

## References

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**Structure of barium chlorate monohydrate,  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ .** By GOPINATH KARTHA, *Department of Physics, Indian Institute of Science, Bangalore, India*

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A series of isomorphous compounds of the type  $A(\text{BO}_3)_2 \cdot \text{H}_2\text{O}$ , where  $A$  is a divalent metal and  $B$  is a halogen, are known to exist. The most common among these being barium chlorate monohydrate, a complete structure analysis of the crystal has been undertaken and the results are given below.

Rotation and Weissenberg photographs gave the following data (Kartha, 1951):

$$a = 8.86 \pm 0.02, \quad b = 7.80 \pm 0.02, \quad c = 9.35 \pm 0.02 \text{ \AA}, \\ \beta = 93^\circ 30',$$

whence the number of molecules per unit cell is four. The systematic absent reflexions were found to be  $hkl$  for  $h+k+l$  odd and  $h0l$  for  $h$  or  $l$  odd. Further, since the morphological studies (Groth, 1906-19, vol. 2, p. 114) showed the crystal to belong to the monoclinic prismatic class, the space group of the crystal is  $C_{2h}^2-I2/c$  with the above unit cell, which corresponds to the morphological axial ratios. By a transformation of axes this can be brought to the standard orientation  $C2/c$  as given in the *International Tables*.

The structure amplitudes were obtained from Weissenberg photographs (Mo radiation) using three films interleaved with silver foils. The crystals being elongated with  $c$  as needle axis, the  $c$ -axis zero-level photograph was taken by the normal-beam method, whereas the  $a$ -axis and  $b$ -axis zero-level photographs were obtained by the anti-equi-inclination method. The intensities were estimated visually by comparison with standard intensity spots. They were corrected for Lorentz and polarization factors, according to Buerger & Klein (1945) in the case

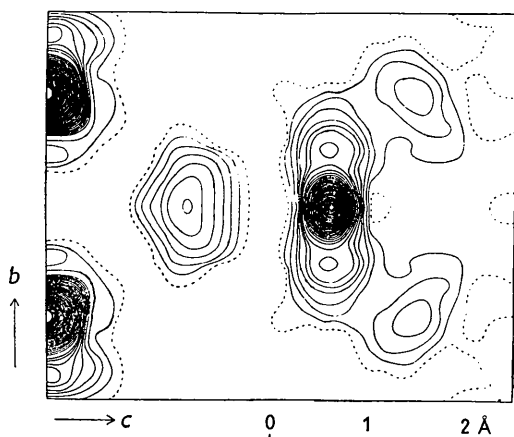


Fig. 1. The (100) Fourier projection showing one quarter of the unit cell. Contours at intervals of 2, 4 and 8  $\text{e} \cdot \text{\AA}^{-2}$  around oxygen, chlorine and barium respectively.

of the  $c$ -axis photograph and according to Kartha (1952) for  $a$ - and  $b$ -axis photographs. The relative sets of intensities thus observed were put on an absolute scale using the statistical method of Wilson (1942). This method also gave the temperature factors for the various zones.

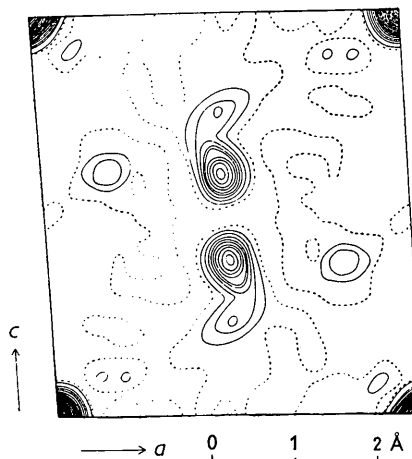


Fig. 2. The (010) Fourier projection showing one quarter of the unit cell. Contours at intervals of 10  $\text{e} \cdot \text{\AA}^{-2}$  around barium and 5  $\text{e} \cdot \text{\AA}^{-2}$  around other atoms.

The structure determination was based on two-dimensional Patterson and Fourier projections along three axes. The  $c$ -axis Patterson projection helped to fix the barium and chlorine positions in the projection. The signs of the combined barium and chlorine contributions to the  $hk0$  reflexions were calculated and these signs were used in making the Fourier synthesis. After Fourier refinement a good set of  $x$  and  $y$  coordinates were obtained for those atoms which were well resolved in the projection. In the  $b$  projection, the projected unit cell is only a quarter of the complete unit cell and contains only one barium atom. The atomic number of barium being far more than that of any other atom in the unit cell, the heavy-atom method was used to obtain the Fourier projection. This projection after refinement gave the  $x$  and  $z$  coordinates. Patterson and Fourier projections were also made on the (100) plane. The  $a$  and  $b$  Fourier projections are given in Figs. 1 and 2 respectively, while Fig. 3 gives a perspective diagram of the unit cell.

