Acknowledgment. The financial support of the MPI and CNR, Rome, is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

Registry No. 1a, 103835-81-0; **1b**, 103835-83-2; **1c**, 103835-85-4; **2a**, 103835-87-6; **2b**, 103835-89-8; **2c**, 103835-91-2; **2d**, 103835-93-4; **3a**, 103835-95-6; **3b**, 103835-97-8; **3c**, 103835-99-0; $FeH_2\{P(OEt)_3\}_4$, 34503-40-7.

Supplementary Material Available: Tables of thermal parameters and a full list of bond lengths, bond angles, and torsion angles for **1a** and **3a** (18 pages); tables of structure factors (32 pages). Ordering information is given on any current masthead page.

Fluorides and Fluoro Acids. 12.[1] Complex–Anion Homology and Isomerism in the Crystal Structures of Two Potassium Poly(hydrogen fluorides), KF·2.5HF and KF·3HF[2]

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Abstract: The compounds KF·2.5HF and KF·3HF were prepared as single crystals and characterized by structure analysis from Mo Kα diffractometer data measured at −100 °C. The structures found are those of poly(hdyrogen fluorides) with anions $H_nF_{n+1}^-$ of three types, formed by strong F–H···F hydrogen bonds. The structural formula of KF·2.5HF (monoclinic, space group $P2_1/a$, Z = 8 formula units per unit cell) is $K_2[H_2F_3][H_3F_4]$ with two different, homologous anions. An isomeric $H_3F_4^-$ anion is present in the structure of KF·3HF or KH_3F_4 (rhombohedral, $R\bar{3}c$, Z = 6 with hexagonal axes). Evidence for the subsolidus existence below −100 °C of a new, dimorphic compound of the system KF–HF with a very high HF content (KF·7HF?) was obtained by difference thermal analysis.

The system potassium fluoride–hydrogen fluoride is of practical importance for the electrolytic production of elemental fluorine. Its melting diagram[3] shows the existence of five intermediary compounds KF·xHF with x = 1, 2, 2.5, 3, and 4. Those with x = 1, 2, and 4 have been subjected to crystal structure analysis and characterized as complex acid fluorides KHF_2: α[4] and β[5], KH_2F_3[2,6] and KH_4F_5,[7] respectively. The present paper deals with the crystal and in particular the anionic structures of the remaining compounds, KF·2.5HF and KF·3HF.

Experimental and Calculations

The solid phases in the system potassium fluoride–hydrogen fluoride in the region 60–100 mol % HF and their melting behavior were checked by difference thermal analysis with apparatus and techniques as described and referred to elsewhere.[8] The samples were prepared by combining in PTFE vessels and ampules weighed amounts of potassium hydrogen difluoride of controlled purity and hydrogen fluoride distilled from 70–75% technical grade hdyrofluoric acid.

For crystal growth of KF·2.5HF and KF·3HF, molten samples of 72 and 78 mol % HF, respectively, were introduced into polyethylene tubings (ca. 10 mm long, 0.3 mm diameter), which then were sealed at both ends by melting the polymer and fixed in thin-walled glass capillaries. In a temperature-controlled gas stream, single crystals were obtained by simple cooling or miniature zone melting using focused heat radition from a halogen lamp.[9] The crystal symmetry, unit cell dimensions, and reflection intensities were determined on a Syntex $P2_1$ diffractometer (Mo Kα radiation, graphite monochromator, ω scan). The instrument was equipped with a modified LT-1 low-temperature attachment, and all measurements were carried out at −100 °C.

Table I. Crystallographic Data and Some Numbers Related to the Crystal Structure Determinations

	KF·2.5HF	KF·3HF
mp,[a] °C	64.3	65.8
measuring temp, °C	−100	−100
crystal system	monoclinic	trigonal
space group; Z	$P2_1/a$; 8	$R\bar{3}c$; 6
lattice const		
a, pm	831.5 (6)	745.8 (4)
b, pm	838.4 (5)	
c, pm	1003.1 (7)	1181.8 (6)
β, deg	101.63 (5)	
calcd density, g/cm^3	2.10	2.07
θ scan range, deg	1.5–30	1.5–30
unique data: obsd;[b] all	1850; 1998	188; 189
parameters refined[c]	102	12
c in weighting scheme[d]	0.0004	0.0
R: obsd; all	0.035; 0.041	0.011; 0.011
R_w: obsd; all	0.065; 0.067	0.015; 0.015

[a] See ref 3. [b] $|F_o| \geq 3.92\sigma_F$. [c] Minimizing $\sum w(|F_o| - |F_c|)^2$. [d] $w = 1/(\sigma_F^2 + c|F_o|^2)$.

