The Crystal Structure of Indium Oxide Chloride and Indium Oxide Bromide

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InOCl, and InOBr, have been investigated by X-ray methods. They have an orthorhombic unit cell. Their unit cell dimensions are

<i>InOCl</i>	<i>InOBr</i>
$a = (4.065 \pm 0.005) \text{ \AA}$	$a = (4.049 \pm 0.005) \text{ \AA}$
$b = (3.523 \pm 0.005) \text{ \AA}$	$b = (3.611 \pm 0.005) \text{ \AA}$
$c = (8.080 \pm 0.005) \text{ \AA}$	$c = (8.649 \pm 0.005) \text{ \AA}$
$Z = 2$	$Z = 2$

A structure is proposed with atomic positions for the indium, halogen, and oxygen atoms in space group No. 59, *Pmmn*. The parameters of the atoms were determined mainly from Patterson and Fourier projections.

The structures are built up of infinite In-O sheets separated by double halogen sheets. They may be described as being of a deformed BiOCl type and are isomorphous with the iron(III)oxide chloride, FeOCl.

Previously, in the Department of Inorganic Chemistry of the Royal Institute of Technology, Stockholm, the hydrolysis of In^{3+} has been studied and polynuclear complexes like In_2O^{3+} have been proved to occur.¹ In connection with this solution work, it was of interest to investigate the coordination between indium and oxygen in solid indium oxide salts. This paper presents a structure determination of indium oxide chloride and indium oxide bromide.

PREPARATION OF THE CRYSTALS

White microcrystalline powders were obtained using the methods described in Gmelin-Kraut's Handbuch (1936)² for preparing InOCl and InOBr. By hydrothermal hydrolysis of solutions of indium(III)chloride, only indium hydroxide could be prepared. However, by heating a mixture of indium(III)halide, indium hydroxide and some water at 300°C, crystals of indium oxide chloride and indium oxide bromide were obtained.

Indium(III)chloride and indium(III)bromide were prepared by dissolving indium metal (99.96 % pure from the Consolidated Mining and Smelting Company of Canada)

in hot conc. hydrochloric or hydrobromic acid, as described by Enslin and Dreyer^{3,4}. To oxidize lower oxidation states of indium to In^{3+} , some hydrogen peroxide was added towards the end of the reaction and the solution was then evaporated to dryness, giving $\text{InCl}_3(\text{H}_2\text{O})_4$ or InBr_3 .

Indium(III)hydroxide was prepared by precipitation from a solution of indium(III)-nitrate using aqueous ammonia. The precipitate was filtered off, washed with water several times and dried in air at room-temperature. It contained 64.3 % In, corresponding to a hydrated $\text{In}(\text{OH})_3$.

Indium oxide chloride was then prepared as follows. A mixture of 280 mg $\text{In}(\text{OH})_3$, 2 g $\text{InCl}_3(\text{H}_2\text{O})_4$ and 0.1 ml H_2O was sealed in a thick-walled glass tube and kept at 300°C in an oven. After 24 h, the tube was cooled and the melt leached with ethanol, thus dissolving the excess of InCl_3 . The residue was then filtered off and washed with ether. It consisted of clear crystals (plane needles) of InOCl and some indium hydroxide.

Indium oxide bromide was prepared in an analogous manner. The initial mixture consisted of 280 mg $\text{In}(\text{OH})_3$, 2.4 g InBr_3 and 0.2 ml H_2O . The crystals were of the same shape as those of InOCl .

The crystals of InOCl and InOBr are very slightly soluble in water but dissolve completely in dilute acids.

Analysis

A sample, dried in air, was decomposed by fusion with sodium carbonate. After cooling, the melt was leached with water and the residue filtered off. In the filtrate, the amount of *halide* was determined gravimetrically as silver halide⁵.

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

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

<i>InOCl</i>	Found	Calculated for <i>InOCl</i>
% Cl	19.8	20.0
% In	68.1	67.8
Density	4.6 ₄	4.6 ₄
		4.77
<i>InOBr</i>	Found	Calculated for <i>InOBr</i>
% Br	35.0	35.0
% In	55.2	55.2
Density	5.3 ₂	5.4 ₀
		5.53

The differences between the experimentally determined percentages of indium and halogen and those calculated from the formula InOX are probably due to slight contaminations of the samples, *e. g.* indium hydroxide.

