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The Crystal Structure of α-ICl

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α-ICl belongs to the space group $P2_1/c$ with 8 molecules per unit cell. The approximate coordinates of the iodine atoms were found from Patterson syntheses of the three projections and by trial and error. The x and z coordinates of all atoms were refined by successive Fourier syntheses of the [010] projection, the y coordinates by computing the three-dimensional electron-density distribution along lines parallel to the b axis through the atoms. The estimated standard deviations in the interatomic distances are rather large: they amount to approximately 0·04 Å for the I–Cl and to 0·02 Å for the I–I distances between adjacent atoms.

The structure consists of molecules ICl, belonging to two non-equivalent sets. Their bond lengths are 2·37 and 2·44 Å respectively.

These molecules are arranged in puckered zigzag chains in which the intermolecular distances (I–I = 3·08 Å and I–Cl = 3·00 Å) indicate a strong interaction between the molecules.

Different chains are separated by normal van der Waals distances.

Experimental

α-ICl was prepared by adding solid iodine to liquid chlorine (*Inorganic Synth.*, 1939). Since the crystals are very volatile and unstable in moist air, they had to be mounted in glass capillaries. Even then, small crystals tended to move by sublimation during the exposure. Most X-ray photographs were therefore made from crystals obtained in the following way: A narrow capillary was completely filled with liquid ICl. The crystallization was then started at one end of the capillary by cooling with solid CO_2 or by adding a small crystal. The crystals thus formed were oriented with their b axis along the axis of the capillary.

Unit cell and space group

Weissenberg photographs about the b axis showed the crystals to be monoclinic. The lattice constants were obtained from Weissenberg and oscillation photographs about the b axis and from one Weissenberg and one oscillation photograph about the c axis. Using Cu $K\alpha$ ($\lambda = 1{\cdot}542$ Å) and Mo $K\alpha$ ($\lambda = 0{\cdot}711$ Å) radiations, the cell constants were found to be

$$a = 12{\cdot}60 \pm 0{\cdot}04,\quad b = 4{\cdot}38 \pm 0{\cdot}02,\quad c = 11{\cdot}90 \pm 0{\cdot}04\ \text{Å};\quad \beta = 119{\cdot}5 \pm 0{\cdot}5^\circ\,.$$

The density calculated for eight molecules per unit cell is 3·78 g.cm.$^{-3}$, which is in fair agreement with the experimental value of 3·85 g.cm.$^{-3}$ at 0° C. (Birk, 1928). The systematic absences indicate the space group $P2_1/c$.

Structure factors

On account of the volatility of the crystals, no X-ray photographs about the a axis and only one oscillation and one Weissenberg photograph about the c axis could be obtained. The reflexion intensities derived from these photographs were not very reliable as they could be corrected only roughly for absorption. The intensities of most reflexions hkl were measured on Weissenberg photographs about the b axis, using Zr-filtered Mo radiation.

Correction for the Lorentz and polarization factors was made in the usual way. An approximate correction for absorption was applied, assuming a cylindrical shape for the crystals. The reflexions were obtained from two crystals for which μR was 1·1 and about 3·5 respectively. The intensities from different layer lines were related approximately by comparing the exposure times of the different photographs and by making use of oscillation photographs about the b axis. The reflexion spots on the Weissenberg photographs were rather extended and it was not possible to measure their intensities accurately. Since, in addition to this, the correction made for absorption was quite uncertain, the values of the observed structure factors are not very accurate. By comparing the intensities of reflexions measured on photographs from different crystals, the errors in the structure factors were estimated to be 10–15%.

Determination of the structure

The [010] *projection*

As the eight molecules in the unit cell lie on fourfold positions, the coordinates of only two iodine and two chlorine atoms had to be determined.