Crystals of KF·2.5HF were invariably twinned as indicatd by pseudoorthorhombic symmetry with nonconventional space group extinctions. The twin law (twin plane (001), $a \simeq -4c \cos \beta$) and true symmetry (monoclinic) could be recognized and were used to collect an appropriate data set of a twin specimen (twin ratio 6.8:1 as determined from noncoinciding reflections) and to reduce it to that of a single crystal for the subsequent structure analysis.

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Table II. Atomic Parameters with Standard Deviations in Parentheses

	x	y	z	B^a
		KF·2.5HF		
K(1)	0.000 15 (5)	0.249 30 (4)	0.500 50 (4)	1.17 (1)
K(2)	0.637 11 (5)	0.273 82 (6)	0.038 69 (4)	1.76 (1)
F(1)	0.215 0 (2)	0.871 2 (2)	0.353 0 (1)	1.65 (3)
F(2)	0.155 5 (2)	0.754 4 (2)	0.135 5 (1)	2.26 (3)
F(3)	0.210 7 (2)	1.147 7 (2)	0.337 8 (1)	1.95 (3)
F(4)	0.351 4 (2)	0.501 9 (1)	0.351 1 (1)	1.59 (3)
F(5)	0.077 6 (2)	0.502 5 (1)	0.352 9 (1)	1.64 (3)
F(6)	−0.078 2 (2)	0.451 9 (2)	0.123 3 (1)	2.68 (4)
F(7)	0.390 7 (2)	0.449 9 (2)	0.124 4 (1)	2.09 (3)
H(2)	0.179 (7)	0.803 (7)	0.197 (6)	7 (1)
H(3)	0.215 (6)	1.034 (6)	0.345 (5)	5 (1)
H(45)	0.209 (7)	0.499 (6)	0.360 (5)	6 (1)
H(6)	−0.040 (7)	0.474 (6)	0.210 (5)	6 (1)
H(7)	0.387 (5)	0.475 (4)	0.192 (4)	2.7 (7)
		KF·3HF		
K	0.0	0.0	0.0	1.33 (1)
F(1)	0.0	0.0	0.25	1.76 (2)
F(2)	0.321 95 (6)	0.0	0.25	1.93 (1)
H	0.218 (2)	0.0	0.25	4.6 (3)

[a] The isotropic thermal parameters of the K and F atoms were derived from the anisotropic B_{ij} values by $B = {}^1/_3(B_{11}a^2a^{*2} + B_{23}bcb^*c^* \cos\alpha + ...)$.

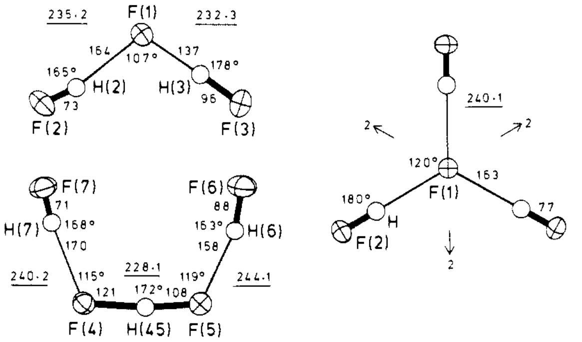

Figure 1. Structures of the $H_nF_{n+1}^-$ anions. The ellipsoids represent 50% probability; the isotropic B values of the H atoms were uniformly reduced to 10^4 pm^2. Interatomic distances (pm), underlined for F···F, and angles (deg). Left: homologous anions $H_2F_3^-$ and $H_3F_4^-$ of KF·2.5HF; esd's for F···F, 0.2 pm; all others, 4–6 pm and 3–7°. Right: isomeric $H_3F_4^-$ anion of KF·3HF; esd's for F···F, 0.04 pm; all others, 2 pm and 0.0°.

