THE PREPARATION AND PROPERTIES OF INDIUM DICHLORIDE.

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Although the existence of indium dichloride has never been questioned, it has equally never been satisfactorily proved. The usual preparative methods yield a substance whose composition approximates to $InCl_2$ but analyses vary considerably; and the reaction with water, the final products of which are metallic indium and the trichloride,[1] is very unusual in a halide. Also, from the position of indium in the Periodic Table the expected chlorides would be InCl and $InCl_3$ and not $InCl_2$ as such, although the latter might be considered as a loose molecular associate of the two stable chlorides. The vapour density evidence of Nilson and Pettersson [2] is inconclusive since the values obtained (at 606° C. obs. 8·15; calc. for $InCl_2$ 7·58) might equally well be produced by mixtures of InCl, $InCl_3$ and chlorine.

The customary method of preparation, *i.e.* by the action of dry HCl on metallic indium [1, 3] has several disadvantages, *e.g.* if the slightest trace of moisture is present irreversible formation of $InCl_3$ occurs and, in the presence of oxygen, the oxychloride InOCl is formed. Klemm,[4] using carefully controlled temperatures and in the presence of carbon dioxide, still found a tendency for the formation of the trichloride even at temperatures as low as 420°, while below 320° the chlorine content was too low (37·14 per cent. obs.; 38·18 per cent. calc.). Klemm [4] also examined the interaction of the metal and the trichloride as a possible preparative method and concluded that the liquid dissociates to some extent into the mono- and tri-chlorides :—

$$2\ InCl_2 \rightarrow InCl + InCl_3.$$

By the use of a mixture of hydrogen and HCl the presence of any traces of InOCl or $InCl_3$ can be avoided. It was found that if the trichloride was heated in a stream of hydrogen in an apparatus similar to that used by Mathers [5] for the preparation of the trichloride, a gradual reduction to the metal took place; the stage $InCl_3 \rightarrow InCl_2$ readily and quantitatively at about 600° C (just above the sublimation point of the trichloride) and the stage $InCl_2 \rightarrow InCl$ with more difficulty at about 700°. The oxychloride, although only slowly affected by hydrogen alone, is readily attacked by a mixture of hydrogen and HCl.

If the mixture of gases contained rather less than 20 per cent. HCl, and the working temperature did not exceed 600°, the reduction was completely stopped at the dichloride stage. The complete absence of water and oxygen in the HCl (difficult to ensure) is now unnecessary since any formation of InOCl and $InCl_3$ is precluded. Another advantage of this method is that the starting material need not be metallic indium, but may

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[1] A. Thiel, *Z. anorg. Chem.*, 1904, **40**, 328.
[2] Nilson and Pettersson, *Z. physik. Chem.*, 1888, **2**, 657.
[3] L. de Boisbaudran, *Comptes Rend.*, 1888, **100**, 701.
[4] Klemm, *Z, anorg. Chem.*, 1926, **152**, 252.
[5] Mathers, *J. Am. Chem. Soc.*, 1907, **29**, 495.

be the hydroxide or the trichloride, the latter probably being the better. The trichloride was prepared by the method of Mathers [5] from $In(OH)_3$ which had been dried at 100°. The presence of iron chlorides colours the $InCl_3$ yellow; these can be easily separated by fractional sublimation. The same apparatus was used for the reduction to the dichloride, it being possible to pass in pure dry HCl, hydrogen or nitrogen either together or separately. A slow stream of hydrogen containing about 15 per cent. HCl was passed over the $InCl_3$, while the tube was heated to low redness at the constriction. The dichloride collected as a yellow liquid in the second bulb and was gradually distilled along the tube in the same gaseous mixture. It was then heated just above its melting-point in a slow stream of nitrogen for about ½ hour to remove HCl, allowed to cool and sealed off.

The final product was a white glassy solid melting *sharply* to a very pale yellow liquid, which solidified equally sharply. The melting-point, measured in an atmosphere of nitrogen with a micro-thermocouple (copper-constantan in a Pyrex capillary), was 235° ± 1° C and the boiling-point approximately 570° C. Cl found = 38·07 per cent.; theoretical value, 38·19 per cent. In found = 61·60 per cent.; theoretical value, 61·81 per cent.

