87. On the Crystal Structure of Tetra-ethyl Ammonium Iodide.

By Isamu NITTA.

Institute of Physical and Chemical Research, Tokyo.

(Rec. June 9, 1928. Comm. by T. TERADA, M.I.A., June 12, 1928.)

In connexion with the X-ray investigation of the structure of organic molecules in crystalline state, it will not be insignificant to make an examination upon the series of alkyl-substituted ammonium iodides well known for the morphotropism of their crystals and also for the importance in the chemistry of electrolyte. The present note deals with the analysis made upon a member of the series, tetra-ethyl ammonium iodide, using the Laue-photographic and ionization-spectrometric data. Groth¹⁾ gives the following crystallographic data concerning it:

Tetragonal scalenohedral, $a : c = 1 : 0.5544$.

Specific gravity, 1.566.

Cleavage, m (110).

The substance from C.A.F. Kahlbaum was recrystallized from aqueous solution. Laue photographs were obtained with the incident X-ray beam²⁾ normal to the net plane (001) of the crystal. These photographs showed a dissymmetry, though very slight, as regards the intensity distribution of the spots as in the case of pentaerythritol³⁾, which means that the crystals of tetra-ethyl ammonium iodide have no plane of symmetry parallel to the axis [001]. From the analysis of the Laue photographs, which proved the correctness of the above axial ratio, the curves of the spectral energy distribution of the Laue spots were plotted, the estimated intensity being chosen as ordinate and $n\lambda/2a$ as abscissa. Here a is the length of the side along the a -axis of the unit of structure, n the order of reflexion and λ the wave-length of the reflected X-rays. The curves showed a sudden fall at about 0.015 of the value of $n\lambda/2a$. This is due to the K characteristic absorption of iodine atoms constituting the crystal⁴⁾, the wave-length of the absorption limit being 0.374 Å. Hence the ratio of the number m of chemical molecules in the unit of structure to the cube

1) P.v. Groth, *Chemische Krystallographie*, I. Teil, (1906), 196.

2) The Coolidge tube with tungsten anticathode was used.

3) I. Nitta, *Bull. Chem. Soc. Japan*, **1** (1926), 62.

4) I. Nitta, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **4** (1926), 49.

of the order n of reflexion could be calculated to be equal to 4.0. It was further observed that only the planes with odd integers for all h , k and l are reflecting in the first order region, and this leads to the conclusion that the underlying space lattice is the tetragonal face-centred. According, however, to the theory of crystal structure a tetragonal face-centred lattice is equivalent to a tetragonal body-centred. Thus in the present case it is convenient to take a smaller unit of structure containing 2 molecules of $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ with the underlying lattice of the tetragonal body-centred, the new system of axes being that obtained from the old system of crystallographic axes by a rotation through 45° about the c -axis. From the spectrometric measurements the new unit of structure was found to be of dimensions

$$a=8.85=12.52/\sqrt{2} \text{ and } c=6.93 \text{ \AA.},$$

the new axial ratio and the density being calculated to be $a:c=1:0.783=1:0.553 \times \sqrt{2}$ and $\rho=1.56$.

For the observed dissymmetry in the intensity distribution of the Laue spots it is necessary that the corresponding space group should be isomorphous to one of the tetragonal point groups¹⁾ S_4 , C_4 and C_4^h . Besides it should be based upon the tetragonal body-centred lattice, namely it should be one of the space groups S_4^2 , C_4^5 , C_4^6 , C_{4h}^5 and C_{4h}^6 . The space groups C_4^6 and C_{4h}^6 can further be excluded, because they require the absence of the second order reflexion from (001) whereas it is present. Thus three space groups S_4^2 , C_4^5 , and C_{4h}^5 remain as the possible ones. On account, however, of the manifest disphenoidal development of the crystal form, it may be concluded that the corresponding space group is S_4^2 .²⁾

For the arrangement of two molecules of $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ in the unit, there are following kinds of equivalent positions³⁾ in S_4^2 :

Two-fold equivalent positions

$$\begin{array}{ll} \text{(a)} \ 0\ 0\ 0; \ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}. & \text{(c)} \ 0\ \frac{1}{2}\ \frac{1}{4}; \ \frac{1}{2}\ 0\ \frac{3}{4}. \\ \text{(b)} \ 0\ 0\ \frac{1}{2}; \ \frac{1}{2}\ \frac{1}{2}\ 0. & \text{(d)} \ \frac{1}{2}\ 0\ \frac{1}{4}; \ 0\ \frac{1}{2}\ \frac{3}{4}. \end{array}$$