UNIT CELL AND SPACE GROUP

A crystal was set with (010), the needle axis, as rotation axis and rotation and Weissenberg photographs (*h*0*l* and *h*1*l*) were taken with CuK radiation. From these photographs it was concluded that the crystals are orthorhombic with the following cell dimensions.

<i>InOCl</i>	$a \approx 4.1 \text{ \AA}$	<i>InOBr</i>	$a \approx 4.2 \text{ \AA}$
	$b \approx 3.5 \text{ \AA}$		$b \approx 3.6 \text{ \AA}$
	$c \approx 8.1 \text{ \AA}$		$c \approx 8.6 \text{ \AA}$

Table 1. Powder photograph of InOCl . $\text{Cu K}\alpha_1$ radiation. Photographs were taken with and without KCl as an internal standard. $a = 6.2930 \text{ \AA}$

hkl	$10^4 \sin^2 \Theta$ calc	$10^4 \sin^2 \Theta$ obs	pF^2 calc	I obs	hkl	$10^4 \sin^2 \Theta$ calc	$10^4 \sin^2 \Theta$ obs	pF^2 calc	I obs
001	91	90	29	w +	123	3089		40	
002	364	359	1	vw	115	3109	3090	48	vw
101	450	449	77	st	006	3272	—	1	—
011	569	568	16	w	301	3322	3324	34	w—
102	723	722	37	w	220	3348		80	
003	818	—	3	—	024	3366	3349	55	m—
110	837	836	22	m +	214	3368		1	
012	842	841	135	m +	221	3439	3439	36	w
111	928	928	90	w—	302	3595	3605	18	w
103	1177	1177	34	vw	106	3631		39	
112	1201	—	0	—	205	3708		24	
013	1296	1294	39	vw	310	3709		15	w—
200	1436		70		222	3712	3708	0	
004	1454	1437	42	m	124	3725		3	
201	1527	1528	29	w	016	3750	—	39	—
113	1655	1656	137	w	311	3800	3800	48	w
202	1800	—	0	—	303	4049	4049	20	vw
104	1813	—	2	—	312	4073	—	0	—
020	1912	1914	58	m +	116	4109	—	10	—
014	1932	—	0	—	223	4166	—	8	—
021	2003		27		025	4184	—	20	—
211	2005	2004	23	m	215	4186	—	6	—
203	2254	—	10	—	031	4393	4393	9	vw
005	2272		15		007	4453	—	3	—
022	2276		0		313	4527		78	
212	2278	2276	176	m	125	4543	4520	78	w—
114	2291		73		130	4661		14	
121	2362	2363	84	m	032	4666	4659	62	w
105	2631		55		304	4685	—	1	—
122	2635	2638	48	w—	206	4708	—	0	—
023	2730		12		131	4752	4749	29	vw
213	2732	2735	53	w—	224	4802	4797	84	w
015	2750		4		107	4812		16	
204	2890	2890	62	w					

Reflections systematically absent according to space group No. 59, $Pmmn$ have been omitted.

The intensities were calculated from the expression $0.1 \cdot \frac{p}{8} \cdot F^2$, where p is the number of equivalent reflections.

More accurate values were calculated from powder photographs in focusing cameras of Guinier type. (Tables 1 and 2) (CuK radiation, internal standard KCl . $a = 6.2930 \text{ \AA}$ *).

