ART. XVIII.—*The Symmetry and Crystal Structure of Zinc Bromate Hexahydrate,* $Zn(BrO_3)_2.6H_2O$; by RALPH W. G. WYCKOFF.[1]

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Introduction.

This paper has the two-fold purpose of adding confirmation to the previously assigned structure of nickel nitrate hexammonate[2] by the study of an analogous compound and, more especially, it is intended to be an illustration of the application of those criteria for distinguishing between the cubic space groups which are described in the preceding article.[3]

Excellent crystals of $Zn(BrO_3)_2.6H_2O$, mostly octahedral in habit, are formed from solutions both by slow cooling and by slow evaporation. The crystals that grow from a cooling solution usually exhibit a slight anomalous double refraction with sectoring.[4] The Laue photographs to which these crystals give rise do not, however, show any anomalous effects. Completely isotropic specimens are obtained by gradual evaporation.

$Zn(BrO_3)_2.6H_2O$ is one of a group of isomorphous crystals to which belong the chlorates of nickel, cobalt and probably copper, and the bromates of nickel, cobalt and magnesium.[5]

The Structure of Zinc Bromate Hexahydrate.

A reflection photograph from the octahedral face combined with an estimation of the density of the salt indicates that four chemical molecules are to be associated with the unit cube.[6] The length of the side of this unit was found to be 10.31 A.U. (10.31×10^{-8}cm.).

Laue photographs were prepared through both octahe-

[1] Member of the Staff of the Geophysical Laboratory of the Carnegie Institution of Washington.

[2] Ralph W. G. Wyckoff, Jour. Am. Chem. Soc., June, 1922.

[3] See page 175 of this Journal.

[4] Marbach, Poggendorffs Ann. d. Phys., 99, 465, 1856.

[5] P. Groth, Chemische Krystallographie, II, p. 112, Leipzig, 1908.

[6] Ralph W. G. Wyckoff, Jour. Am. Chem. Soc., 42, 1100, 1920; Ralph W. G. Wyckoff and Eugen Posnjak, ibid. 43, 2292, 1921.

dral and cube faces. These showed clearly an absence of planes of symmetry; hence it is evident that the symmetry of the arrangement of the atoms of this crystal is either tetartohedral or paramorphic hemihedral (pyritohedral). Interpretation of these photographs in the usual manner[1] showed that in general planes of all sorts appear in the first order region. The fundamental lattice must consequently be the simple cubic lattice. There are four zinc atoms within the unit, and it is both natural and in accord with previous experience to consider them equivalent. If, merely to serve as a starting point for considering the various possible space groups, this assumption of the equivalence of the zinc atoms is made, we find that there are four tetartohedral and paramorphic space groups built upon a simple cubic lattice which have as special cases four equivalent positions within the unit, namely the groups T^1,T^4,T_h^2,T_h^6.

An inspection of the criteria for distinguishing between these space groups (see the preceding article) suggests the investigation of those planes having one of the indices zero. Some data for first order reflections of such planes from a Laue photograph with the X-rays roughly normal to an octahedral face are given in Table I.

TABLE I. Laue Photographic Data.

From a Plate taken with the X-rays roughly normal to (111).

Appearing Planes.

Indices of plane	Wave Length	Form of plane
$03\bar{2}$	0.480 A. U.	032
$\bar{3}40$	.285	034
$5\bar{4}0$	.376	054
$0\bar{5}6$	.415	056
$\bar{5}80$	.313	058
$07\bar{4}$	.357	074
$0\bar{7}8$	.264	078
$12,0,\bar{5}$	.443	0,5,12
$0,\bar{7},10$	.379	0,7,10
$0,\bar{7},12$	.434	0,7,12
$\bar{8},0,11$	.281	0,11,8

[1] Ralph W. G. Wyckoff, this Journal 50, 317, 1920.

Absent Planes.

$70\bar{4}$	.453	047
$05\bar{3}$	.431	053
$0\bar{5}9$	.432	059
$\bar{5}06$	.336	065
$0\bar{6}7$	.325	067
$11,0,\bar{6}$	.329	0,6,11
$\bar{5}07$	.460	075
$0\bar{7}9$	.330	079
$0,\bar{7},11$	.400	0,7,11
$8\bar{5}0$	.448	085
$0,\bar{8},11$	.318	0,8,11
$0,\bar{8},13$	.351	0,8,13
$09\bar{5}$	.304	095
$\bar{7},0,10$	.338	0,10,7
$0,11,\bar{5}$	.362	0,11,5

From this table it will be seen that the only planes of this type which appear in the first order region are of the forms $\{h0l\}$, where h is even and l is odd; it is also apparent that many planes of the forms $\{0hl\}$ and of the forms $\{0kl\}$, where both k and l are odd, were in suitable positions to reflect but did not do so. Results in complete agreement with these data and from planes of still different forms are obtained from the interpretation of a photograph taken with the X-rays approximately normal to a cube face. In comparing the data obtained from two different Laue photographs of either a tetartohedral or paramorphic crystal, it must of course be remembered to choose the H and K axes in the same way in both cases; this is readily accomplished by observing planes of two forms $\{hkl\}$ and $\{khl\}$ which show marked differences in reflecting power and are common to the two photographs to be compared.

