

The Crystal Structure of $I_2Cl_6(ICl_3)$

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I_2Cl_6 crystallizes in complexly twinned triclinic crystals; space group $P\bar{1}$, one I_2Cl_6 per unit cell. The crystal structure was determined by the use of three-dimensional Patterson and Fourier syntheses. The final value of the disagreement factor R was 0.12. The bond lengths are subject to an uncertainty of 0.02 Å and in addition to this to a standard deviation of 0.01 Å. The structure consists of planar molecules with negligible deviations from the point group symmetry mmm . Each iodine atom is surrounded by two chlorine atoms at a distance of 2.38 and 2.39 Å and by two others at 2.72 and 2.68 Å. A discussion of the twinning and of the atomic distances is given.

1. Introduction

The interhalogen compounds are difficult to handle because of their reactivity. This may be the reason why a direct investigation of the structure of these interesting compounds did not start until a few years ago. Up to now only the structure of ClF_3 has been published (Burbank & Bensey, 1953; Smith, 1953).

The theory of the structure of the interhalogen compounds (Wells, 1945; Fessenden, 1951) is based upon the assumption that directed orbitals are occupied by shared electrons and lone pairs. For ClF_3 and ICl_3 a flat trigonal model was predicted in which the light atoms occupy the vertices of a regular triangle and the heavy atom its centre.

The structures found for these compounds are not in agreement with this model: ClF_3 consists of flat T-shaped molecules; ICl_3 appears to consist of flat units I_2Cl_6 .

2. Experimental

(a) Materials

Iodine trichloride can easily be prepared by adding iodine to liquid chlorine and evaporating the excess of chlorine. Chemical analysis showed it to be pure. By sublimation of the yellow powder small needles were obtained, which later appeared to be bounded by the (100) and (001) planes of complexly twinned triclinic crystals.

(b) Unit cell

The crystals were transferred into a boron silicate glass capillary attached to the vessel in which they were prepared. After sealing the capillary, X-ray photographs about the needle axis of crystals, not exceeding 0.05 mm. in diameter, were made. The photographs were taken at room temperature using filtered Mo radiation.

From a rotation photograph the period in the direction of the needle axis ($b = 10.88$ Å) was deduced.

The reciprocal lattice could then be constructed by making use of equi-inclination Weissenberg photographs of different layer lines. The result, shown in Fig. 1, could be interpreted as an interpenetration of the reciprocal lattices of four triclinic crystals with the following cell dimensions:

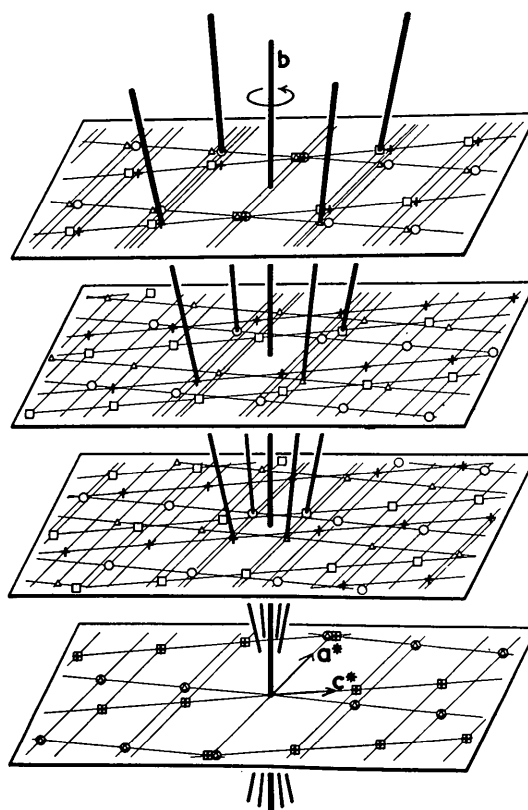


Fig. 1. Twinning of I_2Cl_6 in reciprocal space. Each of the four heavy lines connects the reciprocal lattice points $0k0$ for a given individual, thus representing its b^* axis. The displacements of an $0k0$ lattice point, passing from level to level, amount to $\frac{1}{4}a^*$ exactly and $\frac{1}{3}c^*$ approximately.