InOCl

$$\begin{aligned} a &= (4.065 \pm 0.005) \text{ \AA} \\ b &= (3.523 \pm 0.005) \text{ \AA} \\ c &= (8.080 \pm 0.005) \text{ \AA} \\ V &= 115.7 \text{ \AA}^3 \end{aligned}$$

InOBr

$$\begin{aligned} a &= (4.049 \pm 0.005) \text{ \AA} \\ b &= (3.611 \pm 0.005) \text{ \AA} \\ c &= (8.649 \pm 0.005) \text{ \AA} \\ V &= 126.5 \text{ \AA}^3 \end{aligned}$$

Table 2. Powder photographs of InOBr. CuK α_1 radiation. Photographs were taken with and without KCl as an internal standard. $a = 6.2920$ Å

hkl	$10^4 \sin^2 \Theta$ calc	$10^4 \sin^2 \Theta$ obs	pF^2 calc	I obs	hkl	$10^4 \sin^2 \Theta$ calc	$10^4 \sin^2 \Theta$ obs	pF^2 calc	I obs
001	79	79	20	w	115	2800	—	48	—
002	317	—	0	—	006	2856	—	3	—
101	441	441	135	st	123	2896	2895	68	vw—
011	534	534	1	vvw	024	3089	3088	69	vvw
102	679	680	8	vw	214	3172	—	4	—
003	714	—	4	—	106	3217	—	39	—
012	772	772	218	m+	220	3268	3267	135	m—
110	817	818	2	vw—	016	3311	—	34	—
111	896	896	137	st	301	3336	3336	62	w
103	1076	1076	48	vw	221	3347		23	
112	1134	1136	14	vvw	205	3431	3443	55	vvw
013	1169	1168	32	vw—	124	3451		53	
004	1269	1268	51	vw	302	3574	—	5	—
200	1448	1447	106	m	222	3585	—	1	—
201	1527	1530	18	m	116	3672	3664	102	vvw
113	1531		203		310	3712	—	2	—
104	1631	1631	37	vvw	311	3791	3791	78	w
014	1724	—	4	—	025	3803		51	
202	1765	—	0	—	215	3886	—	5	—
020	1820	1820	141	m	007	3887	—	0	—
021	1899	—	16	—	303	3971	3970	27	vvw
211	1982	1980	1	vvw	223	3981		4	
005	1983		34		312	4029	—	10	—
114	2086	2088	29	vvw	125	4165	4162	90	vvw
022	2137	—	0	—	031	4174	—	0	—
203	2161	—	3	—	107	4249	—	9	—
212	2220	2220	270	m	206	4303	—	4	—
121	2261	2261	160	m—	017	4342	4340	76	vvw
105	2345	2347	62	vvw	032	4412	4407	97	w—
015	2438	—	3	—	313	4426	4426	123	w—
122	2498	—	12	—	130	4457	—	2	—
023	2534	—	3	—	304	4526	4531	22	w
213	2616	2616	68	vw	131	4536		73	
204	2717	2715	72	vw—	224	4537	—	137	—

Reflections systematically absent according to space group No. 59 $Pmmn$ have been omitted.

The intensities were calculated from the expression $0.1 \cdot \frac{p}{8} \cdot F^2$, where p is the number of equivalent reflections.

From the observed densities given above, one could calculate that there must be $1.9_5 \approx 2$ formula units InOX in the unit cell.

The same reflections are systematically absent in both compounds and they are thus isomorphous: $hkl0$ absent with $h+k$ odd, which is characteristic of the space group No. 59, $Pmmn$?

PATTERSON SYNTHESSES

In order to find out the indium and halogen positions in the unit cell the Patterson projections, $P(upw)$, were calculated for both compounds (Fig. 1). Relative intensities of the reflections were estimated visually and the F^2 .

Fig. 1. The Patterson projection $P(uw)$ for InOCl (left) and InOBr (right). In the peak at the origin only every second contour has been shown. Dashed lines indicate negative values.

values calculated using the curves given by Lu⁸. In all syntheses the value of $F^2(000)$ has been omitted. Corrections for absorption have not been applied. The maxima have been located by an interpolation table given by Booth⁹.

Considering the space group, the indium atoms can only be situated in 2(a): $1/4, 1/4, z$; $3/4, 3/4, \bar{z}$; or 2(b): $1/4, 3/4, z$; $3/4, 1/4, \bar{z}$. The In-In vectors would then be $\pm(\frac{1}{2}, 2z)$ in the uw projection.

