The Crystal Structure of InOHF₂

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InOHF₂ has been investigated by X-ray methods. It has a monoclinic unit cell and the unit cell dimensions are

\[
\begin{align*}
a &= (5.780 \pm 0.005) \text{ Å} \\
b &= (5.157 \pm 0.005) \text{ Å} \\
c &= (3.874 \pm 0.005) \text{ Å} \\
\beta &= 98.74^\circ \pm 0.02^\circ \\
V &= 114.1 \text{ Å}^3 \\
Z &= 2
\end{align*}
\]

A structure is proposed with atomic positions for the indium, oxygen and fluorine atoms in space group No. 5-C2. The parameters of the atoms (p. 681) were determined from Patterson projections and improved by back shift calculations.

The indium atoms are surrounded by two oxygen and four fluorine atoms so that a coordination In-OH-F is obtained.

The hydrogen atoms are situated either between the fluorine atoms forming F-H-F bonds or between the fluorine and oxygen atoms forming F-H-O bonds.

The structure may be described as a three dimensional framework (distorted ReO₄ structure).

The crystal structure of the isomorphous compounds InOCl and InOBr has recently been determined and in connection with this investigation attempts were made to prepare indium oxide fluoride. With the method described by Enslin and Dreyer, no crystals large enough for single crystal X-ray investigations were obtained but, by hydrothermal hydrolysis of almost saturated indium(III) fluoride solutions of different acidities, a new compound could be prepared. Its formula proved to be InOHF₂ while Enslin and Dreyer gave the formula of their substance as InOF·aq. This paper presents the structure determination of InOHF₂.

PREPARATION OF THE CRYSTALS

Indium(III) fluoride was obtained by dissolving indium hydroxide, prepared by treating a solution of indium(III) nitrate with aqueous ammonia, in 40 % hydrofluoric acid. The solution was then evaporated until crystals of InF₃(H₂O)₂ separated. After cooling, the crystals were filtered off, washed with water and dried in air.

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CRYSTAL STRUCTURE OF InOHF₃

Indium oxide fluoride was prepared as follows. A solution of 400 mg InF₃(H₂O)₄ dissolved in 6.5 ml HF (2 M) was poured into a Pt-crucible which was then kept at 300°C in an autoclave. After 18 h, the autoclave was cooled and the precipitate filtered off. It consisted of small transparent crystals of InOHF₃.

The crystals are insoluble in water but dissolve completely in hot dilute hydrochloric or nitric acid.

ANALYSIS

A sample, which had been dried in air, was decomposed by fusion with sodium and potassium carbonates. After cooling, the melt was leached with water and the residue filtered off. The amount of fluoride in the filtrate was determined gravimetrically as PbCl₄²⁻.

For the determination of indium, a sample was dissolved in nitric acid, evaporated, and then ignited and weighed as In₂O₃.

The hydroxide was determined as water by Hartwig-Bendig’s modification of Penfield’s method as described by Kolthoff and Sandell.

The density of the crystals was determined from the loss of weight in benzene.

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<thead>
<tr>
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<th>Found</th>
<th>Calculated for InOHF₃</th>
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</thead>
<tbody>
<tr>
<td>% In</td>
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<td>67.6</td>
</tr>
<tr>
<td>% F</td>
<td>22.9</td>
<td>22.38</td>
</tr>
<tr>
<td>% OH</td>
<td>9.5</td>
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<tr>
<td>Density</td>
<td>4.8</td>
<td>4.94 (cf. below)</td>
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</table>

UNIT CELL AND SPACE GROUP

From rotation (around [100], [010] and [001]) and Weissenberg photographs (0kl, 1kl, h0l, hkl, hh0 and hhk1), taken with CuKα radiation, it was concluded that the crystals are monoclinic with a ≈ 5.8 Å, b ≈ 5.1 Å, c ≈ 3.9 Å and β ≈ 90°. More accurate values of the unit cell dimensions were calculated from a powder photograph in a focusing camera of Guinier type (cf. Table 1). (CuKα radiation, internal standard KCl with a = 6.2930 Å).⁶

\[
a = (5.780 \pm 0.005) \text{ Å} \\
b = (5.157 \pm 0.005) \text{ Å} \\
c = (3.874 \pm 0.005) \text{ Å} \\
β = 98.74° \pm 0.02° \\
V = 114.1 \text{ Å}^3
\]

The mean value of the density is 4.90 so that there should be 1.98 ≈ 2 formula units InOHF₃ in the unit cell.

The only reflections systematically absent are

hkl with h+k odd

which is characteristic of the space groups No. 12-C2/m, No. 8-Cm and No. 5-C2.

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Table 1. Powder photograph of InOHF₄. CuKa radiation. Internal standard KCl. 
\(a = 6.2930 \text{ Å}.

<table>
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<td>2016</td>
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</table>

Reflections systematically absent according to space group No. 5-C2 have been omitted.

The intensities were calculated from the expression \(0.05 \cdot \frac{p^2}{\varphi^2}\) where \(p\) is the number.
Fig. 1. The Patterson projection $P(uwp)$ for InOHF$_4$. In the peaks at $P(0p0)$ and $P(4p0)$ only every second contour has been drawn. Dashed lines indicate negative values.

