The Structure of Potassium Tetrahydrogen Pentafluoride

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The compound KF·4HF, prepared by the addition of anhydrous hydrofluoric acid to potassium fluoride, is shown, on the basis of an X-ray structure determination, to be potassium tetrahydrogen pentafluoride, $K[H_4F_5]$. The material crystallizes with four formula units in the tetragonal space group C_{4h}^6–$I4_1/a$ in a cell of dimensions $a = 6.384(3)$, $c = 13.227(7)$ Å. The conventional R factor for the 221 intensities observed above background is 6.2%. The structure is of the scheelite type, with the potassium and the central fluorine atoms residing at special positions of symmetry $\bar{4}$, and the other fluorine atoms hydrogen bonded to the central fluorine atom at an F–H $\cdots$ F distance of 2.453(2) Å. The resultant $H_4F_5^-$ ion, which is crystallographically required to possess $\bar{4}$ symmetry, exhibits a slight but significant distortion from tetrahedral geometry. The F–H $\cdots$ F bond is approximately linear and is unsymmetric with the hydrogen closer to the peripheral fluorine. The fluorine atoms in the immediate environment of the potassium atom form a dodecahedron with triangular faces.

Introduction

Because the three small, strongly electronegative elements fluorine, oxygen, and nitrogen form the strongest hydrogen bonds, their hydrides have been extensively studied by a variety of techniques with a view toward increasing our understanding of the nature of the hydrogen bond (*1*), (*2*). Nevertheless, of the potentially interesting systems of the type MF·*n*HF, where M is either NH_4 or an alkali-metal, only systems with $n = 1$ and $n = 2$ have been characterized structurally. The structures of the compounds MF·HF are well-known, and contain the hydrogen difluoride (bifluoride) anion, HF_2^-, with an F–H $\cdots$ F distance of 2.26–2.28 Å. This HF_2^- anion, on the basis of evidence from diverse experiments, contains a linear, symmetrical F–H–F bond. The compound KF·2HF is known to contain the dihydrogen trifluoride anion, $H_2F_3^-$, with an F–H $\cdots$ F bond length of about 2.33 Å and an average F–F–F bond angle of 135°. Infrared (*3*) and nmr (*4*) evidence suggest that the hydrogen bonds in this anion are unsymmetrical.

Table I summarizes information in the literature concerning melting points of compounds of the type MF·*n*HF. In general the higher members of this series have melting points that are sufficiently high to enable room-temperature diffraction studies to be carried out. This paper reports the preparation of single crystals of the compound KF·4HF, and its characterization, through a three-dimensional X-ray study, as $K[H_4F_5]$.

Experimental

(a) Preparation

A large cylindrical crystal (radius = 1.10 mm, length = 5 mm) of the compound was prepared by placing a dried amount of crystalline potassium fluoride into a piece of "one-eighth inch" (outer diameter = 0.136 in., inner diameter = 0.087 in.) Kel–F (polychlorotrifluoroethylene) tubing about 4 in. long and sealed at one end. The other end was then attached by means of an adapter and a valve to a quarter inch Kel–F vacuum line system (Fig. 1). This system consisted of a cross directly connected to four pieces of quarter-inch Kel–F tubing, *A*, *B*, *C*, and *D*, all about 12 in. long. At the other end of each of these tubes was a valve (*A*, *B*, *C*, or *D*, respectively) all of whose fittings, coming into contact with material enclosed in the system, were also made of Kel–F. The valves *A* and *B* had previously been fitted to mixing tubes *A* and *B* of the type described by Hyman and Katz (*10*), and tube *A* contained very pure liquid hydrogen fluoride, of specific conductivity 7×10^{-6} Ω^{-1} cm^{-1} at 0°C, prepared by distilling the commercially available

TABLE I

The Melting Points in °C of the Compounds[a] MF·nHF

M	0	1	2	2½	3	3½	4	4½	5	6	Ref.
NH₄	Subl.	125.6	30?	–	23	–	–	–	–8.0	–	(5)
Li	842	*	–	–	–	–	–	–	–	–	
Na	988	*	*	–	–	–	–	–	–	–	(6)
K	836	239	72	64	66	–	72	–	–	–	(7)
Rb	775	205	52	–	45	34?	–	23?	–	–	(8)
Cs	682	175	50	–	32	–	–	–	–	–42	(9)

[a] Binary compounds whose existences are not reliably known are quoted "?". Incongruent melting points are denoted by asterisks.