This must correspond to the pronounced maxima A in the projections at $u = \frac{1}{2}$ and $w = 0.244$ (for InOCl) and $w = 0.229$ (for InOBr). If we assume the indium atoms to be situated in the point position 2(a), we thus get the following parameters for the indium atoms (we need only consider the range $0 \leq z_{\text{In}} \leq 1/4$)

$$\text{InOCl: } z \approx 0.122$$

$$\text{InOBr: } z \approx 0.115$$

In addition to the In-In peaks, the Patterson projections show other distinct maxima and we can see that two of them (B_1 and B_2) increase in relative height from the InOCl to the InOBr projection, so they should correspond to distances between indium and halogen atoms. The halogen atoms should then be situated in 2(a) or 2(b) and the In-X vectors in the uw plane would be:

$$\begin{aligned} \text{I} & \pm(0, z_{\text{In}} - z_{\text{Br}}) \\ \text{II} & \pm(\frac{1}{2}, z_{\text{In}} + z_{\text{Br}}) \end{aligned}$$

If we now identify I and II with the peaks B_1 and B_2 in Fig. 1, we get the following values for the parameters of the X atoms (we need only consider the range, $0 \leq x \leq 1/4$, $0 \leq z \leq \frac{1}{2}$, if the range for the corresponding y parameter is $0 \leq y \leq 1$):

InOCl

2 Cl in 2(a) or 2(b) with $z_{\text{Cl}} \approx 0.344$

InOBr

2 Br in 2(a) or 2(b) with $z_{\text{Br}} \approx 0.335$

With this value for the Br parameter we could explain the D maximum as a Br-Br vector. The corresponding maximum for Cl-Cl is concealed by the In-In peak in the InOCl projection.

THE ELECTRON DENSITY FUNCTION

The electron density function was studied in order to locate the oxygen atoms and to get more accurate values for the parameters of the heavy atoms.

Since all the atoms of the structure must occupy twofold point positions (2(a) or 2(b)), the z parameter values may be determined from the line $x = 1/4$ of the projection $\rho(xpz)$ of the electron density function. This function was thus calculated using the signs of F_{obs} given by the indium and halogen contributions. Fig. 2 shows $(1/4, p, z)$ of InOBr. (The InOCl projection is of the

Fig. 2. Electron density of InOBr projected on the xz plane with $x = 1/4$.

Fig. 3. Electron density of InOBr projected on the xz plane and with $x = 1/4$ and the indium and bromine atoms subtracted.

same appearance.) It has two very pronounced maxima giving the positions of the indium atom (the highest maximum) and of the bromine atom (the lower maximum). The small peak at $z \approx 0.98$ might give the position of the oxygen atom. However, the peak may be a little displaced from the correct oxygen position by diffraction effects caused by the heavy atoms. To verify the oxygen position, a new electron density projection was calculated with the heavy atoms subtracted (Fig. 3).

Thus, from the electron density projections, the following parameters could be obtained:

<i>InOCl</i>	2 In	in	No. 59, <i>Pmmn</i>	2(a)	with $z = 0.121$
	2 Cl	»	»	2(a) or 2(b)	» $z = 0.345$
	2 O	»	»	2(a) or 2(b)	» $z = 0.97$
<i>InOBr</i>	2 In	in	No. 59, <i>Pmmn</i>	2(a)	with $z = 0.113$
	2 Br	»	»	2(a) or 2(b)	» $z = 0.336$
	2 O	»	»	2(a) or 2(b)	» $z = 0.98$

With these values for the oxygen parameters, we could explain the small maxima C_1 and C_2 in the Patterson projections in Fig. 1 as In-O distances.

GEOMETRICAL CONSIDERATIONS

From the electron density projections, we have only got values for the x and z coordinates. Now there are two possible values of the y coordinates for the halogen and oxygen atoms, viz. $y = 1/4$ or $3/4$, corresponding to the point position 2(a) or 2(b), and the correct ones can be found by considerations of space.

As 2(a) was arbitrarily chosen as the position of the indium atoms, the only possible sites for the halogen atoms will be in 2(b), since in 2(a) the distances In-X would be too short. (1.8 Å InOCl and 1.9 Å InOBr. In $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$, the In-Cl distance is 2.52 Å. Klug, Kummer and Leroy ¹⁰).

