The Crystal Structure of InOHF_2

HANS-ERIK FORSBERG

*Department of Inorganic and Physical Chemistry, University, and
Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden*

InOHF_2 has been investigated by X-ray methods. It has a monoclinic unit cell and the unit cell dimensions are

$$\begin{aligned} a &= (5.780 \pm 0.005) \text{ \AA} \\ b &= (5.157 \pm 0.005) \text{ \AA} \\ c &= (3.874 \pm 0.005) \text{ \AA} \\ \beta &= 98.74^\circ \pm 0.02^\circ \\ V &= 114.1 \text{ \AA}^3 \\ Z &= 2 \end{aligned}$$

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-6X 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 ReO_3 structure).

The crystal structure of the isomorphous compounds InOCl and InOBr has recently been determined¹ and in connection with this investigation attempts were made to prepare indium oxide fluoride. With the method described by Enslin and Dreyer², 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 InOHF_2 while Enslin and Dreyer gave the formula of their substance as $\text{InOF}\cdot\text{aq}$. This paper presents the structure determination of InOHF_2 .

PREPARATION OF THE CRYSTALS

Indium(III) fluoride^{2,3} 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 $\text{InF}_3(\text{H}_2\text{O})_3$ separated. After cooling, the crystals were filtered off, washed with water and dried in air.

Indium oxide fluoride was prepared as follows. A solution of 400 mg $\text{InF}_3(\text{H}_2\text{O})_3$ 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 InOHF_2 .

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 PbClF_4 .

For the determination of *indium*, a sample was dissolved in nitric acid, evaporated, and then ignited and weighed as In_2O_3 .

The *hydroxide* was determined as water by Hartwig-Bendig's modification of Penfield's method as described by Kolthoff and Sandell⁵.

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

	Found		Calculated for InOHF_2
% In	67.8	67.6	67.60
% F	22.9	23.0	22.38
% OH	9.5	9.5	10.01
Density	4.8 ₀	4.9 ₁	4.94 (cf. below)

UNIT CELL AND SPACE GROUP

From rotation (around $[100]$, $[010]$ and $[001]$) and Weissenberg photographs ($0kl$, $1kl$, $h0l$, $h1l$, $hk0$ and $hk1$), taken with CuK radiation, it was concluded that the crystals are monoclinic with $a \approx 5.8 \text{ \AA}$, $b \approx 5.1 \text{ \AA}$, $c \approx 3.9 \text{ \AA}$ and $\beta \approx 99^\circ$. More accurate values of the unit cell dimensions were calculated from a powder photograph in a focusing camera of Guinier type (cf. Table 1). ($\text{CuK}\alpha$ radiation, internal standard KCl with $a = 6.2930 \text{ \AA}$).⁶

$$\begin{aligned} a &= (5.780 \pm 0.005) \text{ \AA} \\ b &= (5.157 \pm 0.005) \text{ \AA} \\ c &= (3.874 \pm 0.005) \text{ \AA} \\ \beta &= 98.74^\circ \pm 0.02^\circ \\ V &= 114.1 \text{ \AA}^3 \end{aligned}$$

The mean value of the density is 4.90 so that there should be $1.98 \approx 2$ formula units InOHF_2 in the unit cell.

The only reflections systematically absent are

$$hkl \text{ with } h+k \text{ odd}$$

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

Table 1. Powder photograph of InOHF_2 . $\text{CuK}\alpha$ radiation. Internal standard KCl.
 $a = 6.2930 \text{ \AA}$.

hkl	$10^4 \sin^2 \Theta$ calc	$10^4 \sin^2 \Theta$ obs	pF^2 calc	I obs
001	405		53	
110	405	405	100	st
200	727		35	
111	727	728	73	st
111	891		55	
020	892	893	30	st
201	967	968	10	vw
201	1 297		26	
021	1 297	1 297	51	m
002	1 618		35	
220	1 619	1 620	78	m-
112	1 858	1 860	92	
310	1 859		94	m+
221	1 859		89	
202	2 016		24	
311	2 023	2 016	55	w
112	2 188		52	
221	2 189	2 188	49	m-
130	2 190		59	
311	2 505		52	
022	2 510	2 512	54	m-
131	2 512		48	
202	2 676		44	
131	2 676	2 677	86	m-
222	2 908		58	
400	2 909	2 911	24	vw
401	2 983		24	
312	2 983	2 985	49	vw-
222	3 568		33	
040	3 570	3 569	16	vw
003	3 641		9	
401	3 643	3 644	9	
132	3 643		19	vw
330	3 644		19	
113	3 799		30	
420	3 801	3 798	56	w
331	3 808		35	
402	3 867		34	
203	3 872	3 876	17	vw
421	3 875		33	
312	3 973		43	
132	3 973	3 974	49	w
041	3 975		44	
331	4 290		29	
113	4 293	4 292	32	vw+
240	4 297		29	
023	4 533		48	
421	4 535	4 531	29	w-
241	4 537		49	
313	4 759		27	
422	4 759		28	
511	4 761	4 762	40	w br
223	4 764		33	
510	4 768		34	
332	4 768		46	
203	4 862		23	
241	4 867	4 856	40	vw-