The data recorded in Table I are seen to be in entire accord with the criteria which determine the space group T_h^6. Since these criteria uniquely distinguish this space group from every other group, it is evident that the symmetry of crystals of zinc bromate hexahydrate is that of T_h^6. From this knowledge of the corresponding space group and the fact that four chemical molecules are to be

associated with the unit cube, the manner of arrangement of the atoms of zinc bromate hexahydrate is definitely determined to be as follows:

Zinc atoms: Arrangement 4b,

$$000;\ \tfrac{1}{2}\tfrac{1}{2}0;\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}0\tfrac{1}{2}.$$

Bromine atoms: Arrangement 8h,

$$uuu;\ u+\tfrac{1}{2},\ \tfrac{1}{2}-u,\ \bar{u};\ \bar{u},\ u+\tfrac{1}{2},\ \tfrac{1}{2}-u;\ \tfrac{1}{2}-u,\ \bar{u},\ u+\tfrac{1}{2};$$
$$\bar{u}\bar{u}\bar{u};\ \tfrac{1}{2}-u,\ u+\tfrac{1}{2},\ u;\ u,\ \tfrac{1}{2}-u,\ u+\tfrac{1}{2};\ u+\tfrac{1}{2},\ u,\ \tfrac{1}{2}-u.$$

Bromate oxygen atoms: General positions,

$$xyz;\ x+\tfrac{1}{2},\ \tfrac{1}{2}-y,\ \bar{z};\ \bar{x},\ y+\tfrac{1}{2},\ \tfrac{1}{2}-z;\ \tfrac{1}{2}-x,\ \bar{y},\ z+\tfrac{1}{2};$$
$$zxy;\ \bar{z},\ x+\tfrac{1}{2},\ \tfrac{1}{2}-y;\ \tfrac{1}{2}-z,\ \bar{x},\ y+\tfrac{1}{2};\ z+\tfrac{1}{2},\ \tfrac{1}{2}-x,\ \bar{y};$$
$$yzx;\ \tfrac{1}{2}-y,\ \bar{z},\ x+\tfrac{1}{2};\ y+\tfrac{1}{2},\ \tfrac{1}{2}-z,\ \bar{x};\ \bar{y},\ z+\tfrac{1}{2},\ \tfrac{1}{2}-x;$$
$$\bar{x}\bar{y}z;\ \tfrac{1}{2}-x,\ y+\tfrac{1}{2},\ z;\ x,\ \tfrac{1}{2}-y,\ z+\tfrac{1}{2};\ x+\tfrac{1}{2},\ y,\ \tfrac{1}{2}-z;$$
$$\bar{z}\bar{x}y;\ z,\ \tfrac{1}{2}-x,\ y+\tfrac{1}{2};\ z+\tfrac{1}{2},\ x,\ \tfrac{1}{2}-y;\ \tfrac{1}{2}-z,\ x+\tfrac{1}{2},\ y;$$
$$\bar{y}z\bar{x};\ y+\tfrac{1}{2},\ z,\ \tfrac{1}{2}-x;\ \tfrac{1}{2}-y,\ z+\tfrac{1}{2},\ x;\ y,\ \tfrac{1}{2}-z,\ x+\tfrac{1}{2}.$$

Water oxygen atoms: General positions with different values of x, y and z.

Hydrogen atoms: Two sets of general positions. The coördinates and terminology are taken from the writer's book entitled "An Analytical Representation of the Theory of Space Groups" which is shortly to be published by the Carnegie Institution of Washington.

An inspection of the special cases of the space group T_h^6 shows that the arrangement outlined above is the only reasonable one for the atoms of zinc bromate hexahydrate, since any other would string out sets of eight equivalent atoms along the body diagonals of the unit cube. Though it is impossible at the present time to obtain the positions of other than the zinc atoms, it is probable that the value of u, the parameter defining the bromine atoms, is in the neighborhood of $\frac{1}{4}$ and that the values of x, y and z for the bromate oxygen atoms are such as to cluster these atoms more or less closely about the bromine atoms. It will also be observed that the groups of atoms constituting the water molecules cannot be unequally distributed between the metal atoms and the bromate groups, but must all be related in exactly the same manner to the zinc atoms (or to the bromate groups). This distribution is in accord with that found

for the ammonia groups in the hexammonate nickel halides[8] and in nickel nitrate hexammonate.[9]

Summary.

From a study of the Laue photographs to which crystals of zinc bromate hexahydrate give rise, it is shown that they must have the symmetry of the space group T_h^6. Though it is impossible to determine the positions of the atoms in this crystal, such knowledge of the underlying space group defines uniquely the manner of arrangement of its atoms. The length of the side of the unit cube which contains four chemical molecules is found to be 10.31 A.U.

Pasadena, California,
May, 1922.

[8] Ralph W. G. Wyckoff, Jour. Am. Chem. Soc., June, 1922.
[9] Idem. ibid.