ART. II.—*The Crystal Structure of Hydrazine Dihydro-chloride;* by RALPH W. G. WYCKOFF.

Introduction.—The dihydrochloride of hydrazine $N_2H_4.2HCl$) has been described as crystallizing in regular isotropic octahedrons[2]; the class of cubic symmetry to which these crystals should be assigned seems, however, never to have been determined. Their density[3] is 1.4226 measured at 20° against water at 4°C.

This determination of crystal structure using X-rays has been carried out by the methods and procedure previously outlined.[4] The dimensions of the unit crystal and the value of m/n^3, the ratio of the number of chemical molecules within the unit cell to the cube of the order of reflection, were obtained from a reflection spectrogram from some crystal face; Laue photographic data were used to determine the size of the true unit of structure, to establish the corresponding space group and the manner of arrangement of the atoms within this unit and to estimate the positions of these atoms.

The crystals used in this study were clear octahedrons grown by slow cooling from a solution of hydrazine hydrochloride made strongly acid with hydrochloric acid. Excellent specimens are readily obtained in this manner.

The Determination of the Structure of Hydrazine Hydrochloride.—Measurements upon a comparison reflection spectrum from the (100) face of calcite and the (111) face of hydrazine hydrochloride are shown in Table I. The spacing against the cube face, d_{100}/n, calculated in the usual manner from these data can be used to determine the value of the ratio m/n^3:

$$\frac{m}{n^3} = \left(\frac{d_{100}}{n}\right)^3 \frac{\rho}{M} = 4.04$$

(where ρ is the density and M is the mass of a chemical molecule of the hydrazine hydrochloride). There must consequently be either four or 32 chemical molecules of the composition $N_2H_6Cl_2$ within the unit cube.

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[2] T. Liweh, Zeitsch. f. Kryst., 17, 390, 1890.

[3] H. Schiff and U. Monsacchi, Zeitsch. physikal. Chem., 21, 292, 1896.

[4] Ralph W. G. Wyckoff, J. Am. Chem. Soc. 42, 1100, 1920; this Journal, 50, 317, 1920; etc.

A series of Laue photographs with the X-rays making small, and different, angles with the normal to the (111) face were prepared and analyzed in the usual fashion.

TABLE I.   Measurements upon a (100) Calcite—(111) $N_2H_6Cl_2$ Comparison Spectrum.

Calcite:

Line	Distance from slit image to line	Wave Length[5] (Rh tube)
β (2)	1.86 cm.	0.545 A. U.
α (2)	2.10	.614
β (4)	3.83	.545
α_1(4)	4.34	.612
β (6)	6.13	.545
α_1(6)	7.11	.612

$N_2H_6Cl_2$:

Line	Distance from slit image to line	d_{111}/n'	d_{100}/n
β	1.24 cm.	4.522 A. U.	(7.832) A. U.
α	1.39	4.550	7.881
β	2.48	2.286	7.918
α	2.82	2.275	7.880
			7.89 A. U.

Choosing the smaller unit of structure for the purpose of calculating the wave lengths of the X-rays causing the various spots occurring upon the photographic plate, no values of $n\lambda$ less than 0.24 were found upon the photographs; as a consequence it is permissible to choose this as the correct unit, rather than the larger one containing 32 chemical molecules.   The data given in Table II were

TABLE II.   Laue Photographic Data.

Plane	Wave Length	Intensity
$\bar{4}$ 1 4	0.366 A	s
$\bar{2}$ $\bar{1}$ 4	.474	s
$\bar{1}$ $\bar{2}$ 4	.430	s
1 $\bar{5}$ 6	.355	f+
$\bar{5}$ 3 4	.453	m
5 1 $\bar{4}$	.364	m
$\bar{3}$ $\bar{1}$ 7	.492	f
$\bar{1}$ $\bar{3}$ 7	.455	f
3 $\bar{5}$ 5	.390	f

NOTE: In these tables s, m, f and ab refer to reflections that are classed as strong, medium, faint or absent.

[5] W. Duane, Bull. Nat. Research Council, Vol. I, Part 6, 383, 1920.   Values determined by Siegbahn et al.

obtained from one of these Laue photographs. An inspection of them shows that planes having indices (1) that are all odd, (2) that are two even and one odd and (3) that are two odd and one even are all reflecting in the first order. It must therefore be concluded that the lattice underlying the corresponding space group must be the simple cubic lattice, Γ_c. The Laue photographs show a marked hemihedry; such a lack of complete symmetry is shown, for instance, by the strong appear-ance of spots due to planes of the form {631} and the absence of reflections of the opposite form {613}, even though both types of planes were in excellent positions to reflect the X-rays (see Table II). The symmetry of these crystals is then that of either T or T^h, the tetarto-hedry or the paramorphic hemihedry (pyritohedry) of the cubic system.

