

The Crystal Structure of Cs_2I_3 (CsI_4)

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The crystal structure of CsI_4 has been determined by X-ray analysis. Space group: $P2_1/a$; 4CsI_4 per unit cell. The signs of 60 out of the 71 observed $h0l$ structure factors could be calculated directly from inequalities. Inequalities were not useful in the $[001]$ projection, but a first approximation could be obtained from Buerger's minimum function. The coordinates were refined by Fourier syntheses of the three projections and corrected for the termination of the series. The final value of the disagreement factor R is 0.085, and the standard deviation in the atomic distances is 0.02–0.03 Å.

The structure consists of Cs^+ ions and flat $[\text{I}_3^- \cdot \text{I}_2 \cdot \text{I}_3^-]$ ions, the latter showing a weak interaction between their constituents.

1. Introduction

From the observed diamagnetism of CsI_4 (Hubard, 1942) it is likely that the empirical formula of this compound must be doubled since I_4^- ions should be paramagnetic, because of their odd number of electrons. Formulas as Cs_2I_3 and $2\text{CsI}_3 \cdot \text{I}_2$ have been suggested. It was the purpose of the present investigation to obtain detailed information on the structure of this polyiodide.

2. Experimental

Materials

A mixture of 5.00 g. CsI , 2.015 g. I_2 and 73.69 g. H_2O was heated in a closed vessel at 90°C . until it became homogeneous, and was then cooled slowly to 25°C . After 1–2 days CsI_4 crystallized from this solution in violet monoclinic plates $\{100\}$, showing also the forms $\{001\}$ and $\{201\}$. The crystals were dried in a desiccator over sulphuric acid. The composition was checked by chemical analysis. The m.p. was $139\text{--}140^\circ\text{C}$. (cf. Briggs, Greenawald & Leonard, 1930).

Unit cell and space group

The cell dimensions were obtained from rotation- and Weissenberg photographs about the a , b and c axes, using Ni-filtered Cu radiation and Zr-filtered Mo radiation. With $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ and $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ the following values were observed:

$$a = 11.19 \pm 0.05, \quad b = 9.00 \pm 0.04, \quad c = 10.23 \pm 0.05 \text{ \AA}, \\ \beta = 114^\circ 20' \pm 10'.$$

These cell dimensions agree with old optical goniometric measurements by Penfield (Wells, Wheeler & Penfield, 1893) on a polyiodide, which was thought to be CsI_5 and which was described as triclinic with

$$a' : b' : c' = 0.9890 : 1 : 0.42765, \\ \alpha' = 96^\circ 56', \quad \beta' = 89^\circ 55\frac{1}{2}', \quad \gamma' = 90^\circ 21\frac{1}{2}'.$$

Transforming the axes of CsI_4 by the matrix

$$\begin{vmatrix} 0 & 3 & 0 \\ 1 & 0 & 2 \\ 1 & 0 & 1 \end{vmatrix}, \quad \text{we obtain}$$

$$a' : b' : c' = 0.998 : 1 : 0.430, \\ \alpha' = 96^\circ 44', \quad \beta' = 90^\circ, \quad \gamma' = 90^\circ,$$

in close agreement with Penfield's data. This makes it very probable that Penfield's measurements refer to CsI_4 (see also Briggs & Hubbard, 1941).

With 4CsI_4 per unit cell the calculated density is 4.53 g.cm.^{-3} , which is in satisfactory agreement with the measured density, 4.62 g.cm.^{-3} .

Since it was not possible to find a liquid by which CsI_4 was not decomposed, the density was measured in air using a volumetric method (Henglein & Roth, 1923). These measurements were made by Mr H. A. Tasman, whose assistance is gratefully acknowledged.

The following systematic extinctions were observed: $h0l$ for h odd and $0k0$ for k odd. The space group $P2_1/a$, which accounts for these extinctions, was accepted.

Structure factors

The intensities of the $h0l$, $hk0$ and $0kl$ reflexions were measured on integrated Weissenberg photographs (Wiebenga & Smits, 1950). The very weak reflexions were estimated visually on ordinary Weissenberg photographs of long exposure time. The exposures were taken with Zr-filtered Mo radiation.

