The Structure of Hydroxylammonium Chloride, NH₃OHCl, and Hydroxylammonium Bromide, NH₃OHBr*

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Hydroxylammonium chloride, NH_3OHCl, and hydroxylammonium bromide, NH_3OHBr, are isomorphous and belong to the space group C_{2h}^5-$P\,2_1/c$. The unit cell, which contains $4NH_3OHX$, has the following dimensions:

$$NH_3OHCl : a = 6{\cdot}95 \text{ A.}, \quad b = 5{\cdot}95 \text{ A.}, \quad c = 7{\cdot}70 \text{ A.}, \quad \beta = 120{\cdot}8°,$$

$$NH_3OHBr : a = 7{\cdot}29 \text{ A.}, \quad b = 6{\cdot}13 \text{ A.}, \quad c = 8{\cdot}04 \text{ A.}, \quad \beta = 120{\cdot}8°.$$

The nitrogen and oxygen atoms and the halogen ions occupy general positions $4(e)$. The parameters have been determined. All these atoms and ions are situated close to the planes $(\frac{1}{4}, y, z)$ and $(\frac{3}{4}, y, z)$. The distance between the nitrogen and oxygen atoms of the same NH_3OH^+ group is $1{\cdot}45$ A.

Unit cell and space group

The hydroxylammonium chloride used was prepared according to *Organic Syntheses* (1932) and was recrystallized from water. The crystals obtained formed plates (Groth, 1906) shaped as fairly regular hexagons which, owing to intergrowth, were unsuitable for single-crystal work. Crystallization from 85 % ethanol was then tried, and the more needle-like crystals thus obtained were used for the investigation.

The hydroxylammonium bromide was prepared according to Adams (1902). Crystals of very variable shapes were obtained from a solution in absolute ethanol. A needle-shaped crystal was used for the single-crystal work. The substance is slightly deliquescent, and in order to protect the crystal against moisture it was covered with a film of nitrocellulose by dipping it into a solution of nitrocellulose in amyl acetate.

Both substances were tested for piezo-electricity by means of a sensitive dynamic method which has been developed in this laboratory. No piezo-electric effect could be detected from the chloride, while the method failed in the case of the bromide, presumably as a consequence of the hygroscopic nature of the crystals.

Groth (1906) describes the two substances as isomorphous and crystallizing in the monoclinic system. Axial ratios and angles are given as

$$a : b : c = 2{\cdot}0108 : 1 : 1{\cdot}3028,$$

$\beta = 92°\ 57'$ for the chloride, and

$$a : b : c = 2{\cdot}0374 : 1 : 1{\cdot}3077,$$

$\beta = 93°\ 20'$ for the bromide. These statements were confirmed in the present work, but it was found that the axis systems given by Groth correspond to centred cells. The dimensions of the primitive monoclinic cells which were determined from the rotation and Weissenberg photographs are (expressed in true A.units = 10^{-8} cm.)

$a = 6{\cdot}95$ A., $b = 5{\cdot}95$ A., $c = 7{\cdot}70$ A., $\beta = 120{\cdot}8°$ for the chloride, and $a = 7{\cdot}29$ A., $b = 6{\cdot}13$ A., $c = 8{\cdot}04$ A., $\beta = 120{\cdot}8°$ for the bromide. Here the a axis according to Groth's setting has the indices [201], while the b and c axes are the same. The volumes of the unit cells are $273{\cdot}5$ A.³ for the chloride and $308{\cdot}6$ A.³ for the bromide.

The literature gives the specific gravity values $d\ 17°/4° = 1{\cdot}676$ for the chloride (Schiff & Monsacchi, 1896), and $d\ 22°/4° = 2{\cdot}3514$ for the bromide (Eyer, 1910). With the above cell volumes these values correspond to $3{\cdot}97$ and $3{\cdot}83$ groups of NH_3OHX (X denotes Cl or Br) respectively per unit cell. The real value is evidently 4.

Both the chloride and the bromide crystals were rotated about the b axis. In these photographs reflexions $h0l$ were observed only for $l = 2n$. The chloride was also rotated about [201], and here it was found that reflexions $0k0$ occurred only for $k = 2n$. These data, combined with the values given below of the Patterson function in the plane $(u, \frac{1}{2}, w)$ for the bromide, indicate that the space group is C_{2h}^5-$P\,2_1/c$ for both substances.