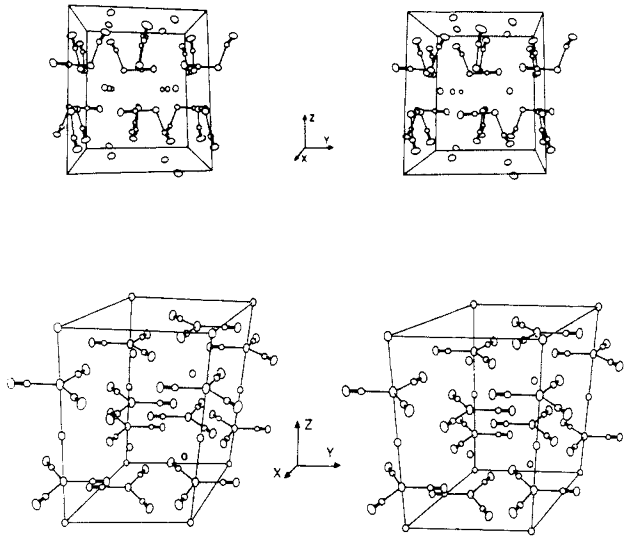

Figure 2. Stereoscopic views of the crystal structures with unit cells. Top: KF·2.5HF. Bottom: KF·3HF.

The structure of KF·2.5HF was solved by direct methods. For KF·3HF use could be made of the closely related structures of $NH_4F·3HF$[10] and NOF·3HF.[11] The structures were refined by the method of least squares. All H atoms were located in difference Fourier maps and included in the refinement. The calculations were performed on an Eclipse S/200 Data General computer with the program system Syntex E-XTL. For the drawings the program ORTEP II[12] was used on a TR 445 Telefunken computer.

Results

The determination of liquidus and eutectic lines above 55 °C was less accurate than in the earlier study of the melting diagram[3] but did not yield contradictory results. Additional thermal effects at −115 and −100 °C could be interpreted as the solid–solid-phase transition and decomposition to the neighboring solids (KF·4HF and HF), respectively, of a further compound of the system with more than 80 mol % HF. By analogy to the related systems NH_4F–HF,[10] NOF–HF,[11] and RbF–HF,[13] a possible composition of the new compound, which could not be determined unambiguously from the thermal analysis, is KF·7HF.

Basic crystallographic data for KF·2.5HF and KF·3HF and some numbers related to the structure determinations are given in Table I, the atomic parameters in Table II. The structures are those of poly(hydrogen fluorides) with complex anions $H_nF_{n+1}^-$ formed by strong F–H···F hydrogen bonds. They thus generally fit into the series of the other compounds of the system. The particular anions present are depicted in Figure 1. The distances are not corrected for thermal motion and the systematic shortening of F–H (and lengthening of H···F) by the X-ray method. Stereoscopic drawings of the crystal structures are shown in Figure 2.

Discussion

The compound KF·2.5HF can be reformulated as $K_2[H_2F_3][H_3F_4]$, presenting a case of two different, *homologous* complex $H_nF_{n+1}^-$ anions in the same crystal structure. The $H_2F_3^-$ anion is of the type established for the first time[6] in the crystal structure of KF·2HF, although that X-ray study as well as a more accurate repetition[2] both failed in locating the H atoms. Recently further $H_2F_3^-$ anions were fully characterized in the crystal structures of $(CH_3)_4NF·2HF$[8] and pyridine·3HF.[14] With the H atoms consistently closer to the two terminal F atoms than to the central one, the appropriate structural formula of these anions is $[F(HF)_2]^-$.

From similar reasoning the other anion, $H_3F_4^-$, in the crystal structure of KF·2.5HF can be formulated as $[(FH)FHF(HF)]^-$; i.e., two HF molecules are hydrogen bonding to one F atom each of a central HF_2^- ion. The geometry of the latter, with the H atom not significantly displaced from the center of a particularly short F···F distance, appears comparable to that of the HF_2^- ion in α-KHF_2.[4] The two terminal hydrogen bonds are much longer than the central one and oriented *cis* to each other (dihedral angle FFFF 0.2°). The only other unbranched-chain $H_3F_4^-$ anion, establishhd so far by crystal structure analysis, is that with a different conformation and pattern of interatomic distances in $H_2O·4HF$.[15]

A branched-chain, i.e., *isomeric*, $H_3F_4^-$ anion of probably similar stability is present in the crystal structure of KF·3HF or KH_3F_4, as has been inferred already from the low-temperature IR spectrum.[16] The anion with the structure $[F(HF)_3]^-$ occupies a special position with the trigonal point symmetry 32 (D_3) and appears to be genuinely planar (i.e., no out-of-plane disorder of the central F atom), as opposed to the flat-pyramidal anions of this type in the crystal structures of $NH_4F·3HF$,[10] NOF·3HF,[11] $(CH_3)_4NF·3HF$,[8] and pyridine·4HF.[14]

The coordination of the cations is square antiprismatic in KF·2.5HF, with an additional F atom above a square face of one

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of the two independent polyhedra, and cube-like in KF·3HF, with K···F contact distances in the range 269.9–313.7 pm.