Small needles along the b or c axis, having cross-sections of approximately $0.03 \times 0.04 \text{ mm.}$, could be obtained by cleavage from larger crystals. This permitted the absorption correction to be neglected for the $h0l$ and $hk0$ reflexions. The $0kl$ reflexions had to be obtained from a crystal of very irregular shape with dimensions varying from 0.02 to 0.1 mm. The influence of absorption was minimized for this specimen by taking an anti-equi-inclination Weissenberg photo-

graph (Kantha, 1952) and applying a graphical absorption correction.

After taking into account the Lorentz and polarization factors the mutually independent structure factors of 71 $h0l$ reflexions, 64 $hk0$ reflexions and 49 $0kl$ reflexions were at our disposal.

3. Determination of the structure

The [010] projection

By applying Wilson's method (Wilson, 1942) the unitary structure factors were obtained. Several high values of U_{h0l} , up to 0.70, were observed, so that an application of inequality relationships between these structure factors looked promising. Making use of the inequalities of Harker & Kasper (1948) in the form given by Gillis (1948*a*, *b*), the signs of 60 $h0l$ structure factors could be obtained.

In the Fourier synthesis based on these 60 terms all atoms were resolved. After calculating the structure factors it appeared that the signs of only 5 of the 60 structure factors had to be changed. The [010] projection was refined by the Fourier method, correcting the coordinates for finite-series errors by the 'back-shift' method (Booth, 1946).

The [001] projection

For this projection the values of the unitary structure factors were too low to make a fruitful application of inequalities possible. Making use, however, of the known x coordinates and the expected minimum distance between the atoms, it proved to be possible to locate a single peak in the [001] Patterson projection (Fig. 1). Starting from this single peak, Buerger's minimum function M_4 (Buerger, 1951) was obtained (Fig. 2). Guided by the minimum function it was possible, after some trial, to get a satisfactory agreement between calculated and observed structure factors, from which the signs of 45 $hk0$ structure factors

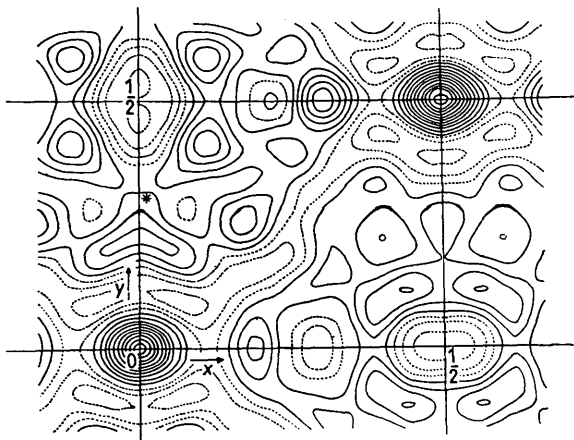


Fig. 1. The [001] Patterson projection. The single peak is indicated by an asterisk. Contours are at equal intervals on an arbitrary scale.

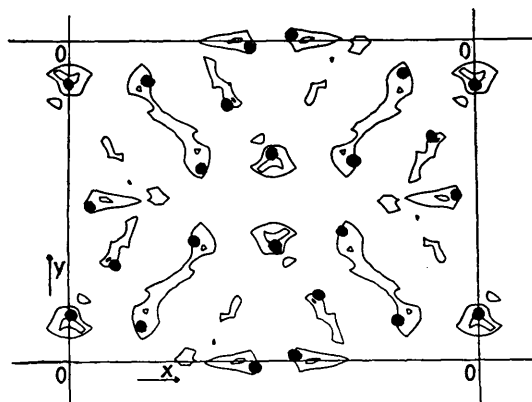


Fig. 2. Buerger's minimum function, M_4 , constructed from the [001] Patterson projection. The final atomic positions are indicated by heavy dots.

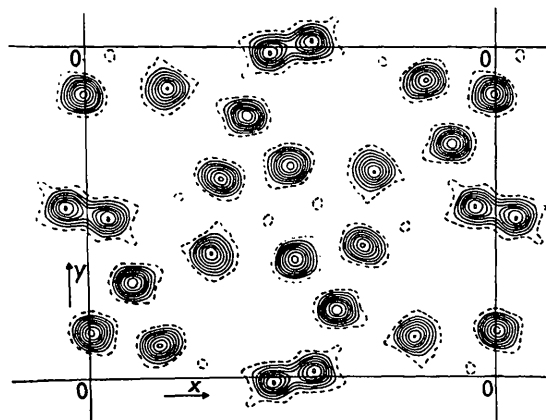


Fig. 3. The final [001] Fourier synthesis of Cs_2I_8 . Contours are drawn at intervals of $10 \text{ e.}\text{\AA}^{-2}$, the $10 \text{ e.}\text{\AA}^{-2}$ line being broken.

could be determined. The coordinates were refined by Fourier syntheses and were corrected for the influence of termination of the series. The final contour map is shown in Fig. 3.