"pure" product in an all Kel–F line (11). Tube B was used as a sink. Valve C led to the tube containing the KF and valve D led to a monel vacuum system fitted with a pressure gauge, two liquid nitrogen traps, and a chemical (soda-lime) trap. All parts of the vacuum system were carefully tested with a helium jet and a leak detector prior to use.

With valves A, B, and C closed and valve D open, the system was evacuated for several minutes to 10^{-3} mm Hg, whereupon valve D was closed. Tube C was then immersed in liquid nitrogen and valves A and C were carefully and partially opened to admit an excess of HF onto the KF in tube C. Both valves were then closed and the liquid nitrogen bath

was removed. Upon slow warming to room temperature, the potassium fluoride completely dissolved. Tube B was then immersed in the cold bath, valves C and B were slightly opened and the excess hydrogen fluoride distilled into the sink B until crystallization just occurred in C. The advantage of using a translucent Kel–F reaction tube instead of the more opaque, but more easily workable, polytetrafluoroethylene is obvious at this stage. Valve C was then closed, valve B was fully opened and most of the residual HF in the line was drawn into the cold sink C. After several minutes, valve C was closed, valve D was opened and the system was taken to a high vacuum. Later, the tube containing the sample was taken from the system, the end containing the sample was inserted in liquid nitrogen and the tube was sealed and broken from the upper parts with warm pliers. The fully sealed tube was about 4 in. long.

It may be noted at this stage that several previous attempts had been made to attach a quarter-inch tube drawn into a capillary and containing a small amount of crystalline KF in order to make a single crystal of the size traditionally suitable for X-ray work, but these had been unsuccessful, since the excess HF tends to stick to the Kel–F walls and thus does not distill off in a smooth way. Also, under these experimental conditions, when a single crystal seemed to be formed, sealing of the capillary with warm pliers forced some residual HF from the walls of the upper tube onto the crystal, which then dissolved. However, the larger tube containing the crystal originally thought ideal for neutron diffraction and unsuited for X-ray work, because of its large size, in fact gave X-ray data which were quite satisfactory.
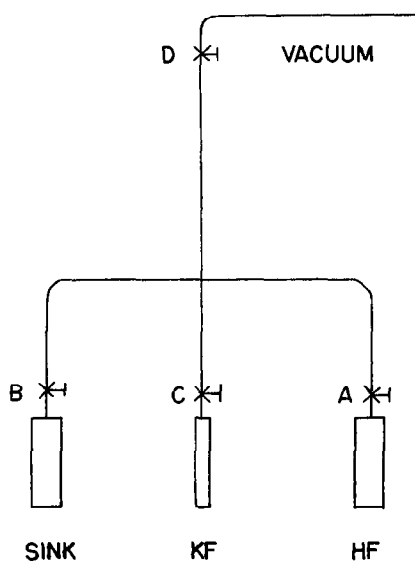

Fig. 1. Diagram of the vacuum line system used in the preparation of K[H₄F₅].

(b) Space Group and Lattice Parameters

The Kel–F tube containing the crystal was attached to a goniometer head by means of Eastman 910 adhesive. Preliminary precession photographs were taken with MoKα radiation. Although the crystal is very large by X-ray standards and the spots on the films were consequently very large, no difficulty was experienced in indexing these photographs.