$a = 5.71 \pm 0.03$, $b = 10.88 \pm 0.02$, $c = 5.48 \pm 0.03$ Å;
 $\alpha = 130^\circ 50' \pm 10'$, $\beta = 80^\circ 50' \pm 1^\circ$, $\gamma = 108^\circ 30' \pm 10'$.

The four crystals join on the (100) plane; in addition to this each individual has the (001) plane in common with one of the three others. Apart from this twinning, the crystals are far from perfect; the streaky appearance of the reflexions on all Weissenberg diagrams indicates that the orientations of the crystallites about the b axis differ by angles up to approximately 8° .

Because of the complexity of the combined reciprocal lattices, photographs about other directions than the b axis were useless.

As may be seen from Fig. 1, the interpenetration of the four reciprocal lattices is such that for $k = 3, 6, 9$ etc. the lattices belonging to individuals with common (100) and (001) planes almost coincide. Because of the inevitable inaccuracy involved in the measurements of the Weissenberg photographs it was not possible to judge from θ -values alone to which of the four reciprocal lattices a given reflexion on one of these layers had to be attributed. Fortunately, however, Weissenberg photographs taken with $Cu K\alpha$ radiation, because of the strong absorption, showed streaks with characteristic shape for each individual. This information could be used for finding the proper relationship between the reflexions of different layer lines.

(c) Space group

A centre of symmetry (space group $P\bar{1}$) was assumed because of the absence of any piezoelectric effect.†

This assumption was confirmed by the subsequent structure determination. With two units ICI_3 per cell the calculated density becomes 3.17 ± 0.06 g.cm.⁻³. This is in agreement with the experimental value, 3.20 g.cm.⁻³ at -70° C. (Birk, 1928).

(d) Structure factors

The intensities of most reflexions were measured on integrated Weissenberg photographs (Wiebenga & Smits, 1950) of all layer lines up to the tenth. The weak reflexions were estimated by eye on ordinary Weissenberg photographs of long exposure time. All photographs were taken with $Mo K\alpha$ radiation, using two films of different speed during each exposure.

Correction for Lorentz and polarization factors were made in the usual way (Lu, 1943). No absorption corrections were made, since, with the small crystals used, these were negligible in relation to the inaccuracy of the intensity measurements. For the same reason a correction for oblique incidence (Cox & Shaw, 1930) was not applied.

It appeared that corresponding reflexions from the four individuals of which the sample was composed

showed somewhat different intensities, indicating different weights of these individuals. This is the reason why Laue photographs perpendicular to the b axis and oscillation photographs about this axis did not show an exact plane of symmetry in the reflexion intensities. The different weight of the individuals was taken into account in the evaluation of the structure factors.

Since only Weissenberg photographs about the b axis were available, the intensities of different layer lines were put on the same scale using oscillation photographs about this axis. Only approximate scaling factors could be obtained in this way as rather large oscillation ranges had to be taken (because of the disorientation of the crystallites) and overlapping of reflexions could hardly be avoided. The oscillation photographs were integrated using the integrating mechanism of the Weissenberg goniometer, the ratchet wheel being operated by an auxiliary motor. The scaling factors appeared to be roughly in agreement with those derived from the exposure times of the different Weissenberg photographs.

As a result of the relatively poor photographs the accuracy of the structure factors obtained was not better than approximately 10% in most cases.

Some reflexions overlapped and could not be measured separately; especially did the approximate overlap of all reflexions on the 3rd, 6th and 9th level give rise to difficulties. On photographs taken with Mo radiation only some of these reflexions could be observed separately. Remarkably enough, the structure factor of each of these reflexions appeared to be equal to that of its neighbouring reflexion. With Cu radiation all reflexions except those on the central lattice lines parallel to a^* (Fig. 1) could be separated; they showed the same striking regularity.