In the liquid phase there is some tendency for the dichloride to dissociate into the mono- and tri-chlorides; this dissociation is also produced by the action of water (*cf.* indium dibromide) followed by the decomposition of the monochloride into indium and the trichloride. Indium oxychloride and trichloride are produced by the action of steam, while moist air produces the metal in addition to these compounds. If the dichloride is heated strongly in moist air, InOCl and $InCl_3$ are first produced, and at higher temperatures the oxychloride decomposes to In_2O_3 and $InCl_3$.

A striking feature of the properties of indium dichloride is its strong resemblance in physical properties to anhydrous stannous chloride (first mentioned by Klemm) [4] *viz.* :—

	Indium Dichloride.	Anhydrous Stannous Chloride.
Appearance.	White glassy solid with a conchoidal fracture. Hygroscopic.	White glassy solid with a conchoidal fracture. Hygroscopic.
Specific gravity.	3·64 *	3·90 †
Melting-point.	235° C.‡	246·8° C.[6]
Liquid.	Pale yellow, darkening with increasing temperature.	Pale yellow, darkening with increasing temperature.
Boiling-point.	*ca.* 570°.	606°.[7]
Crystallographic data (see X-ray section).	Orthorhombic. $b_0 = 9\cdot64 \pm 0\cdot06$ Å. $a : b : c = 0\cdot710 : 1 : 1\cdot093$	Orthorhombic. $b_0 = 9\cdot34 \pm 0\cdot04$ Å. $a : b : c = 0\cdot708 : 1 : 1\cdot069$

* Klemm [4] also gives 3·64. † Klemm gives 3·95. ‡ Klemm gives 235°.

In this connection it is noteworthy that the specific conductivities of the fused substances are unequal; that of stannous chloride being considerably greater than that of indium dichloride.[4] This similiarity gives weight to the supposition that, in the solid state, the dichloride is a definite compound. Since it seemed possible that the two solids might be isomorphous an X-ray examination of the pure chlorides was undertaken.

Preparation of Anhydrous Stannous Chloride.—Commercial $SnCl_2$, $2H_2O$ was heated in a pyrex distillation apparatus in a stream of dry HCl until frothing ceased. It was then distilled over, collected and redistilled in the same apparatus. The distillate was kept just above its melting-

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[6] Kendall, Crittenden and Miller, *J. Am. Chem. Soc.*, 1923, **45**, 963.

[7] Bilz and Meyer, *Z. physik. Chem.*, 1888, **2**, 184.

point, first in dry HCl and then in dry nitrogen and finally poured off and stored in a vacuum desiccator over P_2O_5.

Density Measurements.—The densities of the solid chlorides were measured in dry nitrobenzene which had been stood over anhydrous sodium sulphate and distilled three times. The mean of several determinations gave 3·90 for stannous chloride and 3·64 for indium dichloride.

X-Ray Technique.—Although crystallographic measurements of anhydrous stannous chloride have been reported by Nordenskjöld [8] who stated that the crystals belong to the orthorhombic system with $a : b : c = 0{\cdot}7366 : 1 : 1{\cdot}068$, many attempts in this present work to obtain satisfactory single crystals have been unsuccessful, *e.g.* (a) by sublimation both above and below the melting-point of the chloride (the former in vacuo); (b) by crystallisation from many solvents such as absolute alcohol, ether, benzene, *o*-dichlorobenzene and thionyl chloride; very small clusters of crystals were obtained from absolute alcohol but it was impossible to separate out any single crystals; (c) by the hot-wire method of Bernal and Crowfoot.[9] As no direct experimental details of the method employed by Nordenskjöld were available, his method for the preparation of a single crystal could not be attempted and thus the X-ray analyses could only be carried out on powdered samples of the chlorides.

Similarly it was not found possible to obtain single crystals of indium dichloride by any of the above methods.

Experimental.

The specimens were ground in a desiccator over P_2O_5. During the exposure, the indium dichloride specimens were supported in thin Lithia glass tubes (0·5 mm diameter) which were sealed at both ends. These tubes were used in order to prevent any possibility of the dichloride taking up water during the exposure with its subsequent decomposition.[4] Again for the same reason the exposures were completed as rapidly as possible by using a small diameter camera; the exposure time being about 20 minutes. This limits the accuracy of the ultimate lattice constants but the photographs were poor and the object of the work is more to show the similarity of the two substances rather than the precision determination of the lattice constants. The stannous chloride specimens were supported in thin collodion tubes (0·5 mm. diam.) and photographed in a larger diameter camera as the danger of decomposition is not nearly so great as with indium dichloride. The glass tubes were found to be unsuitable in this case owing to the production of a very high background density.