The final values of the atomic coordinates were obtained by making use of all the projections. The values expressed as fractional coordinates, with the unit cell given above and with the origin at a centre of symmetry, are as follows:

	<i>x</i>	<i>y</i>	<i>z</i>
Ba	0.000	0.396	0.250
Cl	0.250	0.250	0.554
O <sub>1</sub>	0.092	0.342	0.562
O <sub>2</sub>	0.254	0.096	0.650
O <sub>3</sub>	0.267	0.225	0.396
Water oxygen	0.000	0.062	0.250

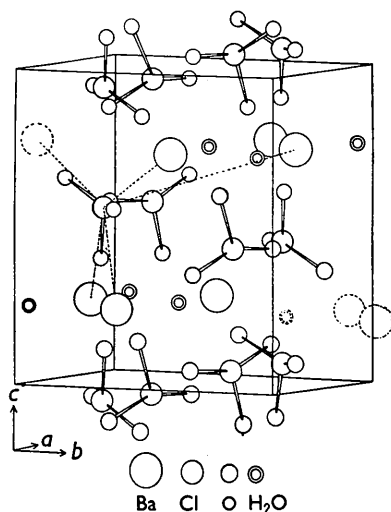


Fig. 3. Perspective diagram of the arrangement of atoms in barium chlorate monohydrate.

It may be pointed out that since the scattering factors of barium and chlorine are far greater than that of oxygen, the coordinates of the oxygen atoms cannot be expected to be as accurate as those of the heavier atoms, where an accuracy of  $\pm 2$  in the last decimal place can be expected. For the three projections about 250 reflexions were used. These gave a reliability coefficient  $\Sigma |F_o| - |F_c| \div \Sigma |F_o|$  of 0.17 which can be considered good since the structure

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**Corrections to Grison's paper on the Harker-Kasper inequalities and to Zachariasen's paper on the 'Statistical method'.** By LOUIS R. LAVINE, *School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.*

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Some errors have been discovered in the papers of Grison (1951) and Zachariasen (1952). The notation used is that of the original papers. Equations not present or not identified in the original papers have been marked with capital letters; numbered equations refer to the original papers.

**Grison's paper**

Inequality (3) was derived by Karle & Hauptman (1950) without internal absolute value signs:

$$|U_H \cdot U_{H'} - U_{H \pm H'}| \leq \sqrt{(1 - U_H^2)(1 - U_{H'}^2)}. \quad (A)$$

The distinction is important because (A) is stronger than (3). However, from (1) we may derive an inequality similar to but stronger than (4):

$$|U_H \cdot U_{H'} - U_{H \pm H'}| \leq \frac{1}{2}(1 - U_H^2) + \frac{1}{2}(1 - U_{H'}^2). \quad (B)$$

is based only on two-dimensional syntheses and projections.

The chlorate ion in this crystal is found to have a distorted low pyramidal structure with an oxygen triangle of average side 2.52 Å, the chlorine being displaced from the oxygen plane by 0.45 Å and the mean Cl—O distance being 1.57 Å. It is interesting to compare these with the values 2.50, 0.50 and 1.48 Å respectively for the chlorate ion in potassium chlorate (Zachariasen, 1929). A chlorine atom is linked to four barium atoms and a barium to eight chlorines at an average distance of 3.90 Å. There is also a barium atom in a line almost normal to the oxygen plane of a chlorate ion at a distance of 5.76 Å from the chlorine. The barium atom is surrounded by ten oxygen atoms at a mean distance of 2.87 Å and by a water oxygen on the rotation axis at a distance of 2.60 Å.

The structure is also in conformity with the strong positive birefringence of the crystal, which may be explained by the manner in which the oxygen planes of the chlorate ions are oriented in the crystal.

Full details of the investigation will be published elsewhere.

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A comparison with (5) shows that the conclusion that (3) is stronger than (1) remains unchanged when we substitute (A) for (3).

Inequality (6) cannot be obtained from (1); this invalidates (7) and (10) which were derived from (6). Inequality (9) is, of course, still valid although this particular derivation of it is not. Actually (6) or its opposite may be true, which means that (9) may be stronger or weaker than (2).

In attempting to show that (3) is weaker than (2), the following inequality:

$$(U_H - U_{H'})^2 \leq 4(1 - U_{\frac{1}{2}(H+H')}^2)(1 - U_{\frac{1}{2}(H-H')}^2), \quad (C)$$

which appears in § 4, was said to be an equivalent form of (3). Then, since (C) is shown to be weaker than (2), it was claimed that (3) is weaker than (2). However,