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The Structures of Yellow and Red Indium Monochloride

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Abstract. InCl (yellow, room-temperature form), cubic, $a = 12{\cdot}373\,(1)$ Å (at 293 K), $Z = 32$, space group $P2_13$. 820 independent reflexions were measured. Conventional R index was 0·03 ($R_w = 0{\cdot}03$). The compound has a highly deformed rock-salt structure. InCl (red, high-temperature form), orthorhombic, β-TlI structure ($B33$), $a = 4{\cdot}242\,(2)$, $b = 12{\cdot}32\,(1)$, $c = 4{\cdot}689\,(4)$ Å (at 430 K), $Z = 4$, space group $Cmcm$. The crystal was not a single crystal but consisted of two individuals. Conventional R index 0·04 ($R_w = 0{\cdot}05$).

Introduction. The monohalides of cations with an $(ns)^2$ outer shell crystallize in the CsCl structure ($B2$) and/or the β-TlI structure ($B33$), with the exception of TlF and InCl. These compounds have different structures, which can both be derived as distortions of the rock-salt structure ($B1$) (van den Berg, 1964). Indium monochloride has a yellow form, which is stable below 390 K, and whose structure has been determined by van den Berg (1964, 1966). This unique and intriguingly complicated structure was described by the author in terms of cation–cation bonding. We, however, are inclined to assume that the stereochemical activity of the monovalent In ion is the most pronounced feature in this structure, instead of cation–cation bonding. Before starting a detailed analysis, we decided to redetermine the structure of yellow InCl in order to verify the previous determination and to obtain more accurate values of all the parameters, with the help of better experimental techniques which are available nowadays.

Indium monochloride has a first-order phase transition at about 390 K (van den Berg, 1964, 1966). Above this temperature a red modification exists, of unknown structure. We decided to determine this crystal structure too, in order to study its relation with respect to the room-temperature structure.

Indium monochloride was prepared from ultra-pure In (Fluka A.G.) and *p.a.* $HgCl_2$ (Merck) following the method of Clark, Griswold & Kleinberg (1958). Small crystals of the red modification were grown from the gas phase in a gradient furnace (700–500 K). These became yellow on cooling to room temperature. Crystals of 60–100 μm were mounted in a glass capillary. Rotation photographs were taken to select single crystals of the yellow phase.

Yellow InCl. A single crystal was measured on a PDP-controlled three-angle single-crystal diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The unit cell appeared to be cubic with cell axes 12·373 (1) Å, in close agreement with van den Berg's value of 12·368 (1) Å. In order to check the absorption corrections the crystal was oriented with the reciprocal vector [410]* as rotation axis. In this orientation 4714 reflexions were measured. The Laue group is $m3$. The only systematic absences are $h00$ for $h \neq 2n$, so the space group is uniquely determined as $P2_13$. The intensities were corrected for absorption (transmission between 0·33 and 0·63) and for a slight decay during the measurements. The intensities of equivalent reflexions were averaged and transformed into structure factors. In this way we obtained 820 independent structure factors hkl (705 significant and 115 not significant) and another 604 structure factors $\bar{h}\bar{k}\bar{l}$ (475 significant, 129 not significant). The three-dimensional Patterson function appeared to be quite similar to van den Berg's. Therefore we used her atomic parameters as starting values in an anisotropic least-squares refinement. Scattering factors for In^+ and Cl^- were taken from *International Tables for X-ray Crystallography* (1974); those for In^+ were interpolated between In and In^{3+}. When convergence was attained we added the imaginary parts of the form factors. Van den Berg's model gave $R = 3{\cdot}91$ and $R_w = 3{\cdot}34\%$, while the inverted structure refined to $R = 3{\cdot}75$ and $R_w = 3{\cdot}15\%$. Going on with the inverted structure we applied an extinction correction (Zachariasen, 1969), resulting in the R value 3·14 and $R_w = 3{\cdot}00\%$.† The final atomic parameters and temperature factors are given in Table 1. Table 2 shows the nearest-neighbour distances. The Cl–In–Cl bond angles, which are 90° in the rock-salt structure, are all between 71·30 and 119·16°.

Red InCl. A yellow single crystal, already mounted on the PDP-controlled three-circle diffractometer and whose orientation at room temperature had been determined, was heated in a warm stream of nitrogen. The

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33742 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Relative atomic coordinates* (Å) *of yellow* InCl

E.s.d.'s in the last digit are given in parentheses. For our crystal the values corresponding to the inverted structure should be taken, but the above figures can be better compared with van den Berg's (1964) result.