3. Determination of the approximate structure

(a) The [010] projection

Apart from the maximum in the origin, the Patterson synthesis (Fig. 2) of this projection showed only one (independent) peak which was almost exactly located in $(10\bar{1})$. It was tentatively assumed that this peak was due to the I-I vector. A Fourier synthesis,

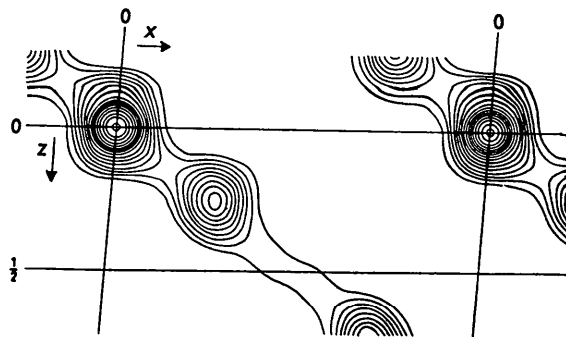


Fig. 2. [010] Patterson projection. Contours are at equal intervals on an arbitrary scale.

† We are much indebted to Prof. Dr P. Terpstra and Dr W. G. Perdok of the Crystallographic Institute, University of Groningen, for putting their apparatus at our disposal for these measurements.

however, based on the signs calculated with the iodine position derived from this Patterson synthesis, did not reveal the chlorine positions and could not be refined.

Since it followed from the [010] Patterson projection that all atoms were located approximately in the $(10\bar{1})$ plane, it was decided to continue by making a $(10\bar{1})$ Patterson section.

(b) The $(10\bar{1})$ section

Before the Patterson synthesis of this section could be computed, it was necessary to make an assumption about the structure factors of the inseparable reflexions with $k = 3, 6$ and 9 . We assumed that the regularity observed for those reflexions which could be separated (see the end of § 2) would hold for all reflexions on these levels. This means that the same value was attributed to the structure factors of the reflexions hkl and $-(h + \frac{1}{3}k), k, -(l + \frac{2}{3}k)$ for $k = 3, 6$ and 9 . Apart from these systematically overlapping reflexions there was a number of reflexions on all layer lines coinciding accidentally with other ones. The latter had to be omitted from the Patterson and Fourier syntheses until an approximate structure was obtained. They were then taken into account by subdividing the combined intensities according to their calculated values. The result of this $(10\bar{1})$ Patterson section (Fig. 3) showed unequivocally that the I-I vector

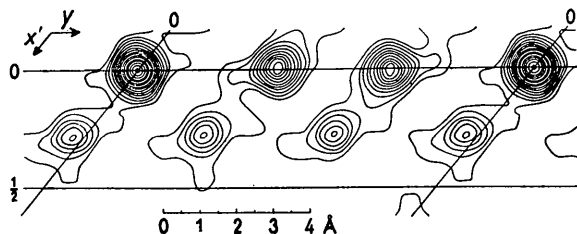


Fig. 3. $(10\bar{1})$ Patterson section. The [101] direction is indicated by x' . Contours are at equal intervals on an arbitrary scale.

coincided with the b axis, contrary to the tentative interpretation of the [010] Patterson projection. Now the vector-convergence method (Beever & Robertson, 1950) was applied to the $(10\bar{1})$ section and revealed clearly the approximate positions of all atoms. With these positions, the signs of most structure factors could be determined and used in a subsequent Fourier synthesis of the $(10\bar{1})$ section. The density map obtained showed almost circular contour lines in the peaks for all atoms, and the coordinates derived from it were only slightly different from the final coordinates.

The three chlorine atoms are separated in the y direction by distances almost exactly equal to $\frac{1}{3}b$. Since, in addition to this, their x (and z) coordinates are the same, the contribution of the chlorine atoms to the structure factor cancels for each value of k which is not a multiple of three. Hence for these reflexions the structure factors are determined only

by the y coordinate of the iodine atom, the x and z coordinates of the latter being zero. This means that, apart from the influence of the Lorentz and polarization factors and the decrease of the scattering factor with θ , the reflexions on each layer line which is not a multiple of three must have very nearly equal intensities in the same layer line. This was indeed one of the most striking features of the rotation photographs about the b axis. The additional peculiarity that the 4th layer line was completely missing, and the 7th almost completely, is readily explained by the value of the y coordinate ($y \approx 66^\circ$) of the iodine atom.

The equal intensities of the double reflexions with $k = 3, 6, 9$ etc. are also a result of the special positions of the chlorine atoms. For $k = 3, 6$ and 9 their contributions to the structure factors are in phase, whereas for one of them a relationship $x + 2z = 6y$ holds almost exactly. This makes the structure factors of hkl equal to that of $-(h + \frac{1}{3}k), k, -(l + \frac{2}{3}k)$.

