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Authors

Forrester, J.D.
Senko, Michael E.
Zalkin, Allan.
et al.

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CRYSTAL STRUCTURE OF KH_2F_3 AND GEOMETRY OF THE H_2F_3^- ION

J. D. Forrester, Michael E. Senko, Allan Zalkin, and David H. Templeton

April 30, 1962

CRYSTAL STRUCTURE OF KH_2F_3 AND GEOMETRY OF THE H_2F_3^- ION^{*}J. D. Forrester, Michael E. Senko,[†] Allan Zalkin, and David H. Templeton

Department of Chemistry and Lawrence Radiation Laboratory

University of California, Berkeley, California, U. S. A.

Crystals of KH_2F_3 contained in polyethylene tubes, because of the high vapor pressure of HF, have been studied by x-ray diffraction. They are orthorhombic, space group $\text{P}2_12_12_1$, with $a = 8.52 \pm 0.02$, $b = 11.09 \pm 0.03$, $c = 6.69 \pm 0.02$ Å. The unit cell contains eight formula units, and the calculated density is 2.06 g cm^{-3} . The structure corresponds to a salt of potassium and hydrogen-bonded ions FHFHF^- . Hydrogen-bond lengths in these ions average 2.33 Å. The F-F-F angles are 130° and 139° , respectively, in the two nonequivalent H_2F_3^- ions.

^{*}Work done under the auspices of the U.S. Atomic Energy Commission.

[†]Now at International Business Machines Corp., Yorktown Heights, N.Y.

Introduction

Alkali fluorides crystallize from HF solutions in the form of many solvates. For example, in the KF-HF system Cady (1934) observed the phases KF.HF, KF.2HF, 2KF.5HF, KF.3HF, and KF.4HF. It is well known that in KF.HF the fluorine atoms are connected in pairs by strong hydrogen bonds, and it is convenient to consider this substance as a salt of K^+ and HF_2^- ions. We speculated that in the higher solvates other polymeric ions occur: $FHFHF^-$, $FHFHFHF^-$, etc. By a determination of the crystal structure by x-ray diffraction, we have confirmed that in KF.2HF the fluorine atoms are grouped into $FHFHF^-$ ions, and consequently we write the formula as KH_2F_3 .

The phase KH_2F_3 melts congruently at 71.7° (Cady, 1934). Because of an appreciable vapor pressure of HF, there was some difficulty in obtaining and photographing suitable crystals. The structure was determined by data from photographs of lower quality than we had hoped to obtain.

Crystals were prepared and photographed (by M. E. S.) in 1954, and the unit cell and space group were determined. The prospect of locating eight atoms in the asymmetric unit of a noncentric crystal with data of doubtful accuracy and with rather inadequate computing facilities was not as interesting as several other problems, and the work was suspended. In 1961 and 1962 the old photographs were examined again and were used to determine the structure which is reported here.

Experimental

Crystals of KH_2F_3 were prepared in a metal vacuum system. A weighed amount of anhydrous HF was allowed to enter an evacuated vessel containing the equivalent amount of reagent grade KF . The system was placed in boiling water for two hours to allow equilibration above the melting point of the product. When cooled and opened in a dry box, the vessel was found to contain a hard transparent mass which was crushed to yield single crystal fragments.

Crystals contained in polyethylene tubes were examined by x-ray diffraction at room temperature, about 24° . Weissenberg photographs were taken with copper radiation ($\lambda = 1.5418 \text{ \AA}$ for $\text{CuK}\alpha$) with rotation about the c axis (layers 0 to 4) and about the a axis (layers 0 and 1). Unit cell dimensions were estimated from the two zero layer photographs. Intensities were estimated on the multiple film Weissenberg photographs ($l=0$ to $l=4$) by visual comparison with a standard film strip on which one reflection was exposed for various times. Intensities were recorded for 524 independent reflections, while 56 others were recorded as too weak to be observed. Lorentz, polarization and velocity corrections were applied. For $\text{CuK}\alpha$ radiation the absorption coefficient is estimated as 138 cm^{-1} , and the intensity data show severe effects of absorption. No absorption correction was made because the dimensions of the crystal are not known. The data from the five layers were placed on a common scale first according to the exposure times, but later the five scale factors were adjusted to improve the agreement of observed and calculated structure factors.