	Position	*x*	*y*	*z*
In(1)	12(*b*)	0·24873 (5)	0·21978 (5)	−0·02881 (6)
In(2)	12(*b*)	0·75270 (5)	0·77805 (5)	0·02948 (6)
In(3)	4(*a*)	0·03016 (5)	0·03016 (5)	0·03016 (5)
In(4)	4(*a*)	0·46731 (5)	0·46731 (5)	0·46731 (5)
Cl(1)	12(*b*)	0·3005 (2)	−0·0504 (2)	0·0005 (2)
Cl(2)	12(*b*)	0·7998 (2)	0·0549 (2)	−0·0110 (2)
Cl(3)	4(*a*)	0·2061 (2)	0·2061 (2)	0·2061 (2)
Cl(4)	4(*a*)	0·7986 (2)	0·7986 (2)	0·7986 (2)

Table 2. In—Cl, In—In *and* Cl—Cl *distances* (Å) *in yellow* InCl (*nearest neighbours only*)

E.s.d.'s are 0·002, 0·001, and 0·004 Å respectively.

In(1)—Cl(1)	3·275	In(2)—Cl(2)	3·510
In(1)—Cl(1)	3·241	In(2)—Cl(2)	3·559
In(1)—Cl(1)	3·423	In(2)—Cl(3)	3·428
In(1)—Cl(2)	2·901	In(4)—Cl(4)	2·924
In(1)—Cl(3)	2·959	In(3)—Cl(1)	3·510
In(1)—Cl(4)	3·527	In(3)—Cl(2)	2·911
In(2)—Cl(1)	2·902	In(4)—Cl(1)	2·908
In(2)—Cl(2)	2·953	In(4)—Cl(2)	3·520
In(1)—In(1)	3·649	In(1)—In(4)	4·705
In(1)—In(1)	4·624	In(1)—In(4)	4·763
In(1)—In(2)	4·629	In(2)—In(2)	4·637
In(1)—In(2)	4·640	In(2)—In(2)	4·667
In(1)—In(2)	4·697	In(2)—In(3)	4·761
In(1)—In(2)	4·740	In(2)—In(3)	4·639
In(1)—In(3)	3·654	In(2)—In(4)	3·591
In(1)—In(3)	4·658	In(2)—In(4)	4·670
Cl(1)—Cl(1)	4·008	Cl(1)—Cl(4)	3·951
Cl(1)—Cl(1)	5·747	Cl(1)—Cl(4)	5·818
Cl(1)—Cl(2)	3·928	Cl(2)—Cl(2)	4·013
Cl(1)—Cl(2)	3·955	Cl(2)—Cl(2)	5·861
Cl(1)—Cl(2)	4·183	Cl(2)—Cl(3)	3·990
Cl(1)—Cl(2)	4·330	Cl(2)—Cl(3)	5·732
Cl(1)—Cl(3)	4·121	Cl(2)—Cl(4)	3·950
Cl(1)—Cl(3)	4·232	Cl(2)—Cl(4)	4·410

temperature in the neighbourhood of the crystal was measured with a thermocouple. While the temperature was raised we watched both the crystal and some reflexions of the crystal (optimizing continuously because of expansion of the crystal). Near the transition point the crystal became increasingly orange and at the transition point (about 390 K) it suddenly became red. At that moment the reflexion of the yellow phase disappeared completely.

Unfortunately no single crystal of red InCl resulted: most crystals consisted of a number of individuals and also gave broad reflexions. We found one crystal consisting of two individuals which both gave not too broad reflexion ranges. Both individuals were measured with graphite-monochromatized Mo $K\alpha$ radiation.

Table 3. *Some information about both individuals of the red* InCl *crystal*

Reflexions	Individual 1	Individual 2
Measured	218	273
Independent	139	169
Significant	100	139
Relative intensity	0·30	0·70
Variation intensity in azimuth scan	± 20%	± 9%
Mosaic spread	0·8°	1·7°
Extinction in *F* of strongest reflexion	12%	~ 0%

According to the systematic extinctions the space group is *Cmcm* (No. 63), $Cmc2_1$ (No. 36), or *C*2*cm* (No. 40) with cell constants $a = 4{\cdot}242\,(2)$, $b = 12{\cdot}32\,(1)$ and $c = 4{\cdot}689\,(4)$ Å; $Z = 2$. For details see Table 3.

No adequate correction for absorption was possible because of the shape of the crystal and the different results of an azimuth scan for both individuals, pointing to a non-homogenous distribution in the crystal. We therefore decided not to apply an absorption correction.

The intensities were reduced to structure factors in the usual way. The structure factors of both individuals were combined without averaging, however. As InBr (Stephenson & Mellor, 1950) has nearly the same cell constants we used its parameters as starting values (in the space group *Cmcm*) for an anisotropic least-squares refinement, with two positional and six thermal parameters and two scale factors, yielding $R = 4{\cdot}91$, $R_w = 5{\cdot}39\%$. After correction for extinction these reduced to $R = 4{\cdot}30$, $R_w = 5{\cdot}19\%$.*

Next the possibilities of space group $Cmc2_1$ and *C*2*cm* were considered. In space group $Cmc2_1$ the *z* parameters of In and Cl, as well as the temperature parameter U_{23}, are released; in *C*2*cm* the extra parameters are the *x* and U_{12} of both In and Cl. In the full-matrix refinement the extra positional parameters of In were fixed. The results of the refinement are given in Table 4.