Cu $K\alpha$ radiation was used for the final experimental work. Mo radiation was tried in the preliminary experiments and produced clearer photographs but the lines were too close for measurement (even when filtered with zirconium oxide). Fe radiation produced photographs whose density was too great for any measurements to be attempted. In all cases dilution of the specimens with pure dry starch (*cf* Davey) [10] had little or no effect.

Pure, dry sodium chloride was used for calibration purposes and was separated from the main sample by means of a plug of cotton wool.

In all cases the strictest precautions were taken to prevent the entrance of moisture during the grinding and exposures of the samples.

The specimens were oscillated through a 10° arc during the exposures. The values of the reflection angles, in angular measure, were averaged from the separate films (two for indium dichloride and three for stannous chloride).

All the resulting powder photographs were very poor, possessing a high background density making measurement difficult and for these reasons

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[8] Nordenskjöld, *Bihang. K. Sv. Vet-Akad. Handl.*, 1874, **2**, no. 2.

[9] Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1032.

[10] W. P. Davey, *Study of Crystal Structure and its Applications* (New York), 1934, p. 118.

the visual intensities reported in the tables must be treated with caution. It was found possible to measure with certainty 17 lines for indium dichloride and 16 lines for stannous chloride; only those lines whose existence on either side of the centre was in no doubt have been used in the calculations.

The calculated values of d for both the chlorides were found to fit the same logarithmic plot for orthorhombic crystals [11] at the approximate axial ratios $a : b : c = 0{\cdot}71 : 1 : 1{\cdot}1$ from which the indices marked * in tables were obtained. The calculated values of the lattice constants obtained from these indices were utilised to index the remaining planes which could not be indexed directly from the plot owing to its complexity at low values of d.

For orthorhombic crystals the quadratic form for each reflection, assuming zero errors, is :—

$$A_0 \,.\, hi^2 + B_0 \,.\, ki^2 + C_0 \,.\, li^2 = \text{Sin}^2\,\theta$$

where : A_0, B_0 and C_0 are respectively $\lambda^2/4a_0^2$; $\lambda^2/4b_0^2$; $\lambda^2/4c_0^2$.

The observation equations for each reflection were combined, by Gauss's method,[12] yielding three normal equations which were solved, by determinants, for A_0, B_0 and C_0† :—

$$\begin{aligned} A_0\Sigma h^4 + B_0\Sigma h^2k^2 + C_0\Sigma h^2l^2 &= \Sigma h^2\,\text{Sin}^2\,\theta \\ A_0\Sigma h^2k^2 + B_0\Sigma k^4 + C_0\Sigma k^2l^2 &= \Sigma k^2\,\text{Sin}^2\,\theta \\ A_0\Sigma h^2l^2 + B_0\Sigma k^2l^2 + C_0\Sigma l^4 &= \Sigma l^2\,\text{Sin}^2\,\theta \end{aligned}$$

TABLE I.—INDIUM DICHLORIDE.

Mean camera diameter = $57{\cdot}48_4$ mm. Cu $K\alpha$ = 1·539 Å.

Indices.	Intensity.	$\theta°$.	$d_{exp.}$	$d_{theor.}$	$\sin^2\theta_{exp.}$	$\sin^2\theta_{theor.}$
*110	vs	7° 59′	$5{\cdot}54_1$	$5{\cdot}58_4$	0·0193	0·0190
*020	s	9 8	$4{\cdot}84_8$	$4{\cdot}82_0$	0·0252	0·0256
*102	m	10 34	$4{\cdot}19_6$	$4{\cdot}17_6$	0·0336	0·0335
*112	m	11 32	$3{\cdot}84_9$	$3{\cdot}83_3$	0·0400	0·0399
*200	vs	12 58	$3{\cdot}42_9$	$3{\cdot}42_5$	0·0504	0·0505
113	s	14 47	$3{\cdot}01_6$	$2{\cdot}97_4$	0·0651	0·0660
220	vs	15 59	$2{\cdot}79_5$	$2{\cdot}79_2$	0·0758	0·0761
224	w	23 31	$1{\cdot}92_9$	$1{\cdot}91_7$	0·1592	0·1597
330	vw	24 27	$1{\cdot}85_9$	$1{\cdot}86_1$	0·1713	0·1711
342	vw	29 5	$1{\cdot}58_3$	$1{\cdot}57_7$	0·2362	0·2368
430	s	30 41	$1{\cdot}50_8$	$1{\cdot}51_1$	0·2604	0·2595
432	m	32 3	$1{\cdot}45_0$	$1{\cdot}45_3$	0·2816	0·2804
532	vw	38 51	$1{\cdot}22_7$	$1{\cdot}22_6$	0·3935	0·3940
505	m	42 16	$1{\cdot}14_4$	$1{\cdot}14_9$	0·4524	0·4526
615	w	50 18	$1{\cdot}00_0$	$0{\cdot}99_9$	0·5920	0·5914
711	w	52 29	$0{\cdot}97_0$	$0{\cdot}97_0$	0·6291	0·6301
713	w	55 6	$0{\cdot}93_8$	$0{\cdot}93_8$	0·6727	0·6719