The approximate x and z coordinates of the iodine atoms could be obtained from a Patterson synthesis of the [010] projection. With these coordinates the $h0l$ structure factors were calculated; the agreement between F_c and F_o was sufficient to determine the signs of 96 out of the 180 observed $h0l$ structure factors. Using these structure factors, a Fourier synthesis was computed. In addition to the high peaks at the known positions of the iodine atoms, the electron-density map showed two lower peaks which indicated the positions of the chlorine atoms. The x and z coordinates from the contour map were refined by successive Fourier synthesis. The final electron-density map is shown in Fig. 1. The coordinates were corrected for series termination by Booth's backshift method (Booth, 1946). These corrected values for the x and z coordinates are listed in Table 1. With these coordinates, a disagreement index $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o| = 0{\cdot}14$ was calculated for the observed $h0l$ structure factors.[*] The temperature factor amounted to $\exp[-2{\cdot}4 \sin^2\theta/\lambda^2]$.

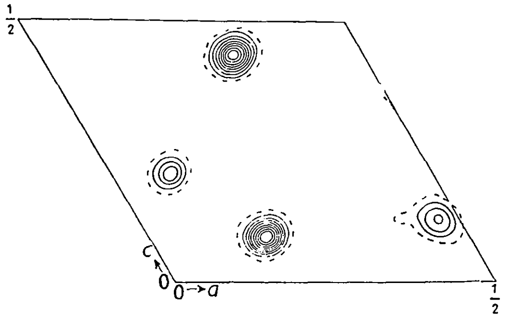

Fig. 1. Final electron-density projection along [010]. Contours at intervals of 5 e.Å^{-2}, the 5 e.Å^{-2} line being broken.

Table 1. *Final atomic coordinates*

	x	z	y	y'
I_1	0·179	0·588	0·366	0·365
I_2	0·297	0·436	0·632	0·633
Cl_1	0·084	0·706	0·152	0·156
Cl_2	0·462	0·620	0·858	0·853

The values y are determined from the three-dimensional electron-density distribution, those of y' from the [100] and [001] projections.

The y coordinates

From Patterson syntheses of the [100] and [001] projection, and by trial and error, the approximate y coordinates of the iodine atoms were found. These atoms are located at a distance of approximately 45° from the glide planes, which explains that almost all reflexions $h2l$ with $l = 2n$ and $h4l$ with $l = 2n+1$ were absent. Fourier syntheses of the [100] and [001] projections showed the approximate positions of the chlorine atoms and gave some refinement of the iodine coordinates. Since only a relatively small number of $0kl$ and $hk0$ reflexions were available, the electron-density maps showed spurious peaks and the y coordinates of the chlorine atoms obtained from the two projections did not agree very well. Therefore, a refinement of all y coordinates was attempted by computing the three-dimensional electron-density distribution along lines parallel to the b axis through the atoms. It appeared that in this way the y coordinates could be determined unambiguously. They were corrected for the finite-series effect and agreed quite well with average values derived from the projections (Table 1).

A disagreement index $R = 0{\cdot}18$ was calculated for the observed hkl reflexions,[*] the temperature factor was assumed to be equal to that obtained from the [010] projection. During the three-dimensional refinement the scaling factors relating the structure factors derived from different layer lines about the b axis were somewhat revised so as to give the best agreement between observed and calculated structure factors.

Discussion

Accuracy

An estimate of the inaccuracies in the atomic coordinates due to errors in the measured intensities was obtained by applying Cruickshank's formula (Cruickshank, 1949). Especially for the y coordinates, the values calculated were considered as a lower limit because slightly incorrect scaling factors relating the intensities from different layer lines may have caused systematic errors in these coordinates. The magnitude of this effect was estimated by changing the scaling factors and examining the resulting change in the y parameters. When also the inaccuracy of the cell constants is taken into account, the total standard deviations in the distances between adjacent atoms are approximately 0·02 Å for I–I and 0·04 Å for I–Cl. The standard deviations in the angles are approximately 1·5° for I–I–Cl and 2° for I–Cl–I and Cl–I–Cl.