As a last peculiarity of the X-ray photographs it was noticed that the equi-inclination Weissenberg photographs for $k = 0$ and $k = 6$, as well as for $k = 3$ and $k = 9$, were almost identical. It may be seen from Fig. 1 that a reflexion $h0l$ or $h3l$ on the photographs of the lower levels, corresponds with a reflexion $(h-1), 6, (l-2)$ or $(h-1), 9, (l-2)$ respectively on the photographs of the higher levels. It is easily verified that the approximate equality of the structure factor for these reflexions is a result of the special positions of the chlorine and iodine atoms.

4. Refinement

(a) The $(10\bar{1})$ section

With the atomic coordinates from the approximate structure all structure factors were calculated. It appeared that the agreement between calculated and observed values was sufficient to determine unequivocally the signs of all structure factors. It was noticed, however, that the discrepancies between F_c and F_o showed a systematic character, indicating slight errors in the scaling factors for the different layer lines, which had already been suspected (see § 2(d)). It was therefore decided to obtain the scaling factors by comparison of the calculated and observed structure factors for the different layer lines.

Since these calculated scaling factors depend for the greater part on the y coordinate of the iodine atom it was necessary first to find this coordinate accurately. Fortunately the possible values for this parameter could be confined between narrow limits using only qualitatively the intensities of the reflexions on consecutive levels. With an inclination angle $\mu = 20^\circ$, a rotation photograph was taken using Mo $K\alpha$ radiation. This photograph showed 16 layer lines. The sequence of the intensities of the higher levels showed that a value $y = 67^\circ (\pm 0.3^\circ)$ had to be attributed to the y coordinate of the iodine atom. With this coordinate, and the chlorine positions from the approximate

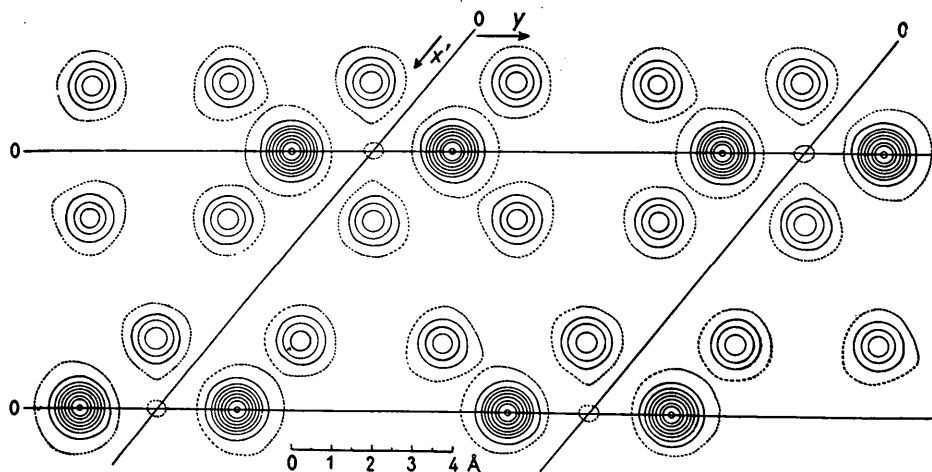


Fig. 4. Final $(10\bar{1})$ Fourier section. The $[10\bar{1}]$ direction is indicated by x' . Contours are drawn at intervals of $2.5 \text{ e.}\text{\AA}^{-3}$ for the chlorine atoms and of $5 \text{ e.}\text{\AA}^{-3}$ for the iodine atoms, the $2.5 \text{ e.}\text{\AA}^{-3}$ line being broken.

Fourier synthesis, all structure factors were recalculated. The scaling factors as well as the value of the temperature factor ($B = 2.25 \text{ \AA}^2$) could now be obtained by minimizing the disagreement between the F_o 's and F_c 's by the method of least squares.