The crystal was found to exhibit Laue symmetry 4/m on the basis of precession photographs of the $h0l$, $2hhl$, hhl, $h2hl$ and $0kl$ nets. Conditions for reflection on these photographs were: hkl, $h + k + l = 2n$; $hk0$, $h = 2n$; $00l$, $l = 4n$. These conditions for reflection are consistent only with the space group $C_{4h}^6 - I4_1/a$.

The lattice parameters, subsequently found through a least-squares refinement (12) of a dozen high-angle reflections that had been carefully centered at room temperature on a Picker four-circle diffractometer, are $a = 6.384(3)$, $c = 13.227(7)$ Å, based on a wavelength of MoKα₁ of 0.7093 Å.

The densities of KF, KF·HF, KF·2HF, and HF are 2.48, 2.37, 2.06, and 1.66 g/cm³, respectively. Thus, the reasonable density of 1.70 g/cm³ for KF·4HF corresponds to four formula units in the above cell.

(c) Collection and Reduction of the X-ray Intensity Data

The Kel–F tube, containing the single crystal, was remounted using epoxy cement on a eucentric goniometer head on the diffractometer with the cylinder axis parallel to the spindle axis. [The cylinder axis of the crystal is not simply related to any of the crystal axes, and is inclined to the c axis at an angle of about 20°. Consequently, this orientation should not lead to appreciable errors from multiple reflections (13)].

The collection of the X-ray data parallels methods previously described (12). Owing to the large size of the crystal, entrance, and exit collimators of 0.19 and 0.20 cm diameter, respectively, were employed, but even so the beam by no means fully intercepted the crystal. As a result some difficulty was experienced in centering the crystal and in centering reflections through the slit system. Nevertheless, the refinement of the high-angle reflections led to suitably small errors in the cell constants. Because of this difficulty in centering, with the consequent variations among the equivalent intensities at their calculated positions, it was concluded that it was not possible to center the crystal reliably for all reflections, and the centering and

subsequent data collection were restricted to a single octant of reciprocal space. At a takeoff angle of 0.3°, open-counter omega scans exhibited half-widths at half-height of about 0.3° and so the θ–2θ scan technique was employed. Data were collected at a takeoff angle of 1.5°. The scan rate was 1° per minute and the scan range was 2.8° in 2θ, symmetrically disposed with respect to the calculated peak center for MoKα₁ radiation. Background counts were taken for ten seconds at each end of the scan range. The pulse-height analyzer was set to accept about 90% of the MoKα window. The diffracted beams were filtered through 7.6 mils of Zr and were collimated through a receiving aperture 7 × 7 mm which was placed 31 cm from the crystal.

A unique set of data out to a 2θ value of 50° was collected; since the number of variables to be determined was small, no further measurements were made.

The observed intensities were reduced to values of F_0^2 through the application of the usual Lorentz and polarization corrections† and a correction for the variation in the irradiated volume of the crystal as a function of orientation. In the estimation of $\sigma(F_0^2)$ a value of p of 0.03 was employed (12). Of the 243 intensities measured, 221 had $F_0^2 > 3\sigma(F_0^2)$ and these were used in subsequent calculations.

Solution and Refinement of the Structure

In general, reflections of the type $2k + l \equiv 2$ (mod 4) were either weak or absent. This condition strongly suggested that the structure could be described by placing a K atom in the special position (4a) and one fluorine atom, F(1), in the other special four-fold position (4b). (Throughout this paper we use the setting of $I4_1/a$ with the origin at $\bar{1}$.) Refinement of this model, followed by a difference Fourier synthesis, led to the placement of the second fluorine atom, F(2), in a sixteen-fold general position of the space group.