The [100] projection

Using the coordinates deduced from the other two projections, the final Fourier synthesis for this projection could be computed. The coordinates from this synthesis were also corrected for the finite-series effect.

As final coordinates (Table I) the average values

Table I. Final coordinates

	x	y	z
Cs	0.200	0.876	0.277
I_1	0.006	0.143	0.446
I_2	0.050	0.485	0.328
I_3	0.107	0.292	0.121
I_4	0.174	0.100	0.941

of each coordinate deduced from two projections were taken.

With these coordinates the value of $R = \frac{\sum\{|F_o| - |F_c|\}}{\sum|F_o|}$ was 0.085, the summations being taken over all observed reflexions. In the calculated structure factors an isotropic temperature factor $\exp[-3.5(\sin \theta/\lambda)^2]$ was introduced.*

4. Discussion

Accuracy

The accuracy of the final coordinates was estimated by comparing the two independent values obtained for 14 coordinates from the three projections. The r.m.s. error of the average value was 0.015 Å for each coordinate direction. The resulting standard error in the atomic distances is 0.02 Å for two symmetrically independent atoms and 0.03 Å for symmetrically related atoms. In addition to these standard deviations the atomic distances are subject to a maximum error of approximately 0.6% due to inaccuracy of the cell dimensions. The standard deviation in the bond angles is approximately 1°.

It was noticed that the standard deviations calculated by the formula of Cruickshank (1949) are approximately three times as small as those calculated in the way mentioned above. It is suspected that the discrepancy is due to an imperfect correction for the termination of the series. The back shifts, which had to be taken into account in subsequent stages of refinement, appeared to be not entirely consistent.

Description and discussion of the structure

From the interatomic distances it may be concluded that the structure (Fig. 4) consists of Cs^+ ions, I_3^- ions and I_2 molecules. Pairs of I_3^- ions form with one I_2

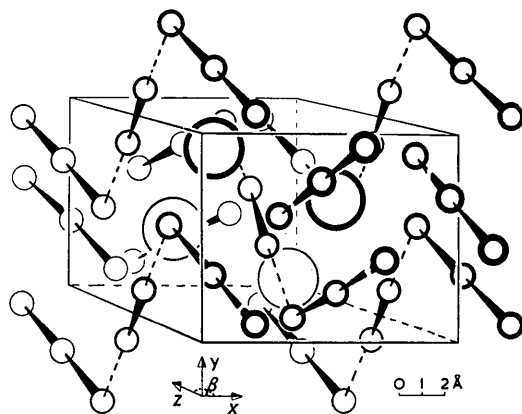


Fig. 4. The crystal structure of Cs_2I_8 .

* A table of observed and calculated structure factors for some 227 reflexions has been deposited as Document No. 4214 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 cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

molecule a larger very nearly flat unit I_8^- (Fig. 5) which is located approximately in the plane

$$6.45x + 0.11y + 2z = 1$$

or the plane related to it by symmetry.

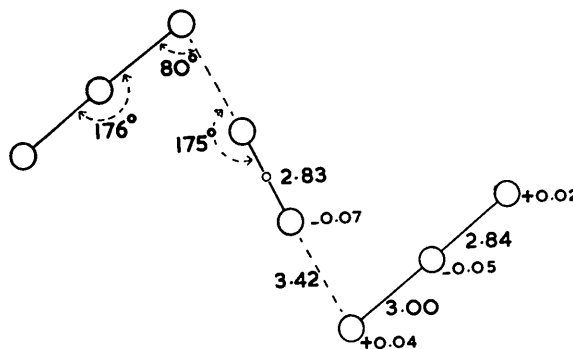


Fig. 5. Bond lengths (Å) and valence angles in the I_8^- ion. The smaller figures represent the deviations from an exactly planar configuration.

The minimum distance between iodine atoms belonging to different I_8^- units is 3.9 Å. Distances between a Cs^+ ion and eight iodine atoms vary from 3.85 to 4.07 Å, those between the Cs^+ ion and two other iodine atoms are 4.33 and 4.38 Å, all other Cs-I distances are larger than 5.3 Å. The minimum distance (3.85 Å) between Cs and I equals the sum of the ionic radii of Cs^+ and I^- .