Four-fold equivalent positions

$$\begin{array}{ll} \text{(e)} \ 0, 0, u; \ 0, 0, -u; \ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u; \ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u. \\ \text{(f)} \ 0, \frac{1}{2}, u; \ \frac{1}{2}, 0, -u; \ \frac{1}{2}, 0, \frac{1}{2}+u; \ 0, \frac{1}{2}, \frac{1}{2}-u. \end{array}$$

1) H. Mark, Die Verwendung der Röntgenstrahlen in Chemie und Technik, Table 67.

2) Thus the symmetry class above-mentioned is not correct, it should be the tetragonal disphenoidal.

3) H. Mark, loc. cit., Table 52; R. W. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space-Groups.

Eight-fold equivalent positions

$$(g) \ x, y, z; \ -y, x, -z; \ \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z; \ \frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z; \\ -x, -y, z; \ y, -x, z; \ \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z; \ \frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z.$$

2 N atoms are to be arranged in a set, and 2 I atoms in another set, of the two-fold equivalent positions (a), (b), (c) and (d). Since all these positions possess the symmetry of S_4 , the tetrahedral nature, if not quite regular, of the valency forces of the ammonium N atom may be concluded.¹⁾ Thus it forms with four equivalent C_2H_5 -groups a radical ion $N(C_2H_5)_4$ of the minimum possible symmetry S_4 . The group (C_2H_5) may be asymmetric, for S_4 has only one axis of tetragonal rotoflexion and consequently the group is not restricted by any condition of symmetry. As to the arrangement of C atoms, it seems unnecessary to take the positions (e) and (f) into consideration. It is partly for the reason that such an arrangement estranges itself from the view of chemistry and partly for the reason that atoms in (e) or (f) cannot contribute to the observed dissymmetry of the intensity distribution of Laue spots. 16 C atoms are divided into two groups of eight equivalent atoms, both being arranged in (g). 40 H atoms will also be divided into five groups of eight equivalent ones (also in (g)).

Now for the arrangement of 2 N and 2 I atoms, there are two possible cases, namely (1) N in (a), I in (b) and (2) N in (a), I in (c), the other cases being reduced to either (1) or (2). To distinguish the alternative, the spectrometric data from (001) may be used. The observed intensity distribution of reflexion from (001) among various orders is very nearly normal. Such a distribution can be accounted for by either of these possible arrangements for N and I atoms with an adequate structure of the group $N(C_2H_5)_4$, in which the tetrahedral nature of C atoms and the ordinary values of atomic radii for the neutral N and C atoms could be well maintained. The values of z for the two kinds of C atoms are about $z_1 \approx \frac{1}{8}$ and $z_2 \approx 0$ in the case (1), and $z_1 \approx \frac{1}{8}$ and $z_2 \approx \frac{1}{4}$ in the case (2). Owing to an ambiguity accompanying the interpretation of the intensity of reflexion, it is not quite free from danger to precise the distinction further only by the data from (001) so as to exclude one of the two. Other intensity data should be made use of also. For this it is necessary to take into account the remaining parameters of x and y , of which the number is

1) In this connection refer to the recent paper of R.W.G. Wyckoff, who analysed the crystal structure of tetramethyl ammonium halides with the result of the probable existence of the tetrahedral ammonium N atom. (Z. Krist. **67** (1928), 91).

so many as to preclude the further determination practically. In case that the structure is based upon (1), it is quite analogous to that of the NaCl type or that of NH_4I crystal at ordinary temperature, the analogy being made clear by returning to the old face-centred unit cell. The shape of the group $\text{N}(\text{C}_2\text{H}_5)_4$ is rather flat, and the lattice becomes remarkably expanded side-ways. In case of the other structure based upon (2), it is somewhat related to that of the CsCl type or that of the low temperature modification of ammonium chloride. The group $\text{N}(\text{C}_2\text{H}_5)_4$ is here probably of the shape of a fylfot. As both structures are equally reasonable, it seems better to retain them equally for the present and to await a decisive conclusion in future.

In conclusion, the author wishes to express his best thanks to Professor S. Nishikawa for his continued interest during the work.