Unit Cell and Space Group

The diffraction patterns show orthorhombic symmetry with unit cell dimensions:

$$a = 8.52 \pm 0.02 \text{ \AA}$$

$$b = 11.09 \pm 0.03 \text{ \AA}$$

$$c = 6.69 \pm 0.02 \text{ \AA}.$$

Reflections are absent for $h00$ with h odd, for $0k0$ with k odd, and for $00l$ with l odd. These absences correspond to space group $P2_1^2 2_1 2_1$ which is confirmed by the success of the structure determination. In this space group there is only one set of equivalent positions:

$$4(a) \quad x, y, z; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z.$$

Therefore the number of formula units per unit cell must be divisible by 4.

Ionic volumes in other crystals suggest that $8(\text{KH}_2\text{F}_3)$ is the only reasonable content of the unit cell. On this basis the calculated density is 2.06 g cm^{-3} .

Determination of the Structure

The asymmetric unit contains two potassium atoms and six fluorine atoms. The coordinates of the potassium atoms were determined uniquely from a three-dimensional Patterson function. We attempted to locate the fluorine atoms in projections (which are centric) based on the $hk0$ and $h0l$ data with phases determined only by potassium, but failed. The number of phases which could be determined was rather small, and the location of both potassium atoms at $z=0$ introduced extra symmetry.

The three-dimensional electron density function was calculated using phases calculated from the potassium atoms. This function was perplexing, but we identified four fluorine atoms by rejecting peaks which corresponded to unreasonably short interatomic distances and those for which we could not find $K_1\text{-F}$ and $K_2\text{-F}$ peaks in the Patterson function.

A second electron density function was calculated with phases determined by the two potassium atoms and the four fluorine atoms. With the same criteria, we were able to identify the remaining two fluorine atoms.

The structure was then refined by least squares. In all calculations we used the atomic scattering factors for K^+ and F^- from the tables of Ibers (1962). The calculations were made with an IBM-7090 computer and a full-matrix program written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, with minor changes. Each reflection was assigned unit weight. Each atom was assigned an individual isotropic temperature factor of the form $\exp(-B\lambda^{-2}\sin^2\theta)$.

Refinement with all the data made it evident that absorption errors were present. Refinement was continued with 551 reflections (of which 56 are zero) where $\sin \theta/\lambda$ exceeded 0.2. For these data the conventional reliability factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was reduced to 0.202 after 6 cycles.

The computer program used had no provision for refining the separate scale factors of the different layers, so these factors were adjusted by hand, and R fell to 0.186. Because the low angle data still seemed to be affected by absorption, further refinement was done with reflections for which $\sin \theta/\lambda$ exceeded 0.3 (487 terms of which 54 are zero). After further rescaling, R was reduced to 0.142. At this stage, shifts of coordinates were negligible. Including scale factors, a total of 37 parameters were used to achieve this fit.

Observed and calculated structure factors for all of the reflections which were measured are listed in Table 1. The calculated values are based on the coordinates and the first set of temperature parameters listed in Table 2. The standard deviations listed in Table 2 are those estimated by the method of least squares assuming that the discrepancies represent random errors.

It is expected that the higher angle data, on which the final parameters are based, include systematic errors due to absorption which are largely compensated by incorrect temperature parameters and scale factors. To the extent that such compensation occurs, the coordinates are not affected by these errors. A second set of temperature parameters, also listed in Table 2, were determined using only the data with $l=0$, and they are systematically greater than the first set. This result implies that further adjustment of the scale factors could improve the fit, but it was decided that the quality of the data did not justify further adjustment. Because of the uncertainty in the relative magnitudes of these thermal parameters, no correction of bond distances for thermal motion has been made. Such corrections are not expected to exceed 0.02 Å for K-F distances or 0.01 Å for F-F distances.