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

The intensities were calculated from the expression $0.05 \cdot \frac{p}{F^2}$ where p is the number

Fig. 1. The Patterson projection $P(upw)$ for InOHF_2 . In the peaks at $P(0p0)$ and $P(\frac{1}{2}p0)$ only every second contour has been drawn. Dashed lines indicate negative values.

PATTERSON SYNTHESSES

In the unit cell there are two indium, two oxygen and four fluorine atoms. To determine their positions, the Patterson projections, $P(upw)$, $P(pvw)$, and $P(uvp)$ 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 Lu⁸. 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 Booth⁹. In the space groups suggested by the extinctions, the possible point positions are as follows:

Fig. 2. The Patterson projections $P(pvw)$ and $P(uvp)$ for InOHF_2 . In the peaks at $P(p00)$ and $P(00p)$ only every third and second contour has been drawn. Dashed lines indicate negative values.

$C2/m$ $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) +$			
$2(a)$	$0,0,0;$	$4(e)$	$\frac{1}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{3}{4}, 0$
$2(b)$	$0, \frac{1}{2}, 0;$	$4(f)$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, \frac{1}{2}$
$2(c)$	$0, 0, \frac{1}{2};$	$4(g)$	$0, y, 0; 0, \bar{y}, 0$
$2(d)$	$0, \frac{1}{2}, \frac{1}{2};$	$4(h)$	$0, y, \frac{1}{2}; 0, \bar{y}, \frac{1}{2}$
		$4(i)$	$x, 0, z; \bar{x}, 0, \bar{z}$
Cm $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0)$ $C2$ $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0)$			
$2(a)$	$x, 0, z$	$2(a)$	$0, y, 0$
$4(b)$	$x, y, z; x, \bar{y}, z;$	$2(b)$	$0, y, \frac{1}{2}$
		$4(c)$	$x, y, z; \bar{x}, y, \bar{z}$

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 $\pm(\frac{1}{2}, \frac{1}{2}, 0)$ appear as pronounced maxima in the Patterson projections at $\frac{1}{2}, p, 0$, $p, \frac{1}{2}, 0$ and $\frac{1}{2}, \frac{1}{2}, p$.

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 $P(udp)$ 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 $w = \frac{1}{2}$ (the corresponding maximum in $P(udp)$ 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 $0 \leq x \leq \frac{1}{2}$, $0 \leq y \leq \frac{1}{2}$ and $0 \leq z \leq 1$).

2 O in $C2$ $2(b)$ with $y \approx 0.125$

The remaining maxima in $P(udp)$ 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 $0 \leq x \leq \frac{1}{2}$, $0 \leq y \leq \frac{1}{2}$ and $0 \leq z \leq 1$).

4 F in $C2$ $4(c)$ with $x \approx 0.325$, $y \approx 0.179$, $z \approx 0.141$ or
 $x \approx 0.325$, $y \approx -0.179$, $z \approx 0.141$

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

FINAL PARAMETERS

The parameters given below are the mean values of those found in the Patterson projections. The only exception is the oxygen y parameter which is obtained only from the $P(pvw)$ projection (in the $P(uvp)$ 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 InOHF_2 :

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

	x	y	z
2 In in 2(a)	0	0	0
2 O in 2(b)	0	$0.14_9 \pm 0.01$	$\frac{1}{2}$
4 F in 4(c)	$0.32_8 \pm 0.01$	$0.18_0 \pm 0.01$	$0.15_4 \pm 0.01$

In Tables 2—4, the calculated structure factors are compared with the observed ones in the Weissenberg photographs $h0l$, $hk0$ and $0kl$. The reliability index

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

is, for $h0l$, $hk0$ 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 InOHF_2 , 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: $a = b = c = (3.874 \pm$

Table 2. Comparison between calculated and observed structure factors $h0l$ from a Weissenberg photograph of InOHF_2 . CuK radiation.