PATTERSON SYNTHSES

In the unit cell there are two indium, two oxygen and four fluorine atoms. To determine their positions, the Patterson projections, $P(uwp)$, $P(pwp)$, and $P(uwp)$ were calculated. (Figs. 1 and 2.) Relative intensities of the reflections were estimated visually and the $F^2$-values were then calculated using the curves given by Lu$^8$. No corrections have been applied for the absorption. In all syntheses, the value of $F^2(000)$ has been omitted. The maxima have been located by an interpolation table given by Booth$^9$. In the space groups suggested by the extinctions, the possible point positions are as follows:

Fig. 2. The Patterson projections $P(pwp)$ and $P(uwp)$ for InOHF$_4$. In the peaks at $P(p00)$ and $P(00p)$ only every third and second contour has been drawn. Dashed lines indicate negative values.

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The indium atoms can be given arbitrarily the twofold point position 2(a) with \( x = 0, y = 0 \) and \( z = 0 \) for all three space groups. The In-In distances of \( \pm (1/2,1/2,0) \) appear as pronounced maxima in the Patterson projections at \( 1/2,0,0 \), \( p,1/2,0 \) and \( 1/2,1/2,p \).

In addition to the In-In peaks, the Patterson projections show other distinct maxima which should correspond to distances between indium and oxygen atoms and indium and fluorine atoms.

Since the unit cell contains two oxygen and four fluorine atoms the oxygen atoms should be situated in a twofold point position and the fluorine atoms either in two twofold or in one fourfold point position. In the Patterson projections \( P(uwp) \) and \( P(pvw) \) we observe a distinct maximum at \( u \approx 0.325, v \approx 0.179 \) and \( w \approx 0.141 \) which can only be explained as being due to atoms in the fourfold point position 4(b) in \( Cm \) or 4(c) in \( C2 \). Thus the fluorine atoms should be situated in one of these point positions.

The other distinct maximum in \( P(pvw) \) at \( v \approx 0.125 \) and \( w = 1/2 \) (the corresponding maximum in \( P(uwp) \) is hidden by the In-In peak) must be explained as an In-O distance with the oxygen atoms in the point position 2(b) in \( C2 \). Thus we get the following parameters for the oxygen atoms (we need only consider the range \( 0 \leq x \leq 1/2, 0 \leq y \leq 1/2 \) and \( 0 \leq z \leq 1 \)).

\[
2 \text{ O in } C2 \quad 2(b) \text{ with } y \approx 0.125
\]

The remaining maxima in \( P(uwp) \) and \( P(pvw) \) on the \( u \) and \( w \) axes are small and probably caused by vectors between light atoms or by diffraction effects.

The parameters of the fluorine atoms are determined from the maximum at \( u \approx 0.325, v \approx 0.179 \), and \( w \approx 0.141 \) and we then notice that there are two possibilities for the sites of the atoms (we need only consider the range \( 0 \leq x \leq 1/2, 0 \leq y \leq 1/2 \) and \( 0 \leq z \leq 1 \)).

\[
4 \text{ F in } C2 \quad 4(c) \text{ with } x \approx 0.325, \quad y \approx 0.179, \quad z \approx 0.141 \text{ or } x \approx 0.325, \quad y \approx -0.179, \quad z \approx 0.141
\]

The latter alternative is excluded by the too short oxygen-fluorine distance of 1.9 Å.
CRYSTAL STRUCTURE OF InOHF₄

FINAL PARAMETERS

The parameters given below are the mean values of those found in the Patterson projections. The only exception is the oxygen γ parameter which is obtained only from the \( P(pvw) \) projection (in the \( P(uwp) \) projection, the In-O distance is hidden by the In-In peak). All values have been corrected by back shift calculations.

Thus the following structure is proposed for InOHF₄:

Space group No. 5-C2. Two formula units per unit cell.

<table>
<thead>
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<th></th>
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<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 In in 2(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2 O in 2(b)</td>
<td>0</td>
<td>0.14 ± 0.01</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>4 F in 4(c)</td>
<td>0.32 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.15 ± 0.01</td>
</tr>
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</table>

In Tables 2—4, the calculated structure factors are compared with the observed ones in the Weissenberg photographs \( h0l \), \( hkh \) and \( 0kl \). The reliability index

\[
R = \frac{|F_{\text{obs}}| - |F_{\text{calc}}|}{|F_{\text{obs}}|}
\]

is, for \( h0l \), \( hkh \) and \( 0kl \) 0.18, 0.20 and 0.15, respectively. However, for crystals like these containing both heavy and light atoms, the reliability index should not be taken as a definite proof that the structure as a whole is true but only that the arrangement proposed for the heavy atoms is essentially correct.

DESCRIPTION OF THE STRUCTURE

Figs. 3 and 4 show the structure of InOHF₄, projected along the \( b \) and \( c \) axes. In both projections, four adjacent unit cells are given so that the building principles of the structure will be more obvious.