Using the somewhat revised values of all observed structure factors, a Fourier synthesis of the $(10\bar{1})$ sections was computed. Since, however, the observed structure factors had been derived from the relatively poor Weissenberg photographs of the first nine levels only, this Fourier synthesis was far from complete and showed considerable false detail. Hence the atomic coordinates were deduced from a Fourier synthesis in which an additional temperature factor ($B' = 4.8 \text{ \AA}^2$) had been introduced. Even in this Fourier synthesis the extra detail had not disappeared completely so that the coordinates were corrected for the remaining termination-of-the-series effect by the 'backshift' method (Booth, 1946a). It was verified that the remaining imperfection of the density map disappeared when another extra temperature factor ($B'' = 3.60 \text{ \AA}^2$) was introduced. The coordinates from the resulting map (Fig. 4) were close to the corrected coordinates from the preceding Fourier synthesis, but were not taken into account in the determination of the final coordinates since, with large temperature factors, random errors in the intensities cause a large uncertainty in the atomic positions (Booth, 1947).

(b) The $[010]$ projection

The position of the atoms in the $(10\bar{1})$ section showed that the peak in the $[010]$ Patterson projection (Fig. 2) was caused by six overlapping I-Cl vectors. The position of this peak indicated that the chlorine atoms are located slightly out of the $(10\bar{1})$ plane. Since in the Patterson synthesis some terms corresponding with overlapping reflexions had been omitted, this conclusion was confirmed by a complete Fourier synthesis of the $[010]$ projection (Fig. 5). The displacement of

the chlorine atoms derived from this Fourier synthesis amounted to approximately 0.04 \AA . In order to

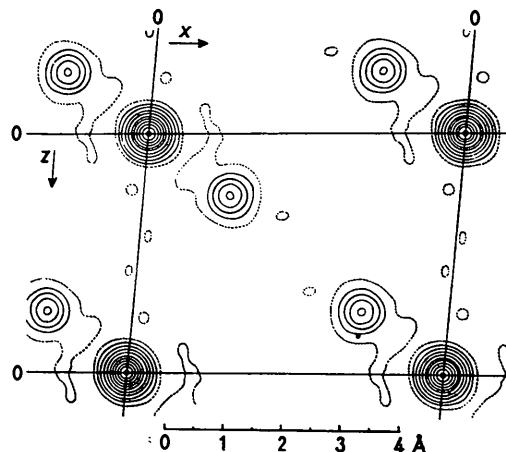


Fig. 5. Final $[010]$ Fourier projection. Contours are drawn at intervals of $20 \text{ e.}\text{\AA}^{-2}$, the $20 \text{ e.}\text{\AA}^{-2}$ contour line being broken.

determine the shift for each chlorine atom individually Booth's differential method (Booth, 1946b) was applied for finding the maxima in the three-dimensional density distribution of the chlorine atoms in the direction $[10\bar{1}]$, which is approximately perpendicular to the $(10\bar{1})$ plane. The displacements found were also corrected for termination of the series by the 'backshift' method. It appeared that the displacement (0.042 \AA) for Cl_1 was somewhat smaller than that for the other chlorine atoms (0.050 \AA). For the iodine atom a negligible shift was found in the same way. The final parameters are shown below.

	$x(^{\circ})$	$y(^{\circ})$	$z(^{\circ})$
I	0	67.0	0
Cl_1	99.1	48.6	94.7
Cl_2	97.9	167.2	92.7
Cl_3	97.8	286.5	92.0

With these coordinates all structure factors (Table 1*) were calculated. The disagreement factor R reached a value of 0.118 if unobserved reflexions are assumed to have zero intensity, and 0.103 if these reflexions were omitted from the calculation. When all overlapping reflexions were omitted the value of R became 0.107.

It appeared that the final values of the calculated structure factors did not change the scaling factors for the layer lines.

5. Discussion

(a) Description of the structure

The position of the atoms in the $(10\bar{1})$ plane is illustrated in Figs. 4 and 6. The structure appears to

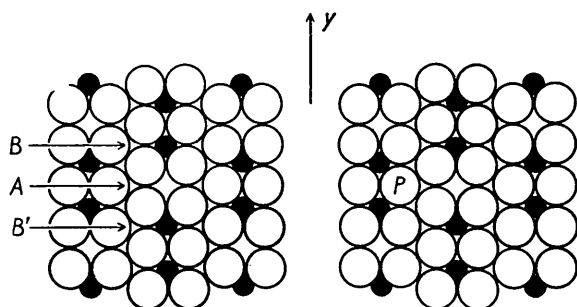


Fig. 6. Type BB' twinning. Two consecutive layers $(10\bar{1})$ are drawn separately. The right layer has to be put on top of the left layer.