Patterson function

All intensities were obtained from Weissenberg photographs with rotation about the b axis. With Cu K radiation only three layer lines in addition to the equator could be used for the determination. In order to get additional data Mo K radiation was tried. Owing to a rapid decrease in intensity with increasing deviation angle the photographs obtained with this radiation, however, did not show more reflexions than the photographs with Cu K radiation. The maximum absolute values obtained with Cu K radiation for h, k and l were for the chloride 8, 3 and 9, and for the bromide 10, 3 and 10.

The intensities were estimated visually using the intensity ratio $I_{a_1} : I_{a_2} : I_\beta = 100 : 50 : 15$ for a given reflexion. For the chloride an attempt was made to

connect the intensities of the reflexions in the different layer lines by means of the equator in a Weissenberg photograph obtained by rotation about [201]. Owing to the very variable shape of the reflexions, however, this method could not be used. The same cause prevented the use of the rotation photograph about the b axis for a similar purpose. It was then thought best to connect the intensities in the different layer lines by direct comparison after exposures of the same length, using the same primary intensity.

(010), $P (u, w)$, and by the values of the function in the plane $(u, \frac{1}{2}, w)$, denoted as $P (u, \frac{1}{2}, w)$, and along the line $(0, v, \frac{1}{2})$, denoted as $P (0, v, \frac{1}{2})$. The plane $(u, \frac{1}{2}, w)$ and the line $(0, v, \frac{1}{2})$ were chosen according to Harker (1936) because of the presence of screw axes 2_1 parallel to the b direction and glide planes c at right angles to this direction. The values for the chloride are shown in Fig. 1 and for the bromide in Fig. 2. The numbers give the relative heights of the maxima, but cannot be used for comparing the different drawings. Corresponding
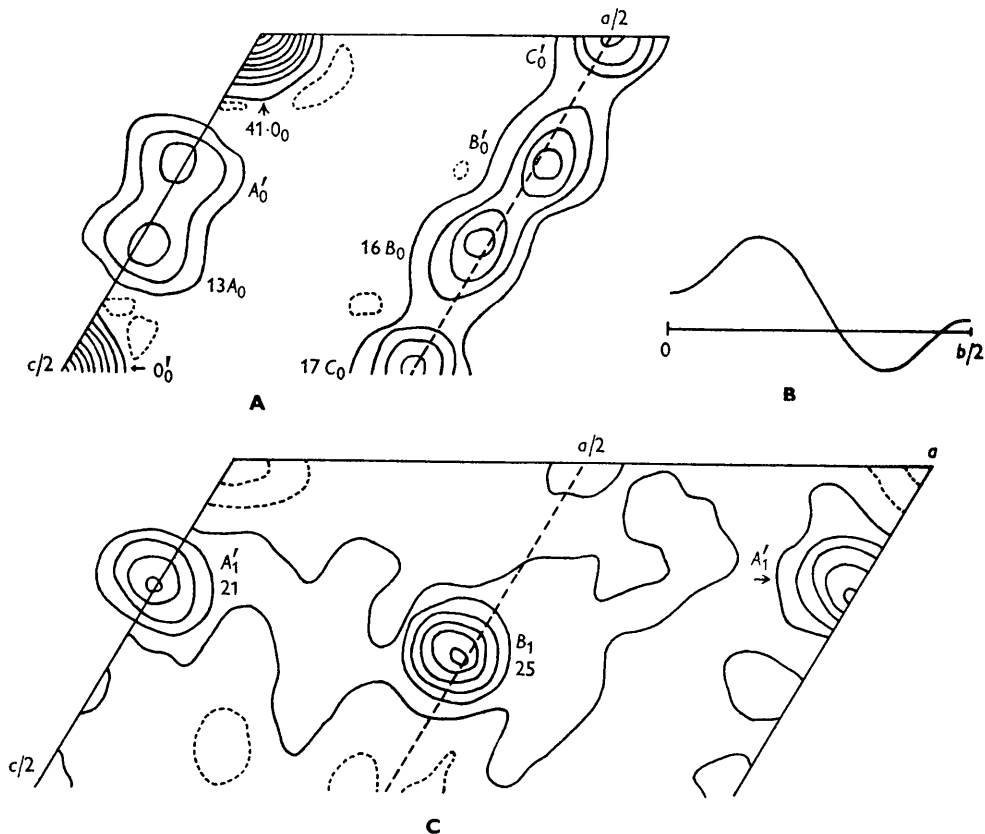

