

ART. XIX.—*On the Symmetry and Crystal Structure of Sodium Hydrogen Acetate, $\text{NaH}(\text{C}_2\text{H}_3\text{O}_2)_2$; by RALPH W. G. WYCKOFF.*¹

[Contribution from the Gates Chemical Laboratory of the California Institute of Technology, No. 17.]

Introduction.

This study of the structure of sodium hydrogen acetate was undertaken in the attempt to find the arrangement of the atoms in some organic compound.

Sodium acid acetate was prepared by the long continued digestion of fused sodium acetate, glacial acetic acid and acetic anhydride in sufficient quantity to remove the small amounts of water which may be present.² It was thus obtained in cubes which under the polarizing microscope prove to be isotropic. Assignment to a particular class of symmetry on the basis of the ordinary crystallographic evidence has never been made.

The Study of the Structure of Sodium Hydrogen Acetate.

Comparison reflection spectra from the (100) face of calcite and the (100) face of sodium acid acetate showed three orders of reflection for the latter which stood in the ratio of 2:3:4 (experimental conditions did not permit of the first order registering itself). Measurements upon these photographs combined with the density, $\rho = 1.402$, as determined by a flotation Westphal balance method, gives the mean value 3.07 for the ratio m/n^3 , m being the number of chemical molecules within the unit cube and n the order of the reflection. There are thus either three or 24 chemical molecules of the composition $\text{NaH}(\text{C}_2\text{H}_3\text{O}_2)_2$ within the unit. The length of the side of the cube having three molecules within it, as determined by these same measurements, is $7.98^\circ \text{ A.U. } (7.98^\circ \times 10^{-8} \text{ cm.})$.

Several Laue photographs taken with the X-rays nearly normal to the cube face of crystals from two dis-

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

² The writer is under obligation to Prof. H. J. Lucas and to L. M. Kirkpatrick for some of these preparations.

tinuous preparations were studied. Some pertinent data from the interpretation of one of these photographs are given in Table I. In this table the wave-lengths of the

TABLE I. Laue Photographic Data.

Indices of plane	Intensity	Wave Length
381	m	0.232 A. U.
581	f	.239
781	f	.227
161	s	.261
341	m	.263
521	s	.217
381	m	.206
1 $\bar{1}0$ 1	f	.243
392	f+	.206
2 13 3	f	.241
6 13 3	f	.244
7 $\bar{1}0$ 1	f	.253
572	m—	.211
752	f	.179
732	f	.233
11 $\bar{5}$ 4	f	.268
752	m	.256
3 14 3	f	.240
592	f	.243

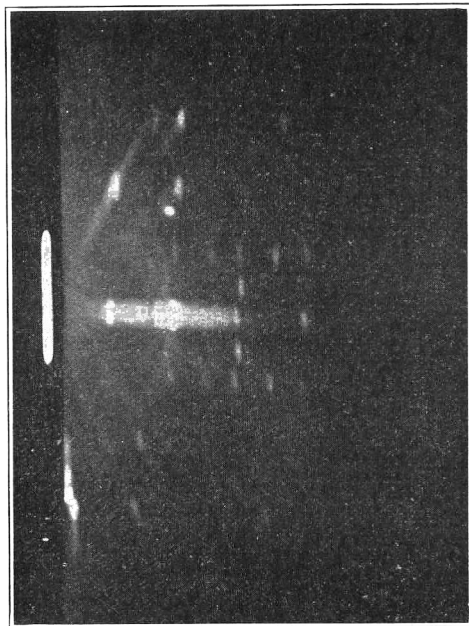
NOTE:—In this table spots having an intensity *f* are faint, those marked *m* are of medium intensity and those designated by *s* are amongst the strongest appearing upon the photograph.

reflected X-rays have been calculated on the basis of a small unit containing three chemical molecules. The voltage applied to the X-ray tube during the making of these photographs was such that no reflections are ordinarily present in wave lengths shorter than $\lambda = 0.24$ A.U. Since, as reference to Table I shows, appreciable effects with values of $n\lambda$ as low as 0.180 are to be found upon the photographs, the correct unit must contain 24 and not three molecules.

This result was sufficiently unexpected, especially in view of the fact that a simple structure containing three

molecules was not only possible on the grounds of symmetry but was chemically plausible, that it seemed worth while to obtain a direct spectrum observation of a reflection in the first order from this larger unit. This could be done by studying the secondary spectra from a cube face reflection. If a spectrum is taken from a crystal face in the usual manner, not only is the reflection from

FIGURE 1.



this face observed upon the photographic plate, but reflections from various other faces which are brought into position by the continuous rotation of the crystal during the course of the experiment will be registered at the same time at various angles to the principal spectrum. Such a composite spectrum was prepared by passing the X-rays through a section of a crystal of $\text{NaH}(\text{C}_2\text{H}_3\text{O}_2)_2$ mounted so that one of the cubic axes was coincident with the axis of its rotation and hence lay in the plane of the slit of the spectrograph. A reproduction of this spectrum is shown in fig. 1.

