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The Crystal Structure of InOOH

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Single crystals of InOOH were prepared hydrothermally. InOOH is orthorhombic; the space-group is *Pnnm* with $a = 5.26$ Å, $b = 4.56$ Å, $c = 3.27$ Å and two formula units per unit cell.

The crystal structure was determined from a Patterson projection and from packing considerations and was refined to a conventional R-value of 6.8 %. The structure may be classified as a deformed rutile type. Each indium atom is octahedrally coordinated to six oxygen atoms. Atomic coordinates, temperature factors and other relevant crystallographic data are reported.

The system In_2O_3—H_2O has been investigated by one of us (ANC) as part of a larger programme concerned with preparation of single crystals by hydrothermal methods.

Previous results by Roy and Shafer [1] on the stability ranges of $In(OH)_3$, InOOH, and In_2O_3 in pure water were confirmed. Roy and Shafer [1] reported d-spacings of InOOH from Debye—Scherrer photographs. We found no other crystallographic data on this compound in the literature.

Hydrothermally prepared samples of InOOH contained single crystals large enough to be mounted on a X-ray goniometer. We decided to determine the crystal structure of this compound because the crystal chemistry of indium is not extensively investigated.

EXPERIMENTAL

Chemistry. InOOH was prepared in the temperature range 330—415°C at a pressure ranging from 120 atm. to 800 atm. by treating amorphous indium hydroxide with water or with a 0.1 to 0.3 M solution of NaOH.

A stainless steel autoclave with internal volume of 100 ml was employed. Solutions were placed in silver ampoules and the balanced pressure technique was used.

Indium was determined by EDTA titration using the method of van Nieuwenburg and van Ligten.[2] (Found: In 78.09. Calc. for InOOH: In 77.68.)

X-ray technique. Powder photographs were obtained with a quadruple Guinier-de Wolff camera using Cu$K\alpha_1$ radiation from a microfocus tube with a focal line of dimensions 6 mm × 0.1 mm The two middle compartments of the camera were employed, one containing highly purified NaCl for reference. The powder diagrams gave sharp lines permitting a reasonable accuracy in determination of unit cell dimensions.

A needle shaped single crystal of dimension: 0.05 × 0.05 × 0.1 mm³ was selected under the polarizing microscope. It was investigated by Weissenberg and precession methods. Integrated precession photographs were taken using Zr-filtered Mo-radiation of *h*0*l*, *h*1*l* and *h*2*l*. The needle axis proved to be 101.

56 independent reflexions were measured photometrically from timed exposures. The usual Lorentz-polarisation correction was done by digital computation. No absorption correction was applied.

STRUCTURE DETERMINATION

InOOH has an orthorhombic lattice with two InOOH units per unit cell. Most of the reflexions of observable intensity have $h + k + l = 2n$. A few reflexions with $h + k + l = 2n + 1$ are of measurable intensity. Systematic absences of the type 0*kl*: $k + l = 2n + 1$, *h*0*l*: $l + h = 2n + 1$ were noted. Possible space groups: *Pnn*2 No. 34 and *Pnnm* No. 58.

Evidently the indium atoms occupy a body centered lattice and the oxygen atoms belong to a primitive lattice. It is not possible to distinguish between oxygen atoms and hydroxyl groups from intensity measurements. Ideally they should be allocated positions not connected by symmetry operations.

The Patterson projection along the *b*-axis, Fig. 1, confirmed the positions of indium atoms upon a body centered lattice. It yielded peaks at 0.36, 0 and 0.14, 1/2. These were interpreted as In—O vectors and yielded directly *x* and *z* parameters.

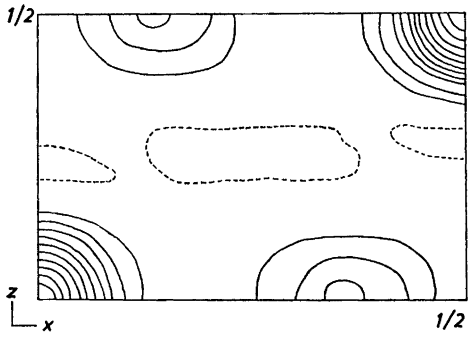

Fig. 1.
Patterson projection along *b*-axis.

