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Publication Date
1962-04-30
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CRYSTAL STRUCTURE OF \( \text{KH}_2\text{F}_3 \) AND GEOMETRY OF THE \( \text{H}_2\text{F}_3^- \) ION

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

April 30, 1962
CRYSTAL STRUCTURE OF KH$_2$F$_3$ AND GEOMETRY OF THE H$_2$F$_3^-$ ION

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Crystals of KH$_2$F$_3$ contained in polyethylene tubes, because of the high vapor pressure of HF, have been studied by x-ray diffraction. They are orthorhombic, space group P2$_1$2$_1$2$_1$, with a = 8.52 ± 0.02, b = 11.09 ± 0.03, c = 6.69 ± 0.02 Å. The unit cell contains eight formula units, and the calculated density is 2.06 g cm$^{-3}$. The structure corresponds to a salt of potassium and hydrogen-bonded ions FHFHF$^-$. Hydrogen-bond lengths in these ions average 2.33 Å. The F-F-F angles are 130° and 139°, respectively, in the two nonequivalent H$_2$F$_3^-$ ions.

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

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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⁻ 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 diffrac- tion, we have confirmed that in KF.2HF the fluorine atoms are grouped into FHFHF⁻ ions, and consequently we write the formula as KH₂F₃⁻.

The phase KH₂F₃ melts congruently at 71.7°C (Cady, 1954). 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 $\text{KH}_2\text{F}_3$ 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 ($\lambda = 1.5418$ Å for CuKα) 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 CuKα 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:

\[ a = 8.52 \pm 0.02 \text{ Å} \]
\[ b = 11.09 \pm 0.03 \text{ Å} \]
\[ c = 6.69 \pm 0.02 \text{ Å} \]

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 \( P2_12_12_1 \) which is confirmed by the success of the structure determination. In this space group there is only one set of equivalent positions:

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

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 \( h00 \) 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 \( K_1^F \) and \( K_2^F \) 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 $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ 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 \( \text{H}_2\text{F}_3^- \) 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$_2$F$_3$ 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$_2$F$_3$ 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$_2$F$_3^-$ ions. The shortest potassium-potassium distance is 4.34 Å. Each potassium atom has eight fluorine neighbors, each a member of a different H$_2$F$_3^-$ ion, at distances averaging 2.83 Å for K$_1$ and 2.82 Å for K$_2$. 
References


Table 1. Observed structure factors (FOB) and calculated structure factor magnitudes (FCAL) and phase angles (PHI) for $\text{KH}_2\text{F}_3$. 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 (*).
Table 2.

Final atomic parameters for $\text{KH}_2\text{F}_3$.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$\sigma(x)$</th>
<th>$\sigma(y)$</th>
<th>$\sigma(z)$</th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>0.2317</td>
<td>0.1789</td>
<td>0.0219</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0009</td>
<td>0.7</td>
<td>1.4</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.1224</td>
<td>0.5974</td>
<td>0.0217</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0010</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td>$F_1$</td>
<td>0.3582</td>
<td>0.1737</td>
<td>0.6544</td>
<td>0.0013</td>
<td>0.0010</td>
<td>0.0025</td>
<td>1.3</td>
<td>1.9</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0.1989</td>
<td>0.0629</td>
<td>0.4338</td>
<td>0.0015</td>
<td>0.0011</td>
<td>0.0027</td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>$F_3$</td>
<td>0.1154</td>
<td>0.3625</td>
<td>0.2402</td>
<td>0.0016</td>
<td>0.0012</td>
<td>0.0030</td>
<td>2.2</td>
<td>2.6</td>
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<tr>
<td>$F_4$</td>
<td>0.0877</td>
<td>0.4681</td>
<td>0.6874</td>
<td>0.0017</td>
<td>0.0014</td>
<td>0.0031</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>$F_5$</td>
<td>0.5022</td>
<td>0.2229</td>
<td>0.2415</td>
<td>0.0016</td>
<td>0.0012</td>
<td>0.0034</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>$F_6$</td>
<td>0.4195</td>
<td>0.3929</td>
<td>0.9246</td>
<td>0.0016</td>
<td>0.0012</td>
<td>0.0030</td>
<td>2.0</td>
<td>3.3</td>
</tr>
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Table 3. Interatomic distances and angles in $\text{KH}_2\text{F}_3$.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Distance</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1-F_2$</td>
<td>2.35 Å</td>
<td>$F_2-F_1-F_3$</td>
</tr>
<tr>
<td>$F_1-F_3$</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>$F_4-F_5$</td>
<td>2.29</td>
<td>$F_5-F_4-F_6$</td>
</tr>
<tr>
<td>$F_4-F_6$</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>$K_1-F_1$</td>
<td>2.69</td>
<td>$K_2-F_4$</td>
</tr>
<tr>
<td>$K_1-F_3$</td>
<td>2.69</td>
<td>$K_2-F_1$</td>
</tr>
<tr>
<td>$K_1-F_5$</td>
<td>2.78</td>
<td>$K_2-F_6$</td>
</tr>
<tr>
<td>$K_1-F_6$</td>
<td>2.80</td>
<td>$K_2-F_2$</td>
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<tr>
<td>$K_1-F_2$</td>
<td>2.81</td>
<td>$K_2-F_4$</td>
</tr>
<tr>
<td>$K_1-F_5$</td>
<td>2.85</td>
<td>$K_2-F_5$</td>
</tr>
<tr>
<td>$K_1-F_6$</td>
<td>2.94</td>
<td>$K_2-F_3$</td>
</tr>
<tr>
<td>$K_1-F_2$</td>
<td>3.05</td>
<td>$K_2-F_3$</td>
</tr>
</tbody>
</table>

The standard deviation of each distance is 0.02 Å.
Table 4. Distances for F-H-F bonds in various crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Average Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF (Atoji and Lipscomb, 1954)</td>
<td>2.49 ± 0.01 Å</td>
</tr>
<tr>
<td>KHF₂ (Helmholz and Rogers, 1939)</td>
<td>2.26 ± 0.01</td>
</tr>
<tr>
<td>NH₄HF₂ (Helmholz and Rogers, 1940)</td>
<td>2.32 ± 0.03</td>
</tr>
<tr>
<td>LiHF₂ (Frevel and Rinn, 1962)</td>
<td>2.27 ± 0.11</td>
</tr>
<tr>
<td>KH₂F₃ (Present work)</td>
<td>2.33 ± 0.01</td>
</tr>
</tbody>
</table>
Fig. 1. Crystal structure of \( \text{KH}_2\text{F}_3 \), projected along \( c \).
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