The identification of the secondary spectra on this photograph can be carried out with the aid of the gnomonic net which has previously been described.⁴ The distance from the crystal to the photographic plate can if necessary be accurately calculated from the measurement of the principal spectrum (in this case the (100) reflection). It is then a simple matter to prepare a gnomonic ruler⁴ for plotting on a radius of five centimeters the projections of the various secondary spectra. By making the distance from the crystal to the plate exactly five centimeters, it would be possible to use directly the same gnomonic ruler which serves for Laue photographs; by making this distance 10 cm., as is more satisfactory, the same ruler can of course be used by dividing by two the readings of the scale giving distances from the central spot. While, during the course of the experiment, the crystal is rotated back and forth, the gnomonic projections of the various reflecting planes will travel along the hyperbolas of the gnomonic net if it is so placed that the zero degree hyperbola (a straight line) coincides in position with the principal spectrum. By rotating the mean projected positions of these reflecting planes (which in the present instance form a simple square network of points) through the angle of rotation suffered by the crystal, portions of hyperbolas will be described which will pass through the gnomonic projections of the observed reflections for those planes that can reflect for this particular setting of the crystal. By superposing, then, the gnomonic projection of the photograph over the series of hyperbolic paths obtained in this manner, it is possible to identify the various reflections upon the photograph. Considerable care must be taken in such a determination and some ambiguity may of necessity arise because it frequently happens that reflections from different planes, especially planes in different orders of reflection, give effects at about the same positions upon the plate.

By making this sort of an interpretation of the transmission spectrum photograph from sodium hydrogen acetate, reflections from planes belonging to a number of forms, such as {161}, {721}, and {521}, were observed in

⁴ H. Hilton, *Min. Mag.*, 14, 18, 1904; Ralph W. G. Wyckoff, *this Journal*, 50, 317, 1920.

the first order from the large unit containing 24 chemical molecules.

The Laue photographs show clearly the absence of planes of symmetry. The crystals of this compound must then have either tetartohedral or paramorphic hemihedral (pyritohedral) symmetry. It was further observed that all of the planes giving reflections in the first order region on the basis of the large unit have two odd and one even indices. This points to an underlying body-centered lattice.⁵ The four space groups T^3 , T^5 , T_h^5 and T_h^7 have the appropriate symmetry and are built upon Γ_c . Distinction between the first three of these is impossible upon the basis of the diffraction effects to which they give rise. Crystals corresponding T_h^7 would give no reflections⁵ in odd orders from planes of the forms $\{0kl\}$, where both k and l are odd. Neither upon the Laue photographs nor upon the transmission spectrum photograph were any such planes found in odd orders, even though some were in suitable positions for reflection. This would make it necessary to assign to crystals of sodium acid acetate the symmetry of T_h^7 . The unit is so large, however, that with moderate degrees of tilt from symmetrical Laue photographs the few planes which reflect in the first order region have complicated indices and are of weak intensity. Consequently in order to place this assignment of symmetry beyond any legitimate questioning, it would be desirable to study Laue photographs from crystals inclined farther from the symmetrical position than those here investigated. It did not, however, seem worth while to make these additional experiments at the present time.

Accepting this assignment to the space group T_h^7 as correct, the general coördinate positions of the atoms in sodium acid acetate are defined. Depending upon what equivalence is assumed for the two acetate groups and for the atoms within these groups, all of the atoms of the crystal will be arranged according to either the 48 generally equivalent positions⁶ of T_h^7 or the 24 equivalent

⁵ Ralph W. G. Wyckoff, see the first article by the writer in this number of this Journal.

⁶ These general positions are stated in abbreviated form by A. Schoenflies, *Krystallsysteme und Krystallstruktur*, p. 551, Leipzig, 1891. Also in detail by P. Niggli, *Geometrische Krystallographie des Discontinuums*, p. 368, Leipzig, 1919.

positions of the special case 24e. It is of course impossible now to determine the positions of any of these atoms. The coördinates of both of these arrangements are given in the book by the writer entitled "The Analytical Representation of the Theory of Space Groups" which is shortly to be published by the Carnegie Institution of Washington.

When it is considered that such a relatively simple substance as this sodium acid acetate has such a very complicated structure as it has here been shown to possess, it scarcely needs to be emphasized that any studies of the structures of organic compounds should be made with extreme care and in order to be of any value should make use of the most powerful diffraction methods now at our disposal.

Summary.

It is shown that the unit cell of sodium hydrogen acetate must contain 24 chemical molecules. The length of the side of this unit cube is found to be 15.98 A.U. The determination of the underlying space group as probably T_h ⁷ defines the general manner of the arrangement of the atoms of this crystal, though it is impossible to obtain the positions of these atoms. A graphical method is outlined for identifying the planes causing the secondary spectra upon a reflection spectrum photograph.

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