Distinction can be made between the space groups which are built upon the simple cubic lattice and which belong to these two classes of symmetry. For this purpose[6] a study is necessary of planes of the forms one of whose indices is zero. Consideration of the form of the general intensity expressions used in establishing these distinguishing criteria shows that the special cases that are involved in a discussion of the present problem do not introduce into them any significant simplifica-tion. It is therefore legitimate to make use of these general criteria. In Table III are given useful data con-cerning first order reflections from such planes. It will be seen that though various planes of the form {k0l}, where k is odd and l is even, appear, reflections from no planes of the opposite form {0kl} nor any planes of the forms {0hl} or {h0l}, where h also is odd, are found upon any of the photographs though several were favor-ably situated. Only one space group agreeing with the other conditions that have been shown necessary could yield these results. The space group corresponding to crystals of hydrazine hydrochloride can consequently be taken as $T_h{}^6$.

From a knowledge of its corresponding space group the manner of arrangement of the atoms in this crystal can be deduced. The special cases of $T_h{}^6$ are as follows:

[6] Ralph W. G. Wyckoff, this Journal, 4, 175, 1922.

TABLE III.   Laue Photographic Data.

Plane	Wave Length	Intensity	Form
$\bar{3}$ 0 4	0.442	s	0 4 3
$\bar{4}$ 5 0	.335	m	0 4 5
5 0 $\bar{3}$	.437	ab	0 3 5
10 $\bar{3}$ 0	.518	f	0 10 3
0 $\bar{4}$ 7	.395	ab	0 4 7
$\bar{5}$ 8 0	.380	ab	0 5 8
$\bar{5}$ 7 0	.327	ab	0 5 7
0 7 $\bar{4}$	.466	ab	0 7 4
9 0 $\bar{5}$	.291	ab	0 5 9
3 $\bar{2}$ 0	.278	ab	0 3 2
$\bar{4}$ 0 5	.288	ab	0 · 5 4
$\bar{5}$ 0 8	.381	m	0 8 5
3 0 $\bar{2}$	.477	s +	0 2 3
0 5 $\bar{3}$	.473	ab	0 5 3
0 $\bar{3}$ 4	.457	ab	0 3 4
$\bar{5}$ 0 7	.330	ab	0 7 5

Four equivalent positions:

4b.   000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

4c. $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00$.

Eight equivalent positions:

8h. uuu; $u+\frac{1}{2},\frac{1}{2}-u,\bar{u}$; $\bar{u},u+\frac{1}{2},\frac{1}{2}-u$; $\frac{1}{2}-u,\bar{u},u+\frac{1}{2}$;
$\bar{u}\bar{u}\bar{u}$; $\frac{1}{2}-u,u+\frac{1}{2},u$; $u,\frac{1}{2}-u,u+\frac{1}{2}$; $u+\frac{1}{2},u,\frac{1}{2}-u$.

Twenty-four equivalent positions: The generally equivalent[7] positions of $T_h{}^6$.

The only atomic arrangement derivable from these special cases which will associate together the two nitrogen atoms of a hydrazine group gives to both nitrogen and chlorine the arrangement 8h, with different values of course of the parameter u; the hydrogen atoms would then most naturally be considered as all equivalent to one another and occupying the 24 most generally placed positions of $T_h{}^6$.   It is convenient to consider the center of one of the hydrazine groups as located at the corner of the unit cube; the centers of the other hydrazine groups within the unit cell are then to be found at the other positions of 4b: the parameter u defining the position of the nitrogen atoms thus will have a small value.

Because, even excluding the hydrogen atoms, there are two unknown parameters in this structure it would not be feasible to carry out an exact determination of the

[7] Ralph W. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space Groups, Carnegie Institution of Washington Publication No. 318.   1922.

positions of the nitrogen and chlorine atoms. Even if only a rough proportionality to atomic number is maintained, however, the scattering power of the chlorine atoms is enough greater than that of the nitrogen atoms so that an estimation of the positions of the former can be made. Experience with other crystal structures has shown, furthermore, that the two nitrogen atoms in direct chemical combination with one another will in all probability be separated by a distance which is of the same order of magnitude as the diameter of the sphere of influence which has been assigned to nitrogen.[8] The value of this parameter u can consequently be taken to lie between fairly narrow limits which for the present purposes are chosen from $u = 0.02$ to $u = 0.07$. For similar reasons the calculations were not carried out for values of the chlorine parameter outside of $v = 0.11$ to $v = 0.44$. The customary intensity expression[9] in this case becomes for the nitrogen and chlorine atoms only:

$$ \mathrm{I} \propto f\left(\frac{d}{n}\right)(\mathrm{A^2 + B^2}), \qquad \text{where} \qquad (1) $$

$$ \mathrm{A} = 2\overline{\mathrm{N}}\left[\cos 2\pi n u(h+k+l) + \cos 2\pi n\left\{u(h-k-l)\right.\right. $$
$$ \left. + \tfrac{1}{2}(h+k)\right\} + \cos 2\pi n\left\{u(-h+k-l) + \tfrac{1}{2}(k+l)\right\} + \cos 2\pi n $$
$$ \left\{u(-h-k+l) + \tfrac{1}{2}(h+l)\right\}\left] + 2\overline{Cl}\left[\text{a similar term in } v\right];\right. $$
$$ \mathrm{B} = 0. $$

Reference to the data of Table III shows that planes of the form {047} did not appear even though they were favorably situated. The chlorine atoms must then have such a position that the calculated amplitude for planes of this form will be slight. The curve showing the variation of A with the value of the chlorine parameter v is shown in figure 1. It is seen that A either vanishes or becomes relatively small in absolute value in four regions—around $v = 0.16$, 0.21, 0.25-0.29 and 0.35-0.38. A choice between these various possible positions for the chlorine atoms can be made from a study of the other curve shown in figure 1, that for the form {045}. The only one of these values of v which permits reflections from planes of this form to appear strongly upon the photographs are those within the region 0.26-0.28. Cal-

[8] W. L. Bragg, Phil. Mag., (6) 40, 169, 1920.
[9] Ralph W. G. Wyckoff, this Journal, 50, 317, 1920.

culations of amplitude have also been made for those planes for which data are recorded in Table IV. In every case there is satisfactory qualitative agreement with this assignment of position to the chlorine atoms. A study of the {714} form shows further that v cannot
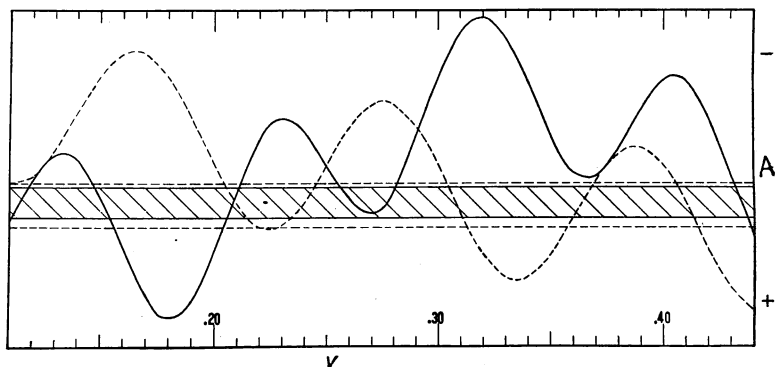
FIG. 1.

FIG. 1.—The full curve shows the variation of A (proportional to the amplitude of the reflected beam) with values of the chlorine parameter for planes of the form {047}, none of which were found in the Laue photographs. For values of u (for nitrogen) between 0.02 and 0.06 the position of zero amplitude will lie somewhere within the shaded area. The dashed curve is a similar one for planes of the form {045}, which appear strongly upon the photographs; in this case the zero position (for the same nitrogen limits) lies between the two horizontal dashed lines.

TABLE IV.   Laue Photographic Data.

Plane	Wave Length	Intensity	Form
0 $\bar{4}$ 7	0.395	ab	0 4 7
$\bar{4}$ 5 0	.335	m ·	0 4 5
$\bar{5}$ 0 8	.381	m	0 8 5
$\bar{4}$ 8 $\bar{1}$	.413	m	8 1 4
$\bar{1}$ 8 $\bar{4}$	.388	ab	8 4 1
3 1 $\bar{3}$	.460	ab	1 3 3
$\bar{3}$ 6 $\bar{1}$	.487	ab	6 1 3
$\bar{1}$ 6 $\bar{3}$	.463	m	6 3 1
10 $\bar{3}$ 0	.518	f	0 10 3
$\bar{4}$ 3 2	.445	s	2 4 3
$\bar{4}$ 2 3	.432	m	4 2 3
$\bar{2}$ 8 $\bar{3}$	.414	m	2 8 3
$\bar{3}$ 8 $\bar{2}$	.420	ab	8 2 3
$\bar{5}$ 2 6	.483	m	5 2 6
$\bar{5}$ 6 2	.508	ab	2 5 6
$\bar{4}$ 7 1	.365	f	4 7 1
1 7 $\bar{4}$	.339	ab	1 7 4