A discussion of the structure of the I_8^- ion may be given by comparing the atomic distances in this ion with those observed in I_2 (Harris, Mack & Blake, 1928; Hassel & Viervoll, 1947), NH_4I_3 (Mooney, 1935) and $\text{N}(\text{CH}_3)_4\text{I}_5$ (Hach & Rundle, 1951). The distance (2.83 Å) between the two central iodine atoms in I_8^- is significantly larger than that observed between two bonded atoms in solid iodine (2.70 Å), whereas the distance (3.42 Å between I_3^- and I_2 in the I_8^- ion is shorter than the distance (3.54 Å) observed between iodine atoms of different molecules in solid iodine. This indicates an interaction between the I_3^- ions and the I_2 molecule in the I_8^- ion. This interaction, however, is much weaker than the interaction between the I^- ion and the two I_2 molecules in the I_5^- ion, in which a distance of 3.14 Å is observed between I^- and I_2 and a distance of 2.93 in I_2 .

The angle (80°) between I_3^- and I_2 in Cs_2I_8 differs somewhat more from 90° than in $\text{N}(\text{CH}_3)_4\text{I}_5$ (94°).

The asymmetry in the I_3^- ion in NH_4I_3 , where the two I-I distances are 2.82 and 3.10 Å and in which a valence angle I-I-I of 177° is observed, appears to exist also in the I_3^- constituents of the I_8^- ion, where the corresponding values are 2.84 and 3.00 Å respectively.

As little is known about the accuracy of the atomic coordinates in the triiodides, a detailed comparison with Cs_2I_8 is not possible. Attempts are being made in our laboratory to determine more accurately the

dimensions of the I₃⁻ ion by a re-investigation of the crystal structure of CsI₃.

We are much indebted to Mr S. van der Burg, whose assistance during the experimental part of this work was of great value. It is a pleasure to thank Theodorus Niemeyer N. V. for putting their I.B.M. equipment generously at our disposal and Mr M. R. van der Velde for his assistance. The support of the Netherlands Organisation of Pure Research (Z.W.O.) is also gratefully acknowledged.

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Sign Determination in Crystal Structure Analysis*

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Selection rules (applying to centrosymmetrical crystals only, but for all types of Bravais lattice) are given in tabular form for the correct choice of three X-ray reflexions to which arbitrary signs may be applied as the initial step towards sign determination by statistical methods.

Certain direct methods of crystal structure determination depend upon the fact that if the signs of a very few strong reflexions from a centrosymmetrical crystal are known, others can be deduced, at least with a considerable degree of probability.

Zachariasen (1952) has pointed out that 'since the origin may be shifted from one inversion center to another, it is possible to choose the signs of three structure factors at will', and by choosing a positive sign for the reflexions (201), (35 $\bar{3}$) and (017) he succeeded in determining the signs of 198 of the largest Fourier coefficients for monoclinic metaboric acid.

This method can be applied with confidence only if a judicious choice of the original three reflexions is made.‡ (These methods are not, of course, always

successful even when correctly applied.) The choice must be such that relative to the eight centres of symmetry in any unit cell (not related by a lattice translation) the signs of the three reflexions will be respectively as shown in Table 1. For certain combina-

Table 1. Possible combinations of signs of three reflexions

$h_1k_1l_1$	+	+	+	+	-	-	-	-
$h_2k_2l_2$	+	+	-	-	-	-	+	+
$h_3k_3l_3$	+	-	+	-	-	+	-	+

tions of reflexions not all these eight possibilities are covered, and in that case the validity of choosing arbitrary signs for three planes is destroyed.

The selection rules depend on the nature of the lattice; apart from this they are independent of system, class or space group, although space-group extinctions may further restrict the choice by reducing to zero intensity some reflexions in axial zones that would otherwise have been allowed.

In this paper we have attempted to show, in a non-mathematical way, the reasons for the selection rules, and to tabulate them so that they can be used directly.

* All derivations and proofs are omitted from this paper to economize space. The complete paper, in which the rules for axial zones and the list of space groups are also given explicitly, is available in duplicated form on application to the authors.

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‡ This was first pointed out to us, in principle, in a private conversation with Dr H. Lipson.