The distance In-O is 2.16 Å in In_2O_3 (Pauling and Shappel ¹¹) and we should expect about the same in InOX. If the oxygen atoms were situated in 2(a) we get too short distances (1.1 Å in InOCl and 1.2 Å in InOBr) and the oxygen atoms must thus be situated in 2(b).

FINAL PARAMETERS

The following structure is proposed for InOCl and InOBr. Space group No. 59, *Pmmn*. Two formula units per unit cell.

<i>InOCl</i>	2 In	in	2(a)	with $z = 0.121 + 0.002$
	2 Cl	in	2(b)	» $z = 0.345 + 0.004$
	2 O	in	2(b)	» $z = 0.97 + 0.01$
<i>InOBr</i>	2 In	in	2(a)	» $z = 0.113 + 0.002$
	2 Br	in	2(b)	» $z = 0.336 + 0.004$
	2 O	in	2(b)	» $z = 0.98 + 0.01$

Table 3. Comparison between calculated and observed structure factors $h0l$ from a Weissenberg photograph of InOCl . CuK radiation

h	$l \rightarrow$	0	1	2	3	4	5	6	7	8	9	10
$\downarrow$	0	—	+42 31	+4 —	-12 18	+51 59	-30 36	+9 —	+14 16	+31 31	+29 27	-5 1
	1	—	-47 59	-34 47	-32 32	-7 —	+41 38	+35 37	+22 22	+14 13	-20 27	-27 21
	2	-66 76	-30 35	-1 —	+12 16	+44 39	+25 17	-2 —	-12 12	-30 27	-26 25	
	3	—	+32 36	+24 37	+25 31	+5 —	-32 19	-29 29	-20 22	-12 9		
	4	+42 38	+20 27	+1 —	-10 15	-35 26	-21 21					
	5	—	-25 23	-19 18								

Table 4. Comparison between calculated and observed structure factors $h1l$ from a Weissenberg photograph of InOCl . CuK radiation

h	$l \rightarrow$	0	1	2	3	4	5	6	7	8	9
$\downarrow$	0	—	-30 20	-86 59	-46 43	+3 —	+15 16	+46 57	+36 42	-12 —	-12 17
	1	-35 34	-50 52	0 —	+61 48	+45 33	+22 38	+16 16	-36 42	-40 45	-23 23
	2	—	+25 36	+69 72	+38 41	-5 —	-13 11	-45 42	+35 38	+12 —	+20 20
	3	+28 46	+36 47	-3 —	-46 48	-38 42	-31 15	-15 10	+26 33		
	4	—	-16 28	-53 56	-28 33	+5 —	+12 11				

Table 5. Comparison between calculated and observed structure factors $h0l$ from a Weissenberg photograph of InOBr . CuK radiation

h	$l \rightarrow$	0	1	2	3	4	5	6	7	8	9	10
$\downarrow$	0	—	+27 13	+1 —	+12 10	-45 42	-37 42	+11 13	0 —	+16 14	+41 42	+5 —
	1	—	+52 67	-13 19	-31 34	-27 18	+35 31	+28 34	+13 22	+31 35	-3 —	-31 29
	2	-65 58	+19 30	+2 —	-7 —	+38 42	+33 29	-9 —	0 —	-15 21	-39 37	
	3	—	+35 45	+10 21	+23 30	+21 17	-27 27	-23 21	-11 20	-27 28		
	4	+44 48	+12 19	-3 —	+5 —	-30 25	-26 20					
	5	—	-26 15	-10 9								

Table 6. Comparison between calculated and observed structure factors $h1l$ from a Weissenberg photograph of InOBr. CuK radiation

$l \rightarrow$	0	1	2	3	4	5	6	7	8	9	10
$h \downarrow$											
0	—	—3	—66	—25	+9	—7	+26	+39	—4	—3	—7
		4	45	31	6	10	31	35	6	4	5
1	—6	—37	—12	+45	+17	+22	+32	—15	—27	—6	—23
	11	54	12	47	16	18	30	19	27	9	25
2	—	+3	—52	+26	—6	+7	—23	—36	+3	+5	
		9	55	31	4	—	21	30	4	—	
3	+6	+28	+10	—35	—17	—17	—27	+14	+24		
	13	36	9	33	19	15	18	16	21		
4	—	—2	—39	—21	+6	—4	+20				
		9	35	23	3	—	19				