Discussion of the Structure

Fluorine atoms occur in the structure in groups of three as was expected for hydrogen-bonded H_2F_3^- ions (Fig. 1). The two nonequivalent groups permit independent measurement of four hydrogen-bond distances and two bond angles which are listed in Table 3. These bond distances average 2.33 Å, and the deviations from this average are of doubtful significance. The difference in the two bond angles is significant, and we infer that the molecule is not very rigid and that it bends to improve the crystal packing. This idea is consistent with the F-F-F angles reported for hydrogen fluoride. In the solid, HF occurs in zig-zag chains with angles of 120.1° (Atoji and Libscomb, 1954). In the gaseous polymer, the angle is observed as 144° by electron diffraction (Bauer, Beach and Simons, 1939).

Distances for hydrogen bonds between fluorine atoms in some other crystals are listed in Table 4. The bond lengths which we observe in KH_2F_3 are close to those observed in the FHF^- ion in various crystals, and they are significantly shorter than the bonds in solid hydrogen fluoride. On the basis of thermodynamic, spectral and dielectric data for KHF_2 , Westrum and Pitzer (1949) concluded that the potential curve for the proton in the bifluoride ion has a single minimum at the midpoint. Peterson and Levy (1952) confirmed by neutron diffraction that in KHF_2 the hydrogen atoms are centrally located in the hydrogen bonds. Atoji and Lipscomb (1954) found evidence in their x-ray study of solid hydrogen fluoride that the hydrogen atoms are unsymmetrically located in these longer hydrogen bonds, as is generally accepted.

The distances which we observe for the hydrogen bonds in KH_2F_3 imply that these bonds approach in stability those in bifluoride ions. This fact suggests that the potential curve for the proton in one of these bonds may also be of the single-minimum type. The accuracy of our x-ray diffraction data does not permit us to test this conjecture, nor do we know of any other evidence which bears on the question. If such a minimum does occur, symmetry does not require it to be at the center of the bond.

The structure as a whole is salt like, with the potassium ions well dispersed among the H_2F_3^- ions. The shortest potassium-potassium distance is 4.34 Å. Each potassium atom has eight fluorine neighbors, each a member of a different H_2F_3^- ion, at distances averaging 2.83 Å for K_1 and 2.82 Å for K_2 .

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Table 1. Observed structure factors (FOB) and calculated structure factor magnitudes (FCAL) and phase angles (PHI) for KH_2F_3 . Each structure factor has been multiplied by 10. Each term for which $\sin \theta/\lambda$ is less than 0.3 was given zero weight and is marked with an asterisk (*).