In subsequent refinements the function minimized was $\sum w(|F_0| - |F_c|)^2$, where $|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w were taken as $4F_0^2/\sigma^2(F_0^2)$. The scattering factors for K and F were from the usual tabulation (14), while those for H were taken from the calculations of Simpson et al. (15). The values of $\Delta f'$ and $\Delta f''$ for K were from the calculations of Cromer (16), and the effects of anomalous scattering

† The following programs were used for a CDC 6400 computer: ORFFE of Busing and Levy, ORTEP of Johnson, local variations of the Busing and Levy ORFLS and Zalkin's FORDAP, as well as several of local origin.

were included in the calculation of F_c. Refinement of the F(2) positional parameters, along with the anisotropic thermal parameters for all atoms and the scale factor, converged to values of R_1 and R_2 of 0.114 and 0.173, respectively, where

$$R_1 = \sum ||F_0| - |F_c||/\sum |F_0|$$

and

$$R_2 = (\sum w(|F_0| - |F_c|)^2/\sum wF_0^2)^{1/2}.$$

Not surprisingly, a comparison of $|F_0|$ and $|F_c|$ at this stage showed evidence of secondary extinction, and in a subsequent calculation a single extinction parameter (17) was added to the variables. This refinement converged to values of R_1 and R_2 equal to 0.088 and 0.134, respectively.

In the usual corrections for absorption it is assumed that the crystal is bathed in the X-ray beam; clearly this assumption is invalid here. Consequently a theory for the correction of absorption of a large, enclosed cylinder which incompletely intercepts the X-ray beam was devised (18). The correction assumes a beam of infinitesimal width, which is incompletely intercepted by the elliptical cross section of a large diffracting cylinder concentric and coplanar with a larger ellipse. The area of the larger ellipse which does not intercept the smaller ellipse is assumed to absorb but not to diffract. This theory was applied to the conditions of the present experiment, and numerical calculation of the absorption ($\mu = 10.17$ cm^{-1}) led to transmission factors which varied between 0.028 and 0.036. Subsequent refinement of the data corrected for absorption resulted in values of R_5 and R_2 of 0.068 and 0.082.

A difference Fourier map computed at this stage showed no peaks with electron density greater than 0.56 e/Å^3. The third highest peak on the map, of height 0.40 e/Å^3, was at a plausible position for the as yet omitted hydrogen atom, since it was 1.59 Å from F(1) and 0.91 Å from F(2) in a nearly linear F(1)$\cdots$H–F(2) arrangement. Subsequent refinement of the hydrogen atom in this position resulted in values of R_1 and R_2 of 0.063 and 0.077. In the process the H atom moved about 0.2 Å closer to F(2), leading to an F(2)–H bond length of 0.70(8) Å. Such a short interaction, though not physically reasonable, is not unexpected from X-ray data (2).

An examination of the values of $w(|F_0| - |F_c|)^2$ as a function of $|F_0|$, scattering angle, and various classes of reflections, suggested that only for the half dozen most intense reflections was there an unexpected trend. It is probable that the single-parameter extinction correction is inadequate for the present crystal, but in view of the other errors in

the data, for example the approximate nature of the absorption correction, no attempt was made to introduce anisotropic extinction. Rather the weighting scheme was readjusted to assure a reasonably uniform variation of $w(|F_0| - |F_c|)^2$ with $|F_0|$. In the final refinement, which converged to values of R_1 and R_2 of 0.062 and 0.069, no significant shifts in the derived parameters occurred. The final value of an error in an observation of unit weight is 1.12 e. A final difference map showed no sign of residual electron density in the interatomic F(1)–F(2) region.

In view of the approximate nature of the absorption correction and the general difficulties of centering the crystal, no further calculations were carried out, although the substitution of K$^+$ and F$^-$ for K and F would be expected to·have a slight, but probably insignificant, effect on the derived structure.

In Table II the final values of $|F_0|$ and $|F_c|$ in electrons ($\times 10$) are tabulated. An examination of $|F_c|$ for those reflections below background revealed no instances where $|F_c|$ was appreciably above $3\sigma(F_0)$.

Table III presents the final positional and thermal parameters, along with the corresponding standard deviations as derived from the inverse matrix.

