	**[(FH)(FH)(FH)F{(HF)(HF)}$_2$]**$^-$
	$NH_3 \cdot 8 HF^{[13]}$

melting the polymer), which in turn were placed in thin-walled glass capillaries for mechanical fixation. Single crystals for the structure determinations were grown in situ on a four-circle diffractometer (Siemens AED2) equipped with an adjustable cold nitrogen gas stream and employed also for the subsequent X-ray measurements. A miniature zone-melting technique with focused heat radiation[16] was applied, for samples prepared in the same way as for the X-ray powder studies. Crystallographic data were obtained as usual and reflection data collected at $-150\,°C$ with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a variable Ω/θ scan. Corrections for absorption were not considered necessary. The structures were solved by direct methods and refined on F^2 with all independent reflections ($F^2 > -3\sigma_{F^2}$). The H atoms were located in difference electron-density maps and, except for three in the structure of $Et_3N \cdot 3 HF$, were freely refined. For structure solution and drawing, the program system SHELXTL PLUS[17] was used on a VAX-Station 3200 (Digital), and for refinement SHELXL-93[18] on a PC. Some experimental and computational details of the structure determinations are included in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100 977. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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