L = 0																			
H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
2	0	211	233	180	4	2	503	567	180	2	4	246	237	0	0	6	0	3	180
4	0	353	424	180	5	2	88	51	90	3	4	284	297	270	1	8	421	407	270
6	0	393	347	180	6	2	131	113	180	4	4	522	597	0	2	6	361	424	180
8	0	519	521	0	7	2	348	271	270	5	4	218	175	270	3	6	193	187	270
10	0	57	65	0	8	2	231	208	180	6	4	221	208	0	4	6	366	320	0
1	1	106	128	270	9	2	272	285	90	7	4	483	419	90	5	6	277	269	90
2	1	255	305	0	10	2	135	114	0	8	4	249	228	180	6	6	218	179	180
3	1	641	1294	270	1	3	360	497	270	9	4	0	30	270	7	6	194	180	270
4	1	291	248	0	2	3	304	314	0	10	4	0	25	0	8	6	0	11	0
5	1	267	191	90	3	3	376	480	90	1	5	583	865	90	9	6	0	3	270
6	1	503	471	180	4	3	288	231	0	2	5	171	179	180	1	7	111	118	270
7	1	358	321	90	5	3	328	286	270	3	5	263	238	90	2	7	513	521	180
8	1	318	249	0	6	3	351	286	180	4	5	0	15	180	3	7	70	84	90
9	1	0	7	270	7	3	180	132	90	5	5	71	67	270	4	7	73	60	180
10	1	98	83	180	8	3	0	45	180	6	5	0	9	180	5	7	94	63	270
0	2	90	131	180	9	3	137	144	270	7	5	464	438	270	6	7	0	33	180
1	2	164	204	90	10	3	227	223	0	8	5	103	110	180	7	7	73	55	270
2	2	161	99	0	0	4	293	759	180	9	5	259	269	90	8	7	336	352	0
3	2	319	358	270	1	4	459	619	90	10	5	175	170	0	9	7	74	108	90
L = 1																			
H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
2	0	331	419	90	4	2	446	371	148	3	4	580	766	177	3	6	119	95	348
3	0	552	768	270	5	2	372	319	95	4	4	437	443	15	4	6	256	224	259
4	0	269	271	270	6	2	366	303	286	5	4	568	555	17	5	6	298	301	168
5	0	272	226	270	7	2	453	408	13	6	4	280	251	75	6	6	413	432	90
6	0	380	324	270	8	2	199	177	66	7	4	100	67	277	7	6	155	131	71
7	0	0	9	90	9	2	311	287	172	8	4	0	42	49	8	6	153	167	249
8	0	141	95	270	10	2	69	65	217	9	4	144	135	239	9	6	0	51	41
9	0	0	30	90	0	3	424	768	270	10	4	228	237	271	0	7	410	388	90
10	0	469	496	90	1	3	50	100	196	0	5	472	550	270	1	7	205	184	17
2	1	277	327	255	2	3	340	440	125	1	5	318	334	12	2	7	368	392	285
3	1	357	388	27	3	3	318	303	35	2	5	408	534	140	3	7	258	241	143
4	1	620	687	84	4	3	368	320	139	3	5	506	564	158	4	7	166	109	98
5	1	125	89	297	5	3	372	313	164	4	5	281	244	244	5	7	157	101	262
6	1	398	357	252	6	3	0	48	338	5	5	93	86	106	6	7	199	180	270
7	1	278	252	169	7	3	273	248	344	6	5	251	228	59	7	7	0	33	4
8	1	0	35	293	8	3	278	293	294	7	5	158	150	301	8	7	360	375	94
9	1	91	99	163	9	3	163	137	189	8	5	0	53	321	9	7	58	79	5
10	1	72	91	292	10	3	65	69	309	9	5	346	347	357	0	8	223	237	0
1	2	295	434	179	0	4	314	436	180	0	6	426	424	180	1	8	92	69	9
2	2	202	261	248	1	4	556	811	300	1	6	75	112	92	2	8	115	116	338
3	2	346	370	62	2	4	381	369	285	2	6	137	145	195	3	8	283	271	9
L = 2																			
H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
1	0	194	293	180	0	2	132	210	0	10	3	249	229	9	0	6	203	222	180
2	0	472	928	180	1	2	451	1033	76	0	4	443	630	180	1	6	275	304	185
3	0	192	167	180	2	2	365	543	44	1	4	100	117	73	2	6	278	258	154
4	0	61	75	0	3	2	523	636	250	2	4	142	162	180	3	6	194	173	84
5	0	160	165	0	4	2	249	184	164	3	4	204	214	234	4	6	630	706	355
6	0	395	352	180	5	2	255	225	263	4	4	0	18	15	5	6	343	375	97
7	0	229	191	0	6	2	402	332	2	5	4	420	393	248	6	6	107	103	205
8	0	228	203	0	7	2	0	40	2	6	4	296	264	76	7	6	132	139	270
9	0	188	193	180	8	2	60	57	15	7	4	123	118	100	8	6	73	45	162
10	0	0	80	180	9	2	437	401	85	8	4	284	248	222	9	6	0	13	50
0	1	105	172	270	10	2	78	156	314	9	4	181	150	319	0	7	130	122	90
1	1	141	236	71	0	3	375	653	270	0	5	181	201	90	1	7	120	103	67
2	1	290	393	10	1	3	227	329	244	1	5	481	582	96	2	7	433	479	192
3	1	418	455	243	2	3	456	709	9	2	5	242	239	267	3	7	238	242	100
4	1	373	386	10	3	3	453	539	111	3	5	122	109	93	4	7	171	149	349
5	1	338	305	86	4	3	271	235	17	4	5	0	21	258	5	7	107	109	270
6	1	447	434	182	5	3	396	339	299	5	5	194	194	34	6	7	86	85	20
7	1	221	215	18	6	3	435	389	169	6	5	151	127	51	7	7	158	166	285
8	1	136	109	5	7	3	195	170	75	7	5	345	373	254	8	7	209	187	358
9	1	76	112	259	8	3	206	125	193	8	5	167	171	116	9	7	121	128	146
10	1	81	93	242	9	3	192	136	299	9	5	199	183	73	0	8	347	345	180
L = 3																			
H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI	H	K	FOB	FCAL	PHI
1	0	282	604	90	10	1	148	138	262	9	3	219	176	152	9	5	294	307	13
2	0	286	377	90	0	2	304	761	180	0	4	196	252	180	0	6	285	311	0
3	0	0	69	270	1	2	346	681	181	1	4	323	463	7	1	6	255	258	278
4	0	0	61	90	2	2	268	365	59	2	4	154	173	218	2	6	378	430	318
5	0	173	177	90	3	2	235	261	266	3	4	327	356	159	3	6	342	304	8
6	0	78	49	270	4	2	287	287	42	4	4	159	117	39	4	6	200	201	202
7	0	81	91	270	5	2	205	220	304	5	4	318	300	22	5	6	222	173	150
8	0	363	296	270	6	2	374	365	307	6	4	229	209	144	6	6	427	432	92
9	0	161	167	90	7	2	334	343	345	7	4	80	101	126	7	6	91	92	239
10	0	306	322	90	8	2	132	135	131	8	4	0	43	58	8	6	219	212	299
0	1	156	322	90	9	2	318	291	190	9	4	0	35	22	0	7	659	785	90
1	1	248																	