consist of almost exactly planar molecules I_2Cl_6 , with negligible deviations from a point group symmetry mmm and with interatomic distances and bond angles as shown in Fig. 7. The I-Cl bond lengths may be compared with those found in ICl (2.303 Å; Weidner, 1948), in $KICl_4$ (2.34 Å; Mooney, 1938*b*), in $N(CH_3)_4ICl_2$ (2.34 Å; Mooney, 1939) and in NH_4ClIBr (2.38 Å; Mooney, 1938*a*).

The distances between neighbouring chlorine atoms of different molecules in one layer are 3.60, 3.55, 3.57 and 3.46 Å, which are comparable with the intermolecular Cl-Cl distances in $KICl_4$ (3.57–4.14 Å; Mooney, 1938*b*).

Consecutive layers are separated by a distance of 3.42 Å; the minimum distance between the chlorine atoms of different layers is 3.68 Å, which is approximately equal to the Cl-Cl distances in a layer; the closest contact between iodine and chlorine atoms of different layers occurs at 3.94 Å.

Two layers $(10\bar{1})$ are shown in Fig. 6. In the crystal

they are superimposed in such a way that a chlorine atom P of the upper (right) layer is located approximately on top of the hole B between three chlorine

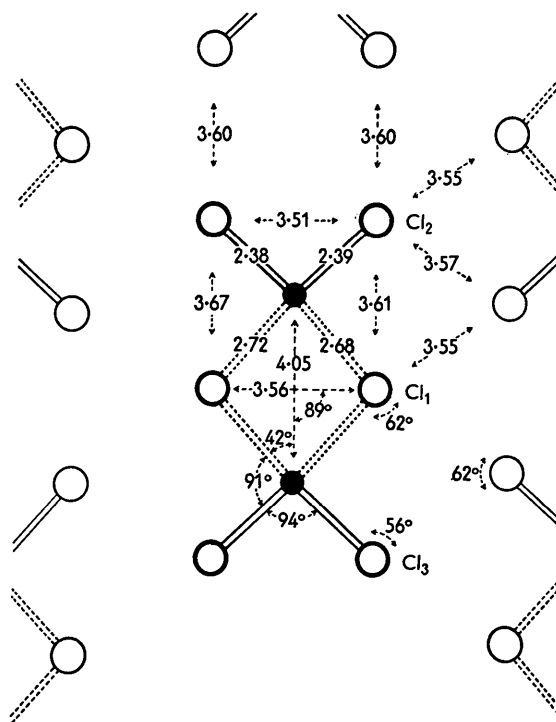


Fig. 7. Atomic distances and valence angles in a layer $(10\bar{1})$.

atoms of the lower (left) layer. All consecutive layers $(10\bar{1})$ of a given individual are related in the same way. However, as can be seen from Fig. 6, hole B' is energetically equivalent to B as far as the superposition of two layers is concerned. Apparently the crystal sometimes

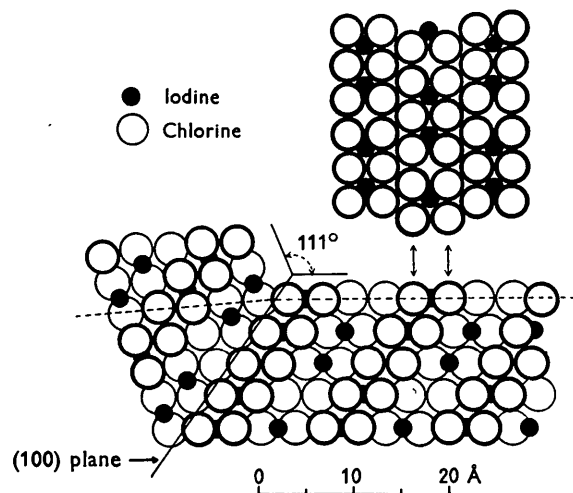


Fig. 8. Second type of twinning. The two individuals are joined on the plane (100) and their $(10\bar{1})$ planes make an angle of 111° . The lower part of the figure represents a projection of the structure along the b axis. The arrangement of the right individual is shown in the upper part of the figure.