The *y*-parameter was estimated from packing considerations. The trial structure was deformed rutile type. The structure could be described in the space groups *Pnn*2 or *Pnnm* assuming oxygen and hydroxyl groups to be equivalent.

This assumption is from a chemical point of view not satisfactory. Therefore refinement was carried out for several space groups:

1. Special form of *P*1: In on 0,0,0 and 1/2, 1/2, *z*, four oxygen atoms in general positions (13 geom. 6 thermal param.).
   $R = 6.32\ \%$
   $R' = \Sigma\,|F_o - k\,F_c|^2 \,/\, \Sigma\,|F_o|^2 = 4.906 \times 10^{-3}$
   $R'/n = R/37 = 1.33 \times 10^{-4}$
   n: = number of observations minus number of parameters.

2. $P2$ with In as in 1 and two oxygens in general two fold positions. (7 geom. 4 thermal param.).
   $R = 6.55\ \%$
   $R' = 5.088 \times 10^{-5}$
   $R'/45 = 1.12 \times 10^{-4}$
3. $Pnn2$: In atoms as in 1 and one oxygen in a general four fold position. (4 geom. 2 thermal param.).
   $R = 6.56\ \%$
   $R' = 5.29 \times 10^{-3}$
   $R'/50 = 1.05 \times 10^{-4}$
4. Special form of $P\bar{1}$: In on 0,0,0 and 1/2, 1/2, 1/2, two oxygens in general two fold positions. (6 geom. 4 thermal param.).
   $R = 6.68\ \%$
   $R' = 5.373 \times 10^{-3}$
   $R'/46 = 1.16 \times 10^{-4}$
5. $P2/m$ with In as in 4. One oxygen in x,y, 1/2 and another one in x,y, 0 (two fold positions). (4 geom. 4 thermal param.).
   $R = 6.77\ \%$
   $R' = 5.453 \times 10^{-3}$
   $R'/48 = 1.15 \times 10^{-4}$
6. $Pnnm$: In atoms as in 4 and one oxygen in a general fourfold position. (2 geom. 2 thermal param.).
   $R = 6.81\ \%$
   $R' = 5.617 \times 10^{-3}$
   $R'/52 = 1.08 \times 10^{-4}$

The refinement was carried out using the method suggested by Bhuiya and Stanley.[3] According to this method each parameter of the structure is varied in turn over a certain range, a residual is computed and the parameter giving the lowest residual is used in the next cycle of computations. An ALGOL programme by Danielsen [4] was used for the refinement. The programme employs individual isotropic temperature factors.

An R-value of 13.1 % was obtained on inserting the In atoms only in the structure factor calculations. The trial structure using space group $P1$ with both In and O atoms yielded an R-value of 7.1 %.

The parameters obtained in the different refinements do not vary significantly. In all cases a non centric space group led to negative temperature factors for the oxygen atoms, whereas all temperature factors have physically reasonable values assuming a centric space group.

Considering the small size of the crystal it is unlikely that absorption correction should be large enough to make temperature factors negative.

The space group $Pnnm$ yields the structure which with a minimum of parameters gives the best agreement between observations and calculations.

CRYSTAL DATA

The quantitative crystallographic data obtained are reported below. Crystal system: orthorhombic

$$a = 5.26 \pm 0.01 \text{ Å}$$
$$b = 4.56 \pm 0.01 \text{ Å}$$
$$c = 3.27 \pm 0.01 \text{ Å}$$

Space group: No. 58 *Pnnm*
Density, calculated (for two formula units in the elementary cell): 6.25 g/cm³. Density determined pycnometrically 7 ± 0.7 g/cm³.

Table 1 shows atomic coordinates and temperature factors with their standard deviations. Table 2 gives interatomic distances. Figs. 2 and 3 are axonometric drawings of the structure.