A compilation of the (averaged) hydrogen-bonding F···F distances (in pm) in all the intermediary compounds of the system KF–HF now studied is as follows: α-KHF_2, 227.7, see ref 4; KH_2F_3, 233.1, average, see ref 2 (and ref 6); $K_2[H_2F_3][H_3F_4]$, 236.0, average, this work; KH_3F_4, 240.1, this work; KH_4F_5, 245.3, see ref 7. The increase with increasing HF content, i.e., with increasing (average) size of the hydrogen-bonded structural unit, is unmistakable. The upper limit of the series is obviously given by the F···F distance in the infinite chain of the pure HF solid, which was recently refined[17] from 249 (1) pm at −125 °C[18] to 250.0 (1) pm at −146 °C. Similar trends, though with less data for any single system, can be seen in the other complex acid fluoride structures referred to above and in some more dealt with in the same references. The correlation is analogous to that known for oxonium cations $[H_3O(H_2O)_n]^+$ in crystalline hydrates of strong acids.[19]

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Registry No. $K_2[H_2F_3][H_3F_4]$, 104090-15-5; KH_3F_4, 104090-16-6.

Supplementary Material Available: Listing of anisotropic thermal parameters of the K and F atoms (1 page); tables of calculated and observed structure factors (5 pages). Ordering information is given on any currrent masthead page.

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Substituent Effects in [3,3]-Sigmatropic Rearrangements. Alkyl Group Effects and Transition-State "Syn-Diaxial" Interactions

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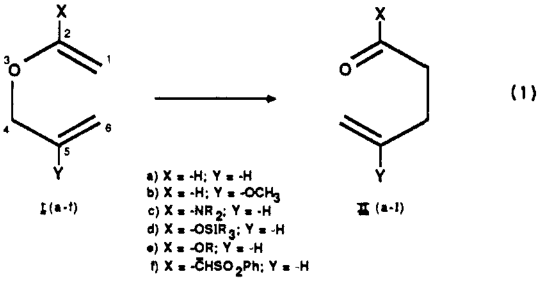
Abstract: Rearrangement rates for nineteen *O*-allyl silylketene acetals {[(1-(allyloxy)-1-ethenyl)oxy]trialkylsilanes} are reported. Whereas rates for rearrangement of **1** and **2** exhibit a linear free energy relationship, no linear free energy relationship is observed between rates for **1** and **3**. These data suggest the possibility of "syn-diaxial" interactions in a chair-like transition state for rearrangements of **3**. The difference in free energy between **2** and **3** is found to be 1.34 kcal/mol and is independent of R. The magnitude of the diaxial interaction ($\Delta\Delta G_{Z^\ddagger/E^\ddagger}$, the difference in free energy between transition states reached from **2** or **3**) was determined to range from 1.2 to 2.5 kcal/mol and is dependent on the nature of R. Finally, comparison of the effect of a (trimethylsilyl)methyl substituent (R = $CH_2Si(CH_3)_3$) with the effects of comparably sized alkyl groups suggests that this C-5 substituent has a rate-decelerating electronic influence on the rearrangement of these acetals. Steric effects in these rearrangements are compared with steric effects in comparably substituted tetrahydropyran derivatives and significant differences are noted.

The aliphatic Claisen rearrangement is a versatile method of carbon–carbon bond formation that is frequently employed in the synthesis of complex molecules of health-related significance.[1] Many variations of this reaction have been devised (eq 1), and the synthetic utility of each of these processes is widely recognized.[2]



Current interest in rearrangements of this type has been stimulated by the remarkably wide range of rates observed within this general family of related reactions. The magnitude of possible substituent effects is dramatically illustrated by the fact that the diene Id rearranges with an apparent first-order rate constant at 35 °C which is 10^6 times greater than that found for the rearrangement of Ib.[3]

Reliable explanations for the effects of substituents on the rates of aliphatic Claisen rearrangements must be founded upon accurate quantitative data. A number of research groups are now

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