		$l \rightarrow$								
		4	3	2	1	0	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$
calc	h $\downarrow$	0				—	45	37	19	21
							52	33	14	21
obs										
calc	2	26	30	42	32	38	20	31	26	27
obs		23	20	48	39	30	15	46	28	30
calc	4	—	21	23	19	31	29	37	27	24
obs			17	19	20	32	21	51	30	25
calc	6	—	—	24	25	31	24	22	16	—
obs				17	23	31	28	25	23	

Table 3. Comparison between calculated and observed structure factors $hk0$ from a Weissenberg photograph of InOHF_2 . CuK radiation.

	$k \downarrow$	$h \rightarrow$	0	1	2	3	4	5	6	7
calc		0	—	—	38	—	31	—	31	—
obs					43		43		41	
calc		1	—	44	—	43	—	25	—	23
obs				32		41		38		32
calc		2	31	—	37	—	31	—	20	—
obs			25		31		33		23	
calc		3	—	33	—	19	—	26	—	
obs				28		16		33		
calc		4	25	—	26	—	23	—		
obs			21		22		24			
calc		5	—	23	—	28	—			
obs				14		26				
calc		6	28	—	21					
obs			25		17					

Table 4. Comparison between calculated and observed structure factors $0kl$ from a Weissenberg photograph of InOHF_2 . CuK radiation.

	$k \downarrow$	$l \rightarrow$	0	1	2	3	4
calc		0	—	46	37	19	21
obs				44	39	24	33
calc		2	33	33	32	30	26
obs			26	30	30	39	30
calc		4	26	29	24	27	—
obs			21	24	23	28	
calc		6	29	23			
obs			24	19			

0.005) 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 ReO_3 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 $(\text{InF}_2^+)_\infty$ 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 Å):

In-In = 3.87	$\text{F}_1\text{—F}_2 = 2.9_3$ and 3.87
In-O ₁ = 2.08	$\text{F—F} = 3.0_8$ and 3.9 ₂ (between layers)
In-F ₁ = 2.06	O—O = 3.87
In-F ₂ = 2.11	O—F ₁ = 2.8 ₇ and 3.7 ₄
F ₁ —F ₁ = 2.4 ₆	O—F ₂ = 2.4 ₉ and 2.9 ₃
F ₂ —F ₂ = 3.8 ₀	

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

Fig. 3. The structure of InOHF_2 , 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 ± 0.05 Å and in the F-F and O-F distances ± 0.1 Å. The In-O distances are about the same as those found in In_2O_3 ¹¹ and InOCl and InOBr ¹. The shortest distance between oxygen and fluorine is somewhat shorter than that found in CeOF ¹² and BiOF ¹³ (2.83 and 2.88 Å).

Fig. 4. The structure of InOHF_2 , viewed along $[010]$. (The range for the y parameter $-0.375 \leq y \leq 0.625$.)

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.

Acknowledgements. The author is indebted to Professor Lars Gunnar Sillén for his helpful criticism and provision of laboratory facilities and to Professor Arne Ölander for his kind interest. The author wishes to thank Dr. Arne Magnéli and Dr. Georg Lundgren for many valuable discussions and Mr. D. G. Gillam for revising the English text.

Thanks are due to the *Consolidated Mining and Smelting Company of Canada, Ltd.* for generously supplying a large amount of indium metal of high purity.

REFERENCES

1. Forsberg, H.-E. *Acta Chem. Scand.* **10** (1956) 1287.
2. Enslin, F. and Dreyer, H. *Z. anorg. allgem. Chem.* **249** (1943) 119.
3. *Gmelins Handbuch der anorganischen Chemie* No. 37 Indium, Verlag Chemie, Berlin 1936.
4. Scott, W. W. *Standard Methods of Chemical Analysis*, D. van Nostrand Company Inc., New York 1948, Vol. 1, p. 404.
5. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*, Mac Millan Company, New York 1943, p. 753.
6. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
7. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1952, Vol. 1.
8. Lu, C.-S. *Rev. Sci. Instr.* **14** (1943) 331.
9. Booth, A. D. *Fourier Technique in X-ray Organic Structure Analysis*, University Press, Cambridge 1948, p. 64 and 101.
10. Meisel, K. *Z. anorg. allgem. Chem.* **207** (1932) 121.
11. Pauling, L. and Shappel, M. *Z. Krist.* **75** (1930) 128.
12. Finkelnburg, W. and Stein, A. *J. Chem. Phys.* **18** (1950) 1926.
13. Aurivillius, B. *Arkiv Kemi, Mineral. Geol.* **26B** (1948) 6.
14. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, New York 1945, p. 284.
15. Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press, 1950, p. 237.

Received January 25, 1957.