Description of the Structure

Some selected interatomic distances and angles, together with their standard deviations as computed from the variance–covariance matrix, are given in Table IV. A stereoview of the unit cell, which consists of well separated K$^+$ and H$_4$F$_5^-$ ions† with 8:8 coordination, is presented in Fig. 2. (For the sake of clarity all illustrations have been drawn using an F(2)–H distance of 0.9 Å, a linear F(2)–H$\cdots$F(1) arrangement, and B$_H$ of 0.5 Å^2.) The crystal falls nicely into the scheelite type (19), the other members of which, as CaWO$_4$ itself, have general formula MXO$_4$, MXO$_3$N, or MXO$_3$F, space group I4$_1$/a, lattice constant ratio c/a of 2.0 to 2.3, 8:8 anion–cation coordination, and imposed $\bar{4}$ symmetry of O (or O disordered with N or with F) about the central X. Since most of the scheelite structures are the results of earlier powder work, possible deviations from tetrahedral symmetry about X in addition to the observed deviations from dodecahedral symmetry about M may be uncertain. The immediate dodecahedral environment about a typical potassium ion is shown in Fig. 3. The two

† The nearest K–F distances in this compound (2.772 Å) are slightly longer than those in crystalline KF (2.66 Å), KHF$_2$ (2.769 Å), and KH$_2$F$_3$ (2.69 Å), suggesting a typically ionic crystal.

TABLE II

Observed and Calculated Structure Amplitudes for $K[H_4F_5]$ in Electrons ($\times 10$)

Structure amplitudes are listed as H, K, FO, FC for each reflection, grouped by L.

L = 0

H	K	FO	FC
0	0		2728
0	4	491	572
0	6	198	218
2	2	907	1150
2	4	321	304
2	6	120	120
4	2	238	233
4	4	271	254
4	6	140	143
6	2	202	195
6	4	94	93

L = 1

H	K	FO	FC
0	1	289	256
0	3	85	94
0	5	130	139
0	7	19	20
1	2	601	580
1	4	124	137
1	6	110	122
2	1	218	193
2	3	317	291
2	5	48	35
2	7	48	49
3	2	23	24
3	4	256	248
4	1	308	303
4	3	19	25
4	5	59	55
5	2	81	89
6	1	26	25
6	3	57	52
7	2	51	48

L = 2

H	K	FO	FC
0	2	145	132
0	4	168	167
0	6	74	79
1	1	641	858
1	3	576	553
1	5	301	297
1	7	104	109
2	2	167	167
2	6	35	34
3	1	586	681
3	3	323	298
3	5	213	217
4	2	208	206
4	4	73	79
5	1	213	209
5	3	269	258
5	5	104	104
6	2	90	89
6	4	50	44
7	1	146	136

L = 3

H	K	FO	FC
0	1	19	14
0	3	428	409
0	7	57	59
1	2	95	97
1	4	198	195
1	6	35	38
2	1	459	463
2	3	153	141
2	5	186	185
2	7	15	15
3	2	102	103
3	6	83	86
4	3	186	177
5	2	75	78
5	4	94	100
6	1	59	56
6	3	38	39
7	2	43	38

L = 4

H	K	FO	FC
0	0	104	90
0	2	847	1138
0	4	262	262
0	6	166	174
1	1	536	597
1	3	159	161
1	5	20	27
1	7	19	28
2	2	268	246
2	4	406	367
2	6	170	174
3	1	182	183
3	3	71	66
3	5	17	20
4	2	418	404
4	4	184	184
4	6	88	87
5	3	34	28
6	2	138	133
6	4	113	113

L = 5

H	K	FO	FC
0	1	380	323
0	3	41	36
0	5	105	120
0	7	44	45
1	2	144	141
1	4	298	286
2	1	255	256
2	3	169	176
2	5	29	24
3	2	323	310
3	4	30	37
3	6	78	79
4	1	28	23
4	3	76	72
4	5	83	85
5	2	21	22
5	4	87	85
6	1	107	102
6	3	37	38