Fig. 1. Patterson function of NH₃OHCl. (A) $P (u, w)$, (B) $P (0, v, \frac{1}{2})$, (C) $P (u, \frac{1}{2}, w)$. Contour lines are drawn at height differences of 5 units, and negative values are denoted by broken lines. The areas limited by full and broken lines lie between 0 and -5.

Relative $| F |^2$ values were calculated from the estimated intensity values by dividing by the polarization and Lorentz factors and by the factor for specific exposure time. These factors were combined into the factor

$$(1 + \cos^2 2\theta)/\cos^2 \beta \sin \alpha,$$

where β is the angle between the primary beam and the equatorial plane and α is the azimuth of the interference counted from the plane through the primary beam and the rotation axis. No correction for absorption was introduced. The Fourier summations were carried out by means of the calculating machine constructed by Hägg & Laurent (1946).

The structure could be determined approximately by means of the projection of the Patterson function on

maxima of the two salts have practically the same situations and have been designed with the same letters.

In the following, only interatomic vectors including at least one halogen atom are discussed. Maxima corresponding to vectors between two light atoms (nitrogen and oxygen) will be too weak to be visible.

All two-fold positions in $C_{2h}^5 - P 2_1/c$ imply a vector $(0, \frac{1}{2}, \frac{1}{2})$. As no such vector can be seen (Figs. 1 C, 2 C), halogen ions cannot occupy two-fold positions but must be placed in $4(e)$. The possibility of nitrogen or oxygen occupying two-fold positions cannot be excluded in this way.

The approximate x and z parameters of the halogen ions could be determined from $P (u, \frac{1}{2}, w)$. Fig. 1 C shows two large maxima of about the same height. One

of them must be ascribed to a vector $Cl^- - Cl^-$, but the other must be caused by special values of the y parameter of others atoms. A_1' can hardly denote a vector between two Cl^- ions connected by the screw axis 2_1. In such a case all Cl^- ions would be situated practically in the plane $(0, y, z)$ (or the equivalent plane $(\frac{1}{2}, y, z)$) which would give a very improbable distribution of the electric charges. The vector $Cl^- - Cl^-$ must then be represented by B_1. This is confirmed by Fig. 2C where B_3 is considerably larger than A_3'. It is evident that a

as in the bromide, but not when it is smaller as in the chloride.