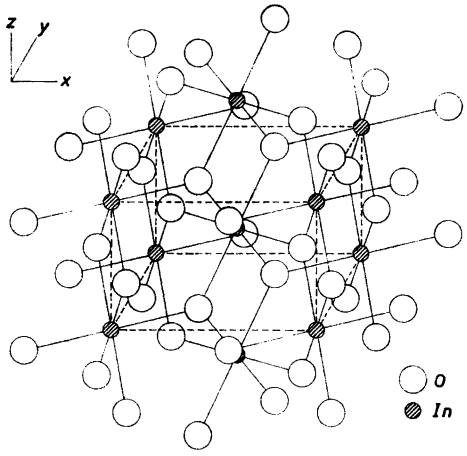

Fig. 2. Axonometric drawing of unit cell showing coordination of indium atoms

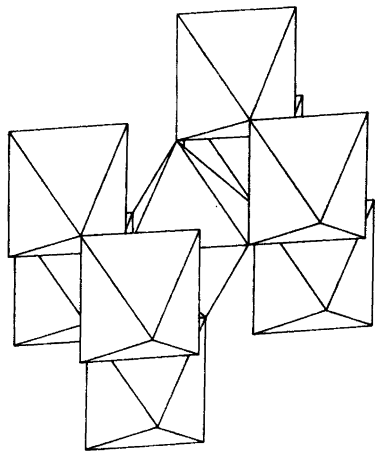

Fig. 3. Packing of In—O_6 octahedra.

A list of calculated and observed structure factors has been sent to the editor but is not printed to save space. The authors will gladly supply copies of this table on request.

The structure factors were calculated using the atomic scattering factors from Vol. III of *International Tables of Crystallography* and the interpolation formula of Bassi.[5] Table 3 shows the indexing of the powder pattern. Optical

Table 1. Atomic coordinates and temperature factors.

Atom	x	y	z	B (Å²)
In	0.000	0.000	0.000	0.50 ± 0.04 two fold position
O	0.3649 ± 0.0045	0.2362 ± 0.016	0.000	04.5 ± 0.36 four fold position

Table 2. Interatomic distances in Å.

	Within octahedrons:		Between neighbouring octahedrons:	
In–O	2.15 ± 0.014		O–O	2.58
In–O	2.20 ± 0.014			
O–O	2.79			
	3.06			
	3.10			
	3.27			

Table 3. Indexing of the powder pattern of InOOH. $a = 5.26$ Å, $b = 4.56$ Å, $c = 3.27$ Å.

d measured	*d* calculated	*hkl*	Optical density *j*
3.444	3.446	110	100
2.776	2.777	101	87
2.658	2.657	011	87
2.629	2.630	200	68
2.367	2.372	111	13
2.279	2.280	020	23
	1.870	021	
1.869			80
	1.869	211	
1.762	1.762	121	57
1.721	1.723	220	32
1.635	1.635	002	66
1.545	1.545	301	63
1.477	1.477	112	50
1.461	1.460	130	17
1.388	1.389	202	28
1.379	1.378	031	8
1.328	1.328	212	13
1.315	1.316	230	11
1.279	1.279	321	18
	1.221	231	
1.220			14
	1.220	401	
1.185	1.185	222	14
1.178	1.179	411	25

densities of the lines were measured using a recording Joyce-Loebl double beam microdensitometer. No effort was made to obtain accurate intensities.

DISCUSSION

Oxygen atoms are octahedrally coordinated to indium atoms. One set of octahedra sharing edges are stacked along the (001) direction. These octahedra contain indium on (000). Another set of octahedra sharing edges and containing indium on (1/2, 1/2, 1/2) are also stacked along 001. The two sets

of octahedra share corners. They are further held together by a hydrogen bond with an O—O distance of 2.58 Å.

The octahedra are distorted. Table 2 shows two sets of In—O distances in the octahedra: 2.20 Å and 2.15 Å. The difference between the two sets of distances is more than three times the standard deviation.

The structure contains a considerable amount of void space, and so the compound probably has ion-exchange properties.

The In—O distances reported here are within 0.05 Å similar to corresponding distances in $InOHSO_4$, $(H_2O)_2$ (Johansson [6]) and in InOCl, InOBr and $InOHF_2$ (Forsberg [7]).

REFERENCES

1. Roy, R. and Shafer, M. W. *J. Phys. Chem.* **58** (1954) 372.
2. van Nieuwenburg, C. J. and van Ligten, J. W. L. *Quantitative Chemical Micro-Analysis* Elsevier, Amsterdam 1963.
3. Bhuiya, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.
4. Danielsen, J. Algol program D45, printed in this laboratory.
5. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
6. Johansson, G. *Acta Chem. Scand.* **15** (1961) 1437.
7. Forsberg, H. E. *Acta Chem. Scand.* **10** (1956) 1287; **11** (1957) 676.

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