Interatomic distances

Atomic distances and angles between lines connecting adjacent atoms are listed in Table 2 and are indicated in Fig. 2. From Fig. 2 it is seen that two sets of non-equivalent ICl molecules may be distinguished; the difference between the observed bond lengths, 2·37 and 2·44 Å respectively, is not, however, signifi-

Table 2. *Bond lengths and angles*

$Cl_2–I_2 = 2{\cdot}37$ Å
$I_2–I_1 = 3{\cdot}08$
$I_1–Cl_1 = 2{\cdot}44$
$Cl_1–I_2' = 3{\cdot}00$

$Cl_2–I_2–I_1 = 94{\cdot}2°$
$I_1–I_2–Cl_1' = 84{\cdot}6$
$Cl_2–I_2–Cl_1' = 178{\cdot}6$
$I_2–I_1–Cl_1 = 179{\cdot}3$
$I_1–Cl_1–I_2' = 102{\cdot}3$

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[*] A table of observed and calculated structure factors hkl has been deposited as Document No. 4750 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $2·50 for photoprints or $1·75 for 35 mm. microfilm. Advance payment is required. Make cheques or money orders payable to Chief, Photoduplicating Service, Library of Congress.

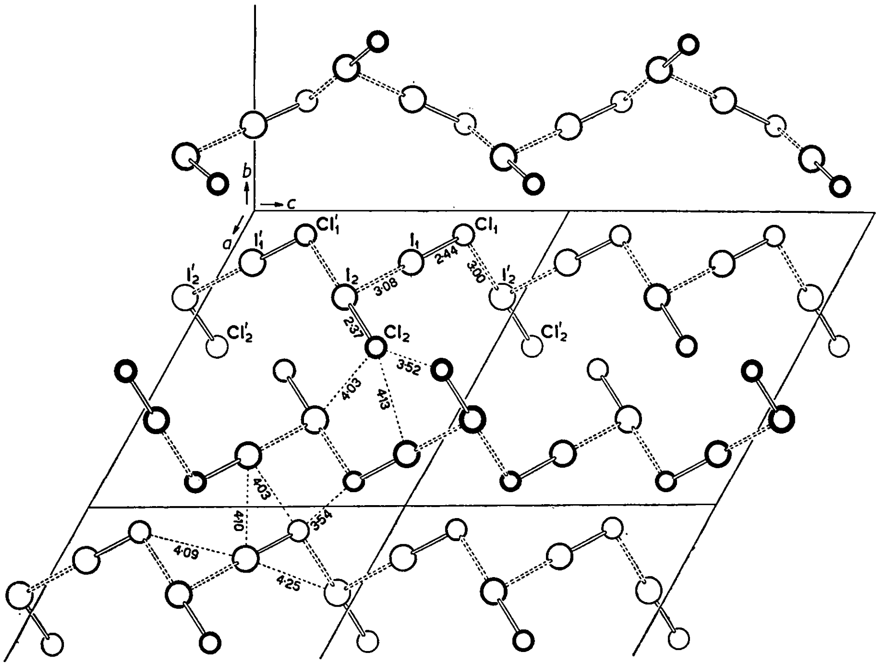

Fig. 2. Lower part: Projection along [010] on the (010) plane. Upper part: Projection of one chain on the (100) plane along the normal to this plane.

cant. Both observed values are somewhat larger than the bond length, 2·303 Å, found for ICl molecules in the vapour phase (Weidner, 1947) and may be compared with the I–Cl distances in I_2Cl_6 (2·39 Å; Boswijk & Wiebenga, 1954), in $KICl_4$ (2·34 Å; Mooney, 1938), in $N(CH_3)_4ICl_2$ (2·34 Å; Mooney, 1939), and in NH_4ClIBr (2·38 Å; Mooney, 1937).

The intermolecular distances show that the molecules ICl are arranged in chains; the puckered zigzag shape of these chains is shown in Fig. 2. The remarkably short intermolecular distances in these chains indicate a strong interaction between the molecules. The distance I_1–I_2 (3·08 Å) is hardly larger than the longer I–I distance in the I_3^- ion, which amounts to 3·04 Å in CsI_3 (Tasman & Boswijk, 1955) and to 3·00 Å in Cs_2I_8 (Havinga, Boswijk & Wiebenga, 1954), and is much smaller than the intermolecular I–I distance in solid I_2 (3·54 Å; Harris, Mack & Blake, 1928). The van der Waals distance I–I is, according to Pauling (1945, p. 189), even 4·3 Å. Also the intermolecular distance I_2'–Cl_1 in the chain (3·00 Å) is much shorter than the sum of the van der Waals radii of I and Cl (3·95 Å).