Combination of the 17 observation equations using the values of $\sin^2\theta_{exp.}$ and solution of the resulting three normal equations yields the final equation :—

$$0{\cdot}0126_2\, h^2 + 0{\cdot}0063_7\, k^2 + 0{\cdot}0053_3\, l^2 = \sin^2\theta$$

from which :—

$a_0 = 6{\cdot}8_5 \pm 0{\cdot}04$ Å. $\quad a_0/b_0 = 0{\cdot}710 \pm 0{\cdot}012$
$b_0 = 9{\cdot}6_4 \pm 0{\cdot}06$ Å.
$c_0 = 10{\cdot}5_4 \pm 0{\cdot}06$ Å. $\quad c_0/b_0 = 1{\cdot}093 \pm 0{\cdot}008$

Density for 8 molecules of $InCl_2$ or 4 molecules of In_2Cl_4 = 3·53.
Experimental density = 3·64.

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[11] Fairbanks, *Laboratory Investigation of Ores* (New York, 1928), p. 79.

[12] Mellor, *Higher Mathematics*, p. 557.

† *Cf.* M. U. Cohen.[13] The correct form of Cohen's equation, *i.e.* with the addition of the "drift constant D" was not used as it was considered unnecessary owing to the large experimental error resulting from the poor powder photographs.

[13] M. U. Cohen, *Rev. Sci. Instr.*, 1935, **6**, 68.

TABLE II.—ANHYDROUS STANNOUS CHLORIDE.

Mean camera diameter = 104·95 mm. Cu $K\alpha$ = 1·539 Å.

Indices.	Intensity.	$\theta°$.		$d_{exp.}$	$d_{theor.}$	$\sin^2 \theta_{exp.}$	$\sin^2 \theta_{theor.}$
*110	vs	8°	11′	5·408	5·402	0·0203	0·0204
*102	m	11	3	4·014	3·983	0·0367	0·0373
*112	s	12	8	3·661	3·664	0·0442	0·0441
*022	s	13	1	3·417	3·411	0·0506	0·0509
130	w	15	52	2·815	2·815	0·0747	0·0748
032	s	16	59	2·634	2·641	0·0853	0·0850
203	vs	19	11	2·342	2·344	0·1080	0·1076
230	w	19	59	2·252	2·265	0·1168	0·1155
310	w	21	4	2·141	2·143	0·1292	0·1289
311	m	21	29	2·101	2·095	0·1341	0·1348
224	m	24	53	1·829	1·832	0·1771	0·1763
313	w	25	13	1·806	1·802	0·1815	0·1822
410	w	28	7	1·624	1·626	0·2245	0·2239
342	vw	30	13	1·529	1·525	0·2533	0·2547
423	m	33	7	1·409	1·410	0·2984	0·2976
404	w	33	56	1·379	1·377	0·3116	0·3119

Solution of the three normal equations yields :—

$$0{\cdot}0135_7 h^2 + 0{\cdot}0067_9 k^2 + 0{\cdot}0059_4 l^2 = \mathrm{Sin}^2\,\theta$$

from which :—

a_0 = 6·61 ± 0·03 Å. a_0/b_0 = 0·708 ± 0·009
b_0 = 9·34 ± 0·04 Å.
c_0 = 9·98 ± 0·04 Å. c_0/b_0 = 1·069 ± 0·006

Density for 8 molecules of $SnCl_2$ or 4 molecules of Sn_2Cl_4 = 4·06.
Experimental density = 3·90.