have a value less than 0.27 (information from the {841} form confirms this). The data as a whole agree best with a value of u (for nitrogen) of about 0.04 and seem to indicate that its effective scattering power may be somewhat less than that which would correspond to a substitution of atomic numbers in expression 1. This is not surprising when it is remembered that all but two
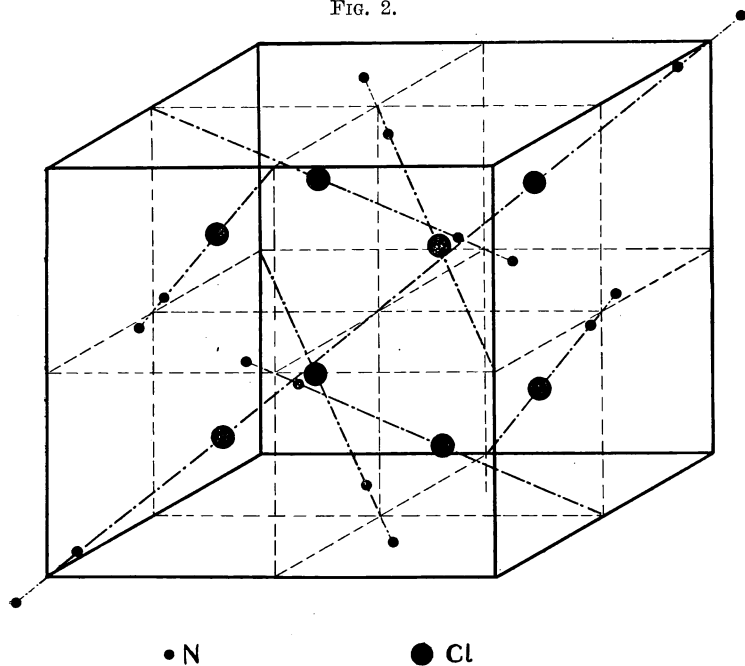
FIG. 2.

• N   ● Cl

FIG. 2.—The unit cell of hydrazine hydrochloride. Both nitrogen atoms of each pair forming a hydrazine group are shown in the figure though one atom in each pair is not within this unit cube.

of the nitrogen electrons may be concerned in binding other atoms and in doing so may occupy positions quite distant from the nitrogen nucleus. These calculations are likewise in entire qualitative disagreement for example with the positions about 0.35-0.38. Especially in view of the impossibility of estimating the true scattering powers of the nitrogen and hydrogen atoms of the hydrazine groups, an attempt to get a more accurate placing of these nitrogen and chlorine atoms would give rise to results of doubtful significance.

Conclusions.—The unit cell of crystals of hydrazine

hydrochloride has been shown to be a cube 7.89 A.U. on a side and to contain four chemical molecules. With the aid of a unique determination of its corresponding space group as $T_h{}^6$, the manner of arrangement of its atoms within this unit is definitely determined. Though it is not now possible to obtain the positions of these atoms with great accuracy, an approximate placing of them has been made. The nature of the resulting structure is shown in figure 2.

In water solutions this salt presumably breaks up into hydrazine ions bearing two positive charges each and two negatively charged chloride ions. It will be noted that in its crystal structure hydrazine hydrochloride resembles such salts of an analogous type as the alkaline earth nitrates,[10] the centers of the hydrazine groups occupying positions analogous to those held by the alkaline earth metal atoms and the chlorine atoms replacing the nitrate groups.

The values which have previously been assigned to atomic radii[11] fail to hold in the present instance: Distance Cl to N, calculated 1.70 A.U., observed 3.14 A.U.; distance Cl to Cl, calculated 2.10 A.U., observed 3.96 A.U.

SUMMARY.

Using Laue photographic and spectographic data and the results of the theory of space groups, the manner of arrangement of the atoms within the unit cell of a crystal of hydrazine hydrochloride, which contains four chemical molecules and is 7.89 A.U. on a side, has been determined. The corresponding space group is $T_h{}^6$. The parameter v defining the positions of the chlorine atoms is found as 0.27+ and the most probable value of the nitrogen parameter is estimated as about 0.04. The distance between adjacent chlorine atoms thus is approximately 3.96 A.U.; between chlorine and nitrogen atoms about 3.14 A.U. It is pointed out that these results are markedly at variance with the hypothesis of constant atomic radii.

Geophysical Laboratory,
    Carnegie Institution of Washington,
        November, 1922.

[10] Nishikawa and Hudinuki, Proc. Tokyo Math. Phys. Soc., (2) 9, 197, 1917.
[11] W. L. Bragg, op. cit.