Table 2.

Final atomic parameters for KH F_{23} .

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B in $\text{\AA}^2$	
							(1)	(2)
K_1	0.2317	0.1789	0.0219	0.0004	0.0003	0.0009	0.7	1.4
K_2	0.1224	0.5974	0.0217	0.0004	0.0003	0.0010	0.7	1.3
F_1	0.3582	0.1737	0.6544	0.0013	0.0010	0.0025	1.3	1.9
F_2	0.1989	0.0629	0.4338	0.0015	0.0011	0.0027	1.7	2.4
F_3	0.1154	0.3625	0.2402	0.0016	0.0012	0.0030	2.2	2.6
F_4	0.0877	0.4681	0.6874	0.0017	0.0014	0.0031	2.5	3.0
F_5	0.5022	0.2229	0.2415	0.0016	0.0012	0.0034	1.9	2.6
F_6	0.4195	0.3929	0.9246	0.0016	0.0012	0.0030	2.0	3.3

Table 3. Interatomic distances and angles in KH_2F_3 .

F_1-F_2	2.35 A	$\text{F}_2-\text{F}_1-\text{F}_3$	$130 \pm 2^\circ$
F_1-F_3	2.34		
F_4-F_5	2.29	$\text{F}_5-\text{F}_4-\text{F}_6$	$139 \pm 2^\circ$
F_4-F_6	2.34		
K_1-F_1	2.69	K_2-F_4	2.67 A
K_1-F_3	2.69	K_2-F_1	2.69
K_1-F_5	2.78	K_2-F_6	2.72
K_1-F_6	2.80	K_2-F_2	2.78
K_1-F_2	2.81	K_2-F_4	2.80
K_1-F_5	2.85	K_2-F_5	2.94
K_1-F_6	2.94	K_2-F_3	2.96
K_1-F_2	3.05	K_2-F_3	2.99

The standard deviation of each distance is 0.02 A.

Table 4. Distances for F-H-F bonds in various crystals.

Crystal	Average Distance
HF (Atoji and Lipscomb, 1954)	2.49 ± 0.01 A
KHF ₂ (Helmholz and Rogers, 1939)	2.26 ± 0.01
NH ₄ HF ₂ (Helmholz and Rogers, 1940)	2.32 ± 0.03
LiHF ₂ (Frevel and Rinn, 1962)	2.27 ± 0.11
KH ₂ F ₃ (Present work)	2.33 ± 0.01

MU-26091

Fig. 1. Crystal structure of KH_2F_3 , projected along c .

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