Apart from the intermolecular distances, the geometry of the chain might also be an indication of a special interaction between the molecules: sets of three atoms I_2'–I_1'–Cl_1', Cl_1'–I_2–Cl_2, I_2–I_1–Cl_1, Cl_1–I_2'–Cl_2' etc. are linearly arranged, similar to the atoms in the I_3^-, $[ICl_2]^-$ and $[BrICl]^-$ ions.

The rods join either at a chlorine atom, where the valence angle is 102°, or at an iodine atom, where it is 94°. Approximately 90° valence angles at an iodine atom are also observed in the I_5^- ion (Hach & Rundle, 1951) and in the I_8^{--} ion, in which they are 94° and 80° respectively.

The distances observed between atoms of different chains (Fig. 2) indicate a normal van der Waals interaction between the chains.

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The Structure of Mercuric Oxide

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The atomic arrangement of mercuric oxide has been determined by neutron and X-ray diffraction methods. The structure is based on zigzag chains of mercury oxide, and the chains in turn are packed to form planar layers. The Hg–O distance within a chain is $2{\cdot}01_5$ Å and the Hg–O–Hg angle is 109·8°.

Introduction

The structures of many heavy metal oxides are not known because it is difficult by X-ray diffraction techniques to locate the positions of light oxygens relative to heavy metal atoms. During the course of a separate investigation, the neutron diffraction pattern of mercuric oxide was required. These data, in conjunction with X-ray data, have led to a solution of the mercuric oxide arrangement.

Mercuric oxide may be prepared as powders which are either yellow or red, and many early investigations were concerned with the question of polymorphism. Careful X-ray work has shown that both materials give identical X-ray powder diffraction patterns (Levi, 1924; Zachariasen, 1927). Zachariasen showed that mercuric oxide crystallized in an orthorhombic unit cell

$$(a_0 = 3{\cdot}296,\ b_0 = 3{\cdot}513,\ c_0 = 5{\cdot}504\ \text{kX.})$$

containing 2 HgO. The mercury atoms are at the origin and body center of the cell, but it was not possible to locate the positions of the oxygen atoms.

A comparison of the coherent scattering amplitudes of mercury and oxygen for neutrons and X-rays shows that neutron diffraction should be more suited for the structure determination:

	Neutron	X-ray
Hg	1·31	80
O	0·58	8

However, since mercuric oxide is orthorhombic and the powder diffraction pattern is quite complex, only the first four diffraction peaks could be resolved with the relatively limited resolution available to the neutron spectrometer. The four neutron diffraction peaks were sufficient to solve the structure in an approximate sense. Once the appropriate structure was known, it was possible to refine the parameters by utilizing the greater resolving power of the X-ray spectrometer.

Neutron diffraction

Neutron diffraction patterns were obtained with the General Electric Company neutron spectrometer located at the Brookhaven National Laboratory. The data were taken by transmission through a flat powder sample of red mercuric oxide contained between spectrographic glass plates. Individual points were measured at angular increments of 08′, and each point was counted for a monitored time interval of 16 min. Integrated intensities were obtained by measuring with a planimeter the areas under peaks on an intensity versus angle plot.

The integrated intensity is given by the expression:

$$P_{hkl} = K(N^2h\varrho'/\varrho)\exp\left[-\mu h \sec\theta\right]\operatorname{cosec}^2\theta \times \exp\left[-2B\,(\sin\theta/\lambda)^2\right]J_{hkl}F^2_{hkl}\,, \quad (1)$$

where K is an instrumental constant which depends upon the incident neutron flux, neutron wavelength and counter slit dimensions, N = number of unit cells per cm.³ of sample, h = thickness of sample, ϱ' = apparent density of powder, ϱ = crystal density, μ = effective linear absorption coefficient, $\exp[-2B(\sin\theta/\lambda)^2]$ = correction for temperature motion, J_{hkl} = multiplicity and F_{hkl} = structure factor for the plane (hkl). The data were placed on an absolute scale by determining that $K = 0{\cdot}3211\times10^{-24}$ from a standard sample of nickel. The absorption coefficient was measured by transmission when $\theta = 0$. The experimental constants are given in Table 1.