L = 6

H	K	FO	FC
0	2	18	23
0	4	48	47
0	6	37	33
1	1	606	647
1	3	460	409
1	5	166	171
1	7	114	120
2	4	20	20
2	6	15	18
3	1	228	231
3	3	431	410
3	5	146	144
4	2	34	35
5	1	321	322
5	3	72	73
5	5	128	123
6	2	33	27
7	1	70	65

L = 7

H	K	FO	FC
0	1	269	259
0	3	27	26
0	5	119	116
1	4	136	144
1	6	32	31
2	1	90	99
2	3	251	230
2	5	22	18
3	2	175	175
3	4	40	45
3	6	44	42
4	1	88	83
4	3	14	3
4	5	107	101
5	2	58	59
5	4	38	32
6	1	55	58
6	3	59	55

L = 8

H	K	FO	FC
0	0	466	482
0	2	398	367
0	4	308	293
0	6	103	105
1	1	401	381
1	3	146	139
2	2	387	373
2	4	185	184
2	6	123	126
3	1	158	156
3	3	64	61
4	2	197	194
4	4	137	145
5	1	27	24
5	3	28	23
6	2	114	118

L = 9

H	K	FO	FC
0	1	35	32
0	3	237	238
1	2	166	175
1	4	30	32
1	6	69	66
2	1	161	162
2	5	99	105
3	4	89	90
4	1	82	81
4	3	86	91
5	2	102	98
6	1	21	21

L = 10

H	K	FO	FC
0	4	17	17
1	1	312	301
1	3	218	219
1	5	167	167
2	2	50	51
2	4	25	27
3	1	285	298
3	3	137	138
3	5	112	109
4	2	46	48
4	4	29	31
5	1	75	80
5	3	152	146

L = 11

H	K	FO	FC
0	1	87	89
0	3	91	91
0	5	41	47
1	2	147	151
2	1	61	59
2	3	51	55
2	5	67	59
3	2	24	29
3	4	97	90
4	1	70	76
4	3	77	72
5	2	54	46

L = 12

H	K	FO	FC
0	0	364	351
0	2	140	147
0	4	145	142
1	1	100	103
1	3	62	56
2	2	227	219
2	4	126	132
3	1	61	59
3	3	27	26
4	2	108	116

L = 13

H	K	FO	FC
0	1	97	100
0	3	16	15
1	2	83	85
1	4	35	32
2	1	30	19
2	3	99	102
3	2	71	70
4	1	77	77

L = 14

H	K	FO	FC
1	1	152	154
1	3	137	135
2	2	17	22
3	1	121	121

L = 15

H	K	FO	FC
0	1	57	53
1	2	40	40
2	1	68	66

independent K–F(2) distances are equal, to a standard deviation (Table IV), and the parameters within the $\bar{4}2m$ symmetry as described by Hoard and Silverton (20) are given in Table V.

The $\bar{4}$ symmetry of a typical tetrahydrogen pentafluoride ion may be visualized in Fig. 4. This tetrahydrogen pentafluoride ion is the largest anion as yet characterized which consists solely of F–H···F

hydrogen bonding. Since the F(1) atom resides at a special $\bar{4}$ symmetry position, all F(1)–H distances within the ion are equal, as are those of F(1)–F(2) and F(2)–H, and the overall symmetry of the ion is close to, but with a distinct tetragonal distortion from, that of a regular tetrahedron. There is no evidence of disordering of the hydrogen atom such as that which might be consistent with a potential

TABLE III

Positional[a] and Thermal Parameters for $K[H_4F_5]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0	$\frac{1}{4}$	$\frac{1}{8}$	0.0244(5)	β_{11}	0.0044(1)	0	0	0
F(1)	0	$\frac{1}{4}$	$\frac{5}{8}$	0.0231(7)	β_{11}	0.0057(2)	0	0	0
F(2)	0.1837(4)	0.0249(4)	0.2805(2)	0.0358(9)	0.0414(9)	0.0081(2)	−0.0137(5)	−0.0032(3)	−0.0068(3)
H[b]	0.13(1)	0.45(1)	−0.309(3)	12(2) A²					

[a] These figures are for space group I4₁/a, origin at $\bar{1}$. However, it is usual to quote the positional parameters for scheelites MXO_4 with respect to an origin at X; in this option, the parameters for F(2) are $x = 0.3163$, $y = 0.2251$, $z = 0.0945$.