If we describe our \( C \)-centered monoclinic lattice by a primitive triclinic lattice, the following unit cell dimensions are obtained: \( a = b = c = (3.874 \pm \ldots

Table 2. Comparison between calculated and observed structure factors \( h0l \) from a Weissenberg photograph of InOHF₄. CuK radiation.

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</table>

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Table 3. Comparison between calculated and observed structure factors \( h k 0 \) from a Weissenberg photograph of InO\(\text{H}^+\)\(\text{F}_2\). CuK radiation.

\[
\begin{array}{cccccccc}
  k & \rightarrow & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
  \text{calc} & k & 0 & - & - & 38 & - & 31 & - & 31 & - \\
  \text{obs} & & 43 & 43 & 43 & 25 & - & 23 & - & 23 & - \\
  \text{calc} & & 32 & 32 & 32 & 32 & 32 & 32 & 32 & 32 & 32 \\
  \text{calc} & & 33 & 33 & 33 & 33 & 33 & 33 & 33 & 33 & 33 \\
  \text{obs} & & 28 & 28 & 28 & 28 & 28 & 28 & 28 & 28 & 28 \\
  \text{obs} & & 21 & 21 & 21 & 21 & 21 & 21 & 21 & 21 & 21 \\
  \text{calc} & & 23 & 23 & 23 & 23 & 23 & 23 & 23 & 23 & 23 \\
  \text{obs} & & 14 & 14 & 14 & 14 & 14 & 14 & 14 & 14 & 14 \\
  \text{calc} & & 28 & 28 & 28 & 28 & 28 & 28 & 28 & 28 & 28 \\
\end{array}
\]

Table 4. Comparison between calculated and observed structure factors \( 0 k l \) from a Weissenberg photograph of InO\(\text{H}^+\)\(\text{F}_2\). CuK radiation.

\[
\begin{array}{cccc}
  l & \\
\hline
  \to & 0 & 1 & 2 & 3 & 4 \\
\hline
  \text{calc} & k & 0 & - & 46 & 37 & 19 & 21 \\
  \text{obs} & & 43 & 39 & 24 & 33 & 33 & 33 \\
  \text{calc} & & 33 & 33 & 33 & 33 & 33 & 33 \\
  \text{obs} & & 30 & 30 & 30 & 30 & 30 & 30 \\
  \text{calc} & & 26 & 26 & 26 & 26 & 26 & 26 \\
  \text{obs} & & 21 & 21 & 21 & 21 & 21 & 21 \\
  \text{calc} & & 29 & 29 & 29 & 29 & 29 & 29 \\
  \text{obs} & & 24 & 24 & 24 & 24 & 24 & 24 \\
\end{array}
\]

0.005 \(\text{Å}\) and \(\alpha = \beta = \gamma = 83.48^\circ \pm 0.02^\circ\). The triclinic cell can be regarded as a distorted cubic cell with approximately the same atomic arrangement as that found in Re\(\text{O}_2\)\(^{10}\). It is thus obvious that the indium atoms have a six coordination in which the calculated distances In-O and In-F are approximately the same.

Alternatively, the structure might be formally described as being built up of layers of (In\(\text{F}_2^+\))\(_{\infty}\) separated by oxygen atoms (Fig. 3) or as containing chains of In-O-In separated by HF\(_2^-\) ions (cf. below).

The interatomic distances for the structure proposed will be (in \(\text{Å}\)):

\[
\begin{align*}
\text{In-In} & = 3.87 \\
\text{In-O}_1 & = 2.08 \\
\text{In-F}_1 & = 2.06 \\
\text{In-F}_2 & = 2.11 \\
\text{F}_1^-\text{F}_2^- & = 2.4_6 \\
\text{O}^-\text{O}^- & = 3.8_6
\end{align*}
\]

* The agreement of the unit cell dimensions with those of a rhombohedral unit cell must be accidental since reflections which should be of equal intensity according to rhombohedral indices differ in intensity in the Weissenberg photographs.

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Fig. 3. The structure of InOHF₃, viewed along [001]. The dotted lines indicate the triclinic unit cell. (The range for the z parameter is $-0.859 \leq z \leq 0.141$.)

The error in the In-O and In-F distances is estimated to be $\pm 0.05$ Å and in the F-F and O-F distances $\pm 0.1$ Å. The In-O distances are about the same as those found in In₂O₃¹¹ and InOCl and InOBr¹. The shortest distance between oxygen and fluorine is somewhat shorter than that found in CeOF¹² and BiOF¹³ (2.83 and 2.88 Å).

Fig. 4. The structure of InOHF₃, viewed along [010]. (The range for the $y$ parameter $-0.375 \leq y \leq 0.625$.)

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The long O-O distances of 3.87 Å exclude the possibility that hydrogen bonds are present between the oxygen atoms. The short distances O-F (2.49 Å) and F-F (2.46 Å) do not differ significantly. They both seem to be consistent with probable values of hydrogen bond lengths (cf. Pauling 14, Wells 15). The fact that fluorine is more electronegative than oxygen might appear in favour of the existence of F-H-F bonds. On the other hand F-H-O bonds would give a more even distribution of the charge of the atoms.

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REFERENCES


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