In Tables 3—6 the calculated structure factors are compared with the observed ones in the Weissenberg photographs $h0l$ and $h1l$ of InOCl and InOBr. In all photographs, there is an absorption effect (*cf.* Wells ¹²) due to the shape of the crystals (plane needles) which is very pronounced for rays passing along the plane of the crystals. The line with this high absorption has been marked and the structure factors on either side of this line must not be compared with each other. Taking this absorption into account the agreement between calculated and observed structure factors is rather good, the reliability index $R = \frac{|F_{\text{obs}}| - |F_{\text{calc}}|}{|F_{\text{obs}}|}$ being for InOCl $h0l$ and $h1l$, 0.17 and 0.18 and for InOBr 0.21 and 0.19 ⁸. (With absent reflections included, InOCl 0.20 and 0.21, InOBr 0.23 and 0.22.) 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

Fig. 4 shows the structure of InOX. The indium and the oxygen ions form In-O-In layers which are separated by double halogen sheets. The arrangement of the metal and oxygen ions in the In-O sheets has been drawn separately in Fig. 5. The figure shows that the indium and oxygen ions form rectangular sheets and that each oxygen ion is tetrahedrally surrounded by four indium ions.

The indium oxide halides are evidently isomorphous with the iron(III)-oxide chloride, FeOCl (Goldsztaub ¹³).

The arrangement of the metal and oxygen ions in the InOX crystals is approximately the same as that found in the corresponding bismuth compounds (Šillén ¹⁴). In BiOX, the bismuth and oxygen ions form square sheets, but in InOX the indium and oxygen ions form rectangular networks.

Fig. 4. The structure of InOX , viewed along (010) .

Fig. 5. The In-O sheet. The figure shows the arrangement of the In^{3+} and O^{2-} ions, viewed along (001) .

The interatomic distances for the structure proposed will be (in Å):

<i>InOCl</i>	$\text{In} - \text{In} = 3.35$
	$\text{In} - \text{O}_1 = 2.1_7$
	$\text{In} - \text{O}_2 = 2.1_6$
	$\text{In} - \text{Cl} = 2.5_1$
	$\text{Cl}_1 - \text{Cl}_1 = 3.52 \text{ and } 4.07$
	$\text{Cl}_1 - \text{Cl}_2 = 3.6_9$
	$\text{Cl}_1 - \text{O}_1 = 3.6_8$
	$\text{Cl}_1 - \text{O}_2 = 3.0_5$
	$\text{O}_1 - \text{O}_2 = 2.7_4$

<i>InOBr</i>	$\text{In} - \text{In} = 3.35$
	$\text{In} - \text{O}_1 = 2.1_8$
	$\text{In} - \text{O}_2 = 2.1_5$
	$\text{In} - \text{Br} = 2.6_4$
	$\text{Br}_1 - \text{Br}_1 = 3.61 \text{ and } 4.05$
	$\text{Br}_1 - \text{Br}_2 = 3.9_4$
	$\text{Br}_1 - \text{O}_1 = 3.8_4$
	$\text{Br}_1 - \text{O}_2 = 3.0_8$
	$\text{O}_1 - \text{O}_2 = 2.7_4$

The error in the distances is assumed to be ± 0.1 Å, the only exception being the X_1-O_2 distances with an accuracy of about ± 0.15 Å. The distances from one indium atom to its four indium neighbours are in good agreement with those of 3.38 Å reported for In_2O_3 (Pauling and Shappel¹¹). The angles $In-O_I-In$ and $In-O_{II}-In$ are 139° and 109° in $InOCl$ and 136° and 114° in $InOBr$. The shortest distance between halogen and oxygen is somewhat shorter than that which is expected from the sums of the ionic radii (Cl^- 1.81 Å, Br^- 1.96 Å and O^{2-} 1.40 Å⁹) and which is usually to be found in structures of this type.

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