[b] Refined isotropically. For all anisotropically refined atoms, temperature factor is

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl).$$
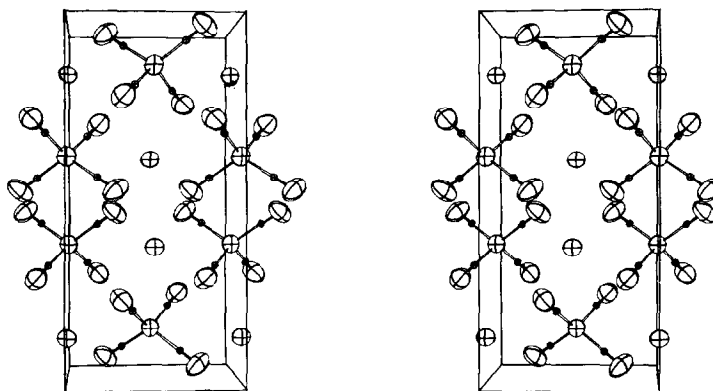
FIG. 2. Stereoview of the unit cell in $K[H_4F_5]$.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES
(DEG) IN $K[H_4F_5]$

F(1)–F(2)	2.453(2) Å	H-bonded
F(1)–F(2)	3.375(4) Å	nonbonded
F(1)–H	1.76(8) Å	
F(2)–H	0.70(8) Å	
F(2)–F(1)–F(2)	118.76(13)°	H-bonded, multiplicity = 2
F(2)–F(1)–F(2)	105.04(6)°	H-bonded, multiplicity = 4
F(1)–H–F(2)	176(8)°	
K–F(2)	2.770(2) and 2.774(2)	Multiplicity = 4 Multiplicity = 4
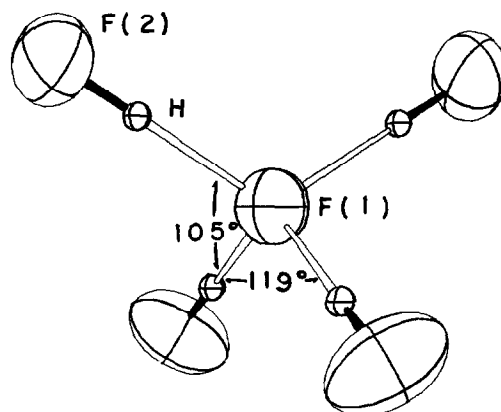
FIG. 4. View of the tetrahydrogen pentafluoride ion in $K[H_4F_5]$.

TABLE V

DODECAHEDRAL PARAMETERS FOR THE
POTASSIUM ENVIRONMENT IN $K[H_4F_5]$

$\theta_A = 42.04(8)°$	$a = 3.710(7)$ Å
$\theta_B = 63.24(6)°$	$b = 4.304(4)$ Å
MA = 2.770(2) Å	$m = 3.368(2)$ Å
MB = 2.774(2) Å	$g = 3.102(5)$ Å
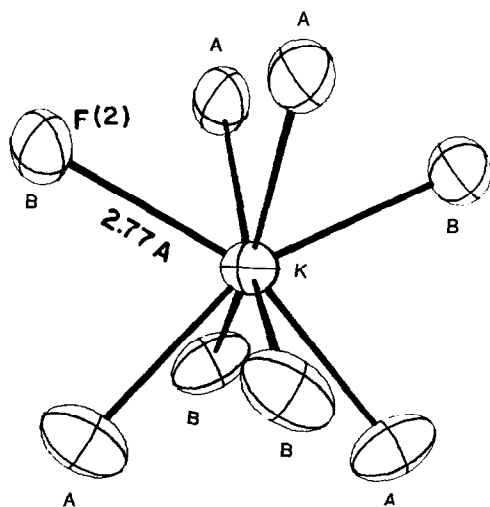
FIG. 3. View of the potassium ion and its nearest F(2) neighbors, which form a triangular dodecahedron, in $K[H_4F_5]$. The two independent "tetrahedra" (20) are denoted by *AAAA* and *BBBB*. The two mutually orthogonal trapezoids *AABB* can be seen.

