

	<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

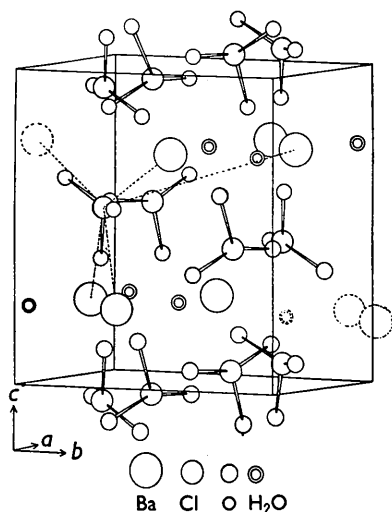


Fig. 3. Perspective diagram of the arrangement of atoms in barium chlorate monohydrate.

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.

The author wishes to express his gratitude to Prof. R. S. Krishnan for his kind interest and to Dr G. N. Ramachandran for his guidance and help throughout the course of the investigation.

#### References

- BUERGER, M. J. & KLEIN, C. E. (1945). *J. Appl. Phys.* **16**, 408.  
 GROTH, P. (1906–19). *Chemische Krystallographie*. Leipzig: Engelmann.  
 KARTHA, G. (1951). *Curr. Sci.* **20**, 151.  
 KARTHA, G. (1952). *Acta Cryst.* **5**, 549.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **152**, 150.  
 ZACHARIASEN, W. H. (1929). *Z. Kristallogr.* **71**, 513.

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,

although (C) may be derived from (A) or (3), neither can be obtained from (C). Therefore, (C) is not equivalent to (3) and the comparison of (C) with (2) yields no information about the relative strengths of (2) and (3) or (2) and (A).

#### Zachariasen's paper

$D_{HK}$  as defined in (5) is not the same as  $D_{HK}$  in (4). If (5) were labelled  $D_{2H,2K}$  or, what is equivalent, if all the angles in (5) were divided by two, (4) and (5) would be in agreement. Furthermore, (5) would then be valid only for the case in which  $S_H = S_K$ . When  $S_H = -S_K$ , the cosine terms must be replaced by sine terms.

In an analysis of the averaging process to find  $\overline{D_{HK}}$  one should first eliminate terms for which  $j = k$  since the determinant is obviously zero in this case. Then, for  $S_H = S_K$ , (using  $\sum_1^{\frac{1}{2}N}$  to indicate that the terms with  $j = k$  are omitted) after expansion and using appropriate trigonometric identities,

$$\begin{aligned} \overline{D_{HK}} = 4 \sum_1^{\frac{1}{2}N} \sum_1^{\frac{1}{2}N} n_j n_k [ & 1 + \cos(\mathbf{H} + \mathbf{K}) \cdot \mathbf{r}_j + \cos(\mathbf{H} - \mathbf{K}) \cdot \mathbf{r}_k \\ & + \cos(\mathbf{H} + \mathbf{K}) \cdot \mathbf{r}_j \cos(\mathbf{H} - \mathbf{K}) \cdot \mathbf{r}_k - \cos \mathbf{H} \cdot \mathbf{r}_j \cos \mathbf{H} \cdot \mathbf{r}_k \\ & - \cos \mathbf{H} \cdot \mathbf{r}_j \cos \mathbf{K} \cdot \mathbf{r}_k - \cos \mathbf{K} \cdot \mathbf{r}_j \cos \mathbf{H} \cdot \mathbf{r}_k \\ & - \cos \mathbf{K} \cdot \mathbf{r}_j \cos \mathbf{K} \cdot \mathbf{r}_k ] . \end{aligned} \quad (D)$$

All terms except the first average to zero when the average is taken over all possible triplets  $\mathbf{H}$  and  $\mathbf{K}$ ; the same is true for  $S_H = -S_K$ . This leaves

$$\overline{D_{HK}} = 4 \sum_1^{\frac{1}{2}N} \sum_1^{\frac{1}{2}N} n_j n_k = 4 \sum_1^{\frac{1}{2}N} \sum_1^{\frac{1}{2}N} n_j n_k - 4 \sum_1^{\frac{1}{2}N} n_j^2 = 1 - 2\sigma^2,$$

which may be compared with  $\overline{D_{HK}} = 1$  in the original paper. This correction is minor, since  $2\sigma^2$  is small compared with 1 for most crystal structures.

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**The unit-cell dimensions and space groups of two modifications of crystalline glycyglycylglycine.\*** By H. L. YAKEL, JR. and E. W. HUGHES, *Gates & Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

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Three crystalline forms of the linear peptide glycyglycylglycine have been investigated previously. Of these, two, reported by Lenel (1932), are anhydrous; they are termed  $\alpha$ - and  $\beta$ -glycyglycylglycine, while the third, studied by Bernal (1931), is an orthorhombic dihydrate. The unit-cell dimensions and space groups found by these authors are listed in Table 1.

In an effort to determine the complete crystal structure of one or more of these compounds, glycyglycylglycine prepared at the Harvard Medical School was recrystallized in these laboratories and X-ray investigations of the crystals were begun. Two distinct modifications were found in the preparations studied. One of these seemed to be identical with the  $\alpha$ -glycyglycylglycine form but

However, in finding  $\overline{D_{K_i, H+K_i}}$  when averaging over all  $K_i$  we are faced with a different process. The substitutions to be made in (D) are  $K = K_i$  and  $H = H + K_i$ . Inspection of these new terms in (D) shows that the third term,  $\cos \mathbf{H} \cdot \mathbf{r}_k$ , will not average to zero; all others except the first will average to zero. Then, in this case

$$\overline{D_{K_i, H+K_i}} = 1 - 2\sigma^2 + U_H - 4 \sum_1^{\frac{1}{2}N} n_k^2 \cos \mathbf{H} \cdot \mathbf{r}_k.$$

For the case in which  $S_H = -S_K$ , the signs of the last two terms are interchanged. When this value of  $\overline{D_{K_i, H+K_i}}$  is used in (9) it is found that

$$\begin{aligned} (\overline{U_{K_i}} + \overline{U_{H+K_i}})^2 &= 2\sigma^2 \\ + \overline{S_{K_i} \cdot S_{H+K_i}} (\overline{U_{H+2K_i}} + 4 \sum_1^{\frac{1}{2}N} n_k^2 \cos \mathbf{H} \cdot \mathbf{r}_k) \\ &+ U_H \cdot \overline{U_{H+2K_i}} . \end{aligned} \quad (E)$$

Thus it seems that Zachariasen's derivation cannot yield (11), the equation which is basic for the method.

Although these corrections show that the derivation is faulty, they give no information about the validity of the method. As Zachariasen points out, there is other less direct evidence supporting it, and his own success in the use of the method is more convincing than anything else.

I would like to thank Dr Grison, whose criticisms and comments have been extremely valuable, and Prof. W.N. Lipscomb and Mr Christer Nordman for their helpful suggestions and encouragement. Support of this work by the Office of Naval Research is gratefully acknowledged.

#### References

- GRISON, E. (1951). *Acta Cryst.* 4, 489.  
KARLE, J. & HAUPTMAN, H. (1950). *Acta Cryst.* 3, 181.  
ZACHARIASEN, W. H. (1952). *Acta Cryst.* 5, 68.

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