* *Editorial note.*—Table 1, comprising 7 pages of typescript, has been withdrawn and is deposited as Document No. 4187 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 \$ 1.25 for photoprints, or \$ 1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

passes from the type B to the type B' packing, thus generating a twin individual. The B and the B' individuals have the (100) and (001) planes in common. The hole denoted by A is not equivalent to B and B' , and the type A packing does not occur.

In addition to the BB' twinning, another type of twinning occurs in which the two individuals have only the (100) plane in common (Fig. 8). Here the (101) planes of the two individuals make an angle of 111° . Presumably this type of twinning is to be explained by the fact that the packing of the chlorine atoms in one individual is approximately continued in the other (see the broken line in Fig. 8).

(b) Accuracy of the coordinates

The accuracy of the atomic coordinates was estimated by applying Cruickshank's formula (Cruickshank, 1949). Some caution was required, however, in making an estimate of the errors ΔF in the observed structure factors. Cruickshank's procedure of taking for ΔF the difference between F_o and F_c would possibly lead in this case to a too optimistic view about the accuracy of F_o , since the scaling factors between reflexions of different layer lines were only roughly determined experimentally and were actually adapted to the calculated structure factors (see § 4(a)). The latter were based on a value of 67.0° for the y coordinate of the iodine atom, which could be determined from the qualitative sequence of the intensities of the different layers with a maximum error of 0.3° . Hence, apart from the experimental random error in the intensity measurements, the F_o values which were used in the Fourier syntheses involve an error as a result of possible incorrect scaling factors. The maximum error due to this uncertainty was determined by calculating the influence on the scaling factors by a change of 0.3° in the iodine y coordinate. Maximum errors of 1, 1.5, 1, 1, 7, 0.5 and 10% were found for $k = 1, 2, 3, 5, 6, 8$ and 9 respectively. The combined errors substituted in Cruickshank's formula gave standard deviations of approximately 0.0015 and 0.005 Å for each coordinate of the iodine and the chlorine atoms respectively.

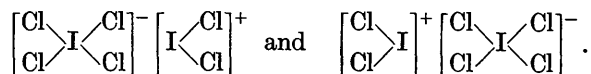
Since the back-shift corrections had been rather large, (0.06 Å on an average) it might not be permissible to assume that the coordinates were exactly corrected for the termination of the series. The consistency of the results, after applying the back-shift correction, suggested, however, that the error involved was very small. It may be safe to represent the combined errors due to inaccuracy of the intensities and the back-shift correction by a standard deviation of approximately 0.005 Å for the iodine and 0.01 Å for the chlorine coordinates, resulting in approximate standard deviations of 0.012 Å in the I-Cl bond lengths and 0.5° in the valence angles.

A reservation had to be made for the y coordinate of the iodine atom since the errors in F_o , due to an

inaccuracy of the scaling factors, are not entirely random errors, but tend to shift systematically the iodine atom in the y direction. A maximum error of $0.3^\circ = 0.01$ Å was retained for this coordinate. This uncertainty in the y coordinate of the iodine atom, and the inaccuracy involved in the measurement of the cell dimensions (§ 2(b)), give rise to an additional uncertainty in the bond lengths and valence angles. The maximum variations of these quantities, obtained by changing the cell dimensions and the iodine y position between their limits of accuracy, were determined to be ± 0.02 Å and $\pm 1^\circ$ respectively.

(c) Discussion of the molecule

It is difficult to explain theoretically why the crystal does not consist of molecules ICl_3 , but is built up from molecules I_2Cl_6 . For the constitution of the hypothetical molecule ICl_3 a theoretical explanation was already given (see § 1). The constitution of I_2Cl_6 might be explained similarly by assuming a mesomerism between structures as