function with asymmetric minima between the fluorine atoms. In addition to the four F(2) atoms hydrogen-bonded to the central F(1) atom at a distance of 2.453 Å, another set of four F(2) atoms, themselves hydrogen-bonded to other F(1) atoms, resides at 3.375 Å from the central F(1). The superset of eight F(2) atoms constitutes a cube, one of whose tetrahedra is extended from, the other contracted toward, the center.

TABLE VI

COMPARISON OF FHF HYDROGEN-BONDED DISTANCES IN VARIOUS CRYSTALS

Compound	Ion	Average distance, Å	Ref.
NaHF$_2$	HF$_2^-$	2.264(3)	(21)
LiHF$_2$	HF$_2^-$	2.27(11)	(22)
NH$_4$HF$_2$	HF$_2^-$	2.269(5)	(23)
KHF$_2$	HF$_2^-$	2.277(6)	(24)
KH$_2$F$_3$	H$_2$F$_3^-$	2.33	(25)
KH$_4$F$_5$	H$_4$F$_5^-$	2.453(2)	This work
HF	—	2.49(1)^a	(26)

^{a} At −125°C.

A comparison of the fluorine–fluorine hydrogen-bonded distance with those in other HF compounds is given in Table VI. One may rationalize the observed trend by assuming that as the electrons of the fluorine atoms become less available for hydrogen-bonding, then the F–H⋯F bond becomes longer. This is consistent with either an increase in the coordination number or especially with a decrease in formal negative charge on the fluorine atoms.

Despite the fact that the present structure was derived from X-ray data that were not collected under the most desirable conditions, there are several lines of evidence that suggest that the determination is a reliable one. Not only is the final value of R_1 of 0.062 fairly low but the atomic mean-square amplitudes of vibration (Table VII) seem reasonable enough as do the directions of thermal motion, and these thermal parameters should be particularly sensitive to residual errors in the data. The peripheral fluorine F(2) is the only atom showing appreciable anisotropic vibration and, as can be seen in the figures, the axis of largest root-mean-square amplitude is roughly perpendicular to the plane formed by its nearest F(1) and K neighbors. In addition,

TABLE VII

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ALONG PRINCIPAL ELLIPSOID AXES (A)

Atom	Minimum	Intermediate	Maximum
K	0.198(3)	0.224(2)	0.224(2)
K(1)	0.219(3)	0.219(3)	0.226(5)
F(2)	0.212(4)	0.243(3)	0.356(3)

the location and refinement of a plausible position for H atom suggest that the data are reasonably free from systematic error.

The structure is completely different from that of the isoelectronic KF·4H$_2$O, (27) where edge- and vertex-sharing K(H$_2$O)$_6^+$ and F(H$_2$O)$_6^-$ octahedra are observed, together with 2.79 Å K–O distances and of course much longer hydrogen bonds than are found in HF systems.

Finally, the analogy between the various hydrofluoric acid anions and the xenon fluorides may be of interest and may give rise to some speculation. As H$^-$ is isoelectronic with He, then HF$_2^-$ is analogous to XeF$_2$, H$_2$F$_3^-$ to Xe$_2$F$_3^+$ and H$_4$F$_5^-$ to Xe$_4$F$_5^{3+}$, a hypothetical cation which could conceivably exist, say, in 4XeF$_2$·3SbF$_5$.

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