On the 0·01 significance level none of the three space groups can be rejected in favour of one of the others. Moreover, the assumption of random distributed errors is not valid here because the absorption correction was not applied. Space group *C*2*cm* gives only very small deviations from *Cmcm* in its positional parameters. The high U_{33} parameter for Cl in space group *Cmcm* might point to space group $Cmc2_1$. Indeed this value decreases. Fixing the U_{33} value in space group $Cmc2_1$ at 0·065 gives an R_w value of 5·22%. Therefore the behaviour of the Cl ion can be described better by an anisotropic thermal motion than by a deviation from the ideal position. As long as no independent test can be made we will describe the results in space group *Cmcm*.

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* See previous footnote.

Table 4. *Fractional coordinates, thermal parameters* (Å^2) *and their e.s.d.'s in the three different space groups* (*red* InCl)

	Cmcm	*C2cm*	*Cmc*2_1
In x	0·0	0·0	0·0
y	0·38811(8)	0·38815 (8)	0·38806 (8)
z	0·25	0·25	0·25
Cl x	0·0	0·001 (4)	0·0
y	0·15475 (31)	0·1549 (4)	0·1551 (3)
z	0·25	0·25	0·234 (9)
In U_{11}	0·0813 (9)	0·0820 (9)	0·0810 (9)
U_{22}	0·0625 (7)	0·0630 (7)	0·0624 (7)
U_{33}	0·0708 (8)	0·0707 (7)	0·0711 (8)
$2U_{12}$	0·0	−0·0154 (45)	0·0
$2U_{23}$	0·0	0·0	0·009 (6)
$2U_{31}$	0·0	0·0	0·0
Cl U_{11}	0·066 (2)	0·068 (2)	0·066 (2)
U_{22}	0·063 (2)	0·065 (2)	0·063 (2)
U_{33}	0·093 (2)	0·093 (2)	0·086 (7)
$2U_{12}$	0·0	−0·045 (13)	0·0
$2U_{23}$	0·0	0·0	−0·007 (16)
$2U_{31}$	0·0	0·0	0·0
R(%)	4·31	4·25	4·27
R_w(%)	5·19	5·07	5·11
Number of parameters	10	13	13

Table 5. *Distances in red* InCl (Å)

In–Cl	$0,y,\frac{1}{4}$	2·875 (5) × 1
	$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$	3·205 (2) × 4
	$\frac{1}{2},\frac{1}{2}-y,\frac{1}{4}$	3·910 (4) × 2
Cl–Cl	$0,y,\frac{5}{4}$	4·242 (2) × 2
	$1,y,\frac{1}{4}$	4·689 (4) × 2
	$0,\bar{y},\frac{3}{4}$	4·476 (7) × 2
	$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$	3·937 (5) × 4
In–In	$0,y,\frac{5}{4}$	4·242 (2) × 2
	$1,y,\frac{1}{4}$	4·689 (4) × 2
	$0,1-y,\frac{3}{4}$	3·619 (3) × 2
	$\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$	4·645 (3) × 4

The distances between In and Cl atoms are given in Table 5.

Discussion. Our investigations have confirmed that yellow InCl has indeed the deformed rock-salt structure as was determined by van den Berg (1964, 1966). This is a unique structure, which will be the subject of further investigation. We have also shown that red InCl has the so-called β-TlI structure (B33). This structure is also found in TlI (Helmholz, 1936), InI (Jones & Templeton, 1955), InBr (Stephenson & Mellor, 1950) and in thin films of TlBr and TlCl (Ungelenk, 1963). The B33 structure can hypothetically be derived from the rock-salt structure (B1) by shearing double-layers of anions and cations perpendicular to a fourfold axis (van Arkel, 1961; Ungelenk, 1963). Since yellow InCl has a deformed B1 structure and red InCl has the B33 structure this shearing of double layers is a possible mechanism of the phase transition between yellow and red InCl. A further investigation of both yellow and red InCl and of related structures is already in progress.

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Structure du Dichromate d'Argent: $Ag_2Cr_2O_7$

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Abstract. $Ag_2Cr_2O_7$, triclinic, $P\bar{1}$, $a = 6{\cdot}968$ (5), $b = 7{\cdot}148$ (5), $c = 6{\cdot}544$ (5) Å, $\alpha = 110{\cdot}82$ (3), $\beta = 96{\cdot}11$ (3), $\gamma = 91{\cdot}05$ (3)°, $Z = 2$. The crystal structure has been determined from 2920 independent reflexions. The final R value is 0·037. Distorted AgO_6 octahedra link Cr_2O_7 groups in a three-dimensional way.

Introduction. Les cristaux de $Ag_2Cr_2O_7$, qui se présentent sous la forme de polyèdres quelconques rouge brique à éclat métallique, sont préparés de la façon suivante: on verse lentement dans une solution diluée de tripolychromate d'ammonium [$(NH_4)_2Cr_3O_{10}$] une solution diluée de nitrate d'argent jusqu'à persistance