The deviation of the theoretical densities from the experimentally measured values, for both the chlorides, lies within the experimental error of the lattice constant determinations. When comparing the above experimental axial ratios for stannous chloride with those given by Nordenskjöld,[8] it must be remembered that although, in his paper, the figures are stated to be only approximate they are given to 4 decimal places; in addition the author appears to be in doubt as to the purity of his sample.

It should be noted that seven preparations of indium dichloride and five of stannous chloride yielded identical powder diagrams; the latter including a preparation by the action of dry HCl on metallic tin.

The preparation and analysis show that, in the solid state, indium dichloride is a definite chemical entity and this is confirmed by the X-ray evidence. Its very close resemblance to anhydrous stannous chloride shows that it cannot be a " molecular " compound of the residual valency type. That this resemblance to some extent persists in the liquid phase is shown by the similar, but by no means equal, specific conductivities and boiling-points.

It is now reasonable to assume that the vapour density values of Nilson and Pettersson [2] are actually due to the presence of associated molecules of In_2Cl_4, more particularly so since this effect is also observed with stannous chloride.[14] The solids are no doubt completely associated to compounds of the type M_2Cl_4, as in the case of anhydrous cupric chloride and other anhydrous metallic chlorides. The fact that molecular weight determinations of stannous chloride in organic solvents [15, 16] indicate that it exists as single molecules cannot be taken

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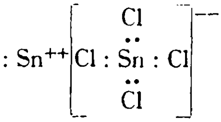
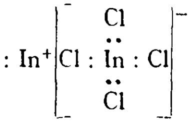
[14] Biltz and Meyer, *Ber.*, 1888, **21**, 22.
[15] Werner and Schuler, *Z. anorg. Chem.*, 1897, **15**, 1.
[16] N. Castoro, *Gazz. Chim. Italiana*, (ii), 1898, **28**, 317.

as evidence for the molecular condition of the soild (*cf.* for example molybdenum dichloride, which is trimolecular in the solid[17] although unimolecular in urethane;[18] the latter being one of the solvents used for the molecular weight determination of anhydrous stannous chloride).[16] Stannous chloride (*cf.* cupric chloride) is probably derived from H_2SnCl_4 with the following structure:



$$:\mathrm{Sn}^{++}\left[\begin{array}{c}\mathrm{Cl}\\ \mathrm{Cl} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Sn}}} : \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right]^{--}$$

Similarly indium dichloride is probably derived from $HInCl_4$:—



$$:\mathrm{In}^{+}\left[\begin{array}{c}\mathrm{Cl}\\ \mathrm{Cl} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{In}}} : \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right]^{-}$$

These structures, although differing in ionic charges, have identical electronic configurations, which would lead to strong physical similarities between the two chlorides. The larger ionic charge of anhydrous stannous chloride would also account for its greater conductivity in the fused state.[4]

It may be supposed that these complex ions are relatively unstable, being decomposed by solvents and partly dissociated on fusion (more particularly so on vaporisation). The breakdown of the complex $SnCl_4^{--}$ ion will lead to the formation of Sn^{++} and Cl^- ions, *i.e.* simply ionised $SnCl_2$, *viz*:—

$$\mathrm{Sn^{++}[SnCl_4]^{--}} \rightarrow 2\,\mathrm{Sn^{++}} + 4\mathrm{Cl^-}$$

while that of the $InCl_4^-$ ion will give In^+, In^{+++} and Cl^- ions, *viz*:—

$$\mathrm{In^+[InCl_4^-]^-} \rightarrow \mathrm{In^+} + \mathrm{In^{+++}} + 4\mathrm{Cl^-}.$$

The above reactions provide a logical explanation of the action of water and heat on indium dichloride. The yellow colour of the fused chlorides can then be explained by the presence of small quantities of stannous chloride ($SnCl_2$) and indium monochloride respectively. This is supported by the observation that if indium dichloride is heated in a sealed, evacuated tube (*i.e.* under conditions favourable to this dissociation) and suddenly cooled, the solid is coloured yellow or red.

We wish to point out that the suggested structures are based on chemical rather than X-ray evidence.

Summary.

A new method for the preparation and the chief properties of indium dichloride are described.

This substance is shown to be similar in physical properties to anhydrous stannous chloride. X-ray analysis shows both substances to belong to the orthorhombic system with similar lattice constants.

Evidence is presented to support the view that both substances are associated in the solid state.

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[17] Blomstrand, *J. prakt. Chem.*, 1861, **82**, 423.

[18] Ephraim, *Inorganic Chemistry* (*English Trans.*), 1934, p. 239.