The $[ICl_4]^-$ ion is known from other structures and its constitution is usually explained as an octahedral sp^3d^2 hybridization. The chlorine atoms occupy the four equatorial positions in these orbitals, whereas the other ones are occupied by lone electron pairs. The $[ICl_2]^+$ ion is not found in other structures, but was suggested (Greenwood & Emeléus, 1950) to account for the electrical conductivity of molten I_2Cl_6 . Its constitution might be explained by trigonal hybrid sp^2 orbitals, two of which are occupied by chlorine atoms and the other by a lone electron pair, or simply by two p bonds. The proposed constitution of I_2Cl_6 implies that not all I-Cl bonds in the molecule are equivalent. The distance from I to Cl_2 (Fig. 7) is expected to be intermediate between the bond length in $[ICl_4]^-$ and $[ICl_2]^+$; the I- Cl_1 distance on the other hand should be intermediate between the length of a single I-Cl bond and the sum of the van der Waals radii of I and Cl. The observed bond lengths fit into this picture.

The question arises whether the existence in the crystal of $[ICl_4]^-$ and $[ICl_2]^+$ ions, instead of I_2Cl_6 molecules, would also be in agreement with the observed intensities. This possibility was considered by assuming an average structure in which chlorine atom Cl_1 (Fig. 7) occupies either of two positions, such that its distance from one of the iodine atoms becomes 2.42 Å. This means that instead of one chlorine atom at $y = 51.3^\circ$ two atoms with half the scattering power of chlorine were located at $y = 51.3^\circ + 14^\circ$ and $y = 51.3^\circ - 14^\circ$ respectively, keeping all other coordinates unchanged. When the structure factors were calculated it appeared that this average structure could be definitely excluded: the disagree-

ment factor, calculated for the $h8l$ reflexions only, increased from 0.067 to 0.230. ($F_o - F_c$) syntheses confirmed this conclusion.

The Patterson and Fourier syntheses were calculated on punched-card machines. We wish to express our gratitude to Theodorus Niemeijer N. V. for generously putting their I.B.M. equipment at our disposal and to Mr M. R. van der Velde for his assistance. We are also indebted to Dra Aafje Vos for some valuable suggestions during this work and to Drs H. Lemmens and W. Heerspink for their cooperation during the first part of this investigation. The support of the Netherlands Organization for Pure Research (Z.W.O.) is gratefully acknowledged.

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The Crystal Structure of Barium Tetrasulfide Monohydrate*

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Barium tetrasulfide monohydrate forms strongly piezoelectric crystals belonging to the orthorhombic system, space group $D_2^3-P2_12_12$, with four molecules in a unit cell of dimensions $a = 9.67$, $b = 7.99$ and $c = 7.81$ Å. The crystal structure has been completely determined, and the values of the 17 atomic coordinates have been refined by double Fourier series and least-squares methods, based upon 296 terms derived from visual intensity measurements in the three principal zones. The barium atom is completely ionized, and is in ionic contact with the sulfur atoms and the oxygen atom of the water molecule. The tetrasulfide ion possesses C_2 symmetry. Like the anion of cesium hexasulfide, the tetrasulfide ion is non-branched and non-planar, and also exhibits a similar alternation in bond length. Two kinds of sulfur-sulfur bonds are present, of length 2.02 and 2.07 Å, allowing a new tentative bond-order v . bond-length curve for sulfur to be established.

Introduction

The crystal structure of cesium hexasulfide has been studied previously (Abrahams & Grison, 1953) in this laboratory, during the course of an investigation of the properties of the VI₆ group of the periodic table. This work unambiguously demonstrated the polysulfide chain to be non-branched and non-planar, and also indicated that two kinds of bond occurred in the hexasulfide ion, of length 2.02 and 2.11 Å, the standard deviation being 0.03 Å. The present study was undertaken to determine whether a similar alternation in bond length also occurred in the tetrasulfide ion.

Barium tetrasulfide is considerably more stable in contact with air than cesium tetrasulfide, although cesium forms the longer stable polysulfide (Schöne, 1862; Biltz & Wilke-Dörfurt, 1905). Barium tetrasulfide is reported to crystallize with varying amounts of water (Veley, 1886), but the conditions of crystallization used (Robinson & Scott, 1931) gave only the monohydrate.

The values of the dihedral angle in the hexasulfide ion were 78.8, 81.9 and 61.4°,† indicating that this angle was largely influenced by the crystallographic environment. Recently, Marsh, Kruse & McCullough

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† The angles quoted by Abrahams & Grison (1953) are, in fact, all complements of the correct values.