The maximum A_3', whose height compared with the $Br^- - Br^-$ maximum B_3 is much less than the height of A_1' compared with the $Cl^- - Cl^-$ maximum B_1, must be caused by a vector from halogen to either nitrogen or oxygen. As $X^- - O$ will give a maximum of practically the same height as $X^- - N$, one cannot decide between these two possibilities. However, the light atom in question is temporarily denoted as 'N'. This atom must
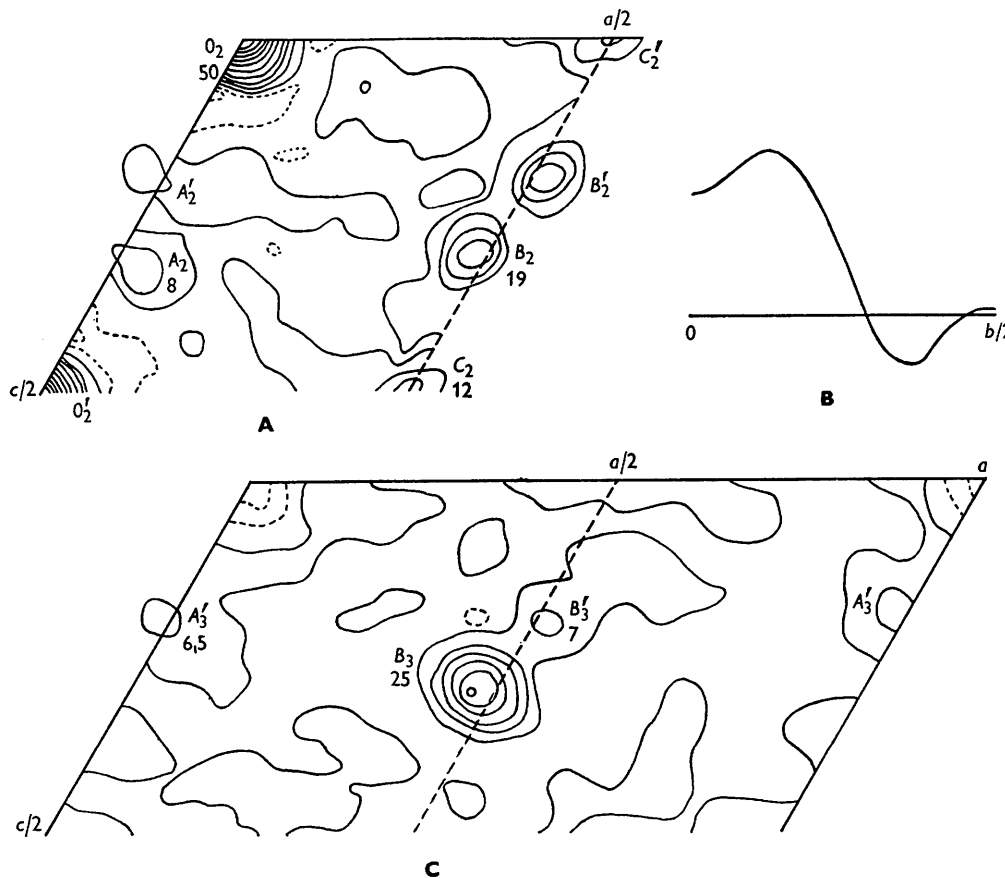

Fig. 2. Patterson function of NH_3OHBr. (A) $P(u, w)$, (B) $P(0, v, \frac{1}{2})$, (C) $P(u, \frac{1}{2}, w)$. Contour lines as in Fig. 1

halogen-halogen maximum compared with the other maxima must be relatively larger in NH_3OHBr than in NH_3OHCl. B defines the x and z parameters of the halogen ions as $x \approx 0.24$, $z \approx 0.395$; or $x \approx 0.26$, $z \approx 0.105$. These two pairs are equivalent and the first is arbitrarily chosen.

From $P(0, v, \frac{1}{2})$ (Figs. 1 B, 2 B) one gets the approximate value 0.18 for the y parameter of the halogen.

Fig. 2 C shows a weak maximum B_3', which has no equivalent in Fig. 1 C. With the halogen parameters now obtained one can explain this maximum as the 'top' of a $Br^- - Br^-$ maximum, whose centre is situated at a distance of 0.14 from the plane $(u, \frac{1}{2}, w)$. This is so close to the plane that the outskirts of the maximum are seen in $(u, \frac{1}{2}, w)$ when the maximum has a high value

occupy a position $4(e)$. As the vector $X^- - 'N'$ is so apparent in $P(u, \frac{1}{2}, w)$, the y parameter of 'N' must differ from the y parameter of the X^- by about $\frac{1}{2}$. This gives $y_{'N'} \approx 0.68$. One further obtains $x_{'N'} \approx 0.26$ and $z_{'N'} \approx 0.22$.

These 'N' parameters require $X^- - 'N'$ maxima in $P(u, w)$ at $(0.50, 0.12)$ and $(0.50, 0.38)$. This explains the elongated form of the maxima B_0, B_0', B_2 and B_2' in Figs. 1A, 2A.

The only maxima hitherto not explained are those called C in the positions $(\frac{1}{2}, \frac{1}{2})$ of Figs. 1A, 2A. The maximum C' in $(\frac{1}{2}, 0)$ is identical with C. The height of C shows it to be caused by a vector from halogen to the kind of light atoms (excluding hydrogen) which is not responsible for the maxima A'. The kind causing C is

temporarily denoted as 'O'. The situation of C and the halogen parameters already obtained show that the 'O' atoms must be situated in $4(e)$ with $x_{.0}. \approx 0.26$ and $z_{.0}. \approx 0.105$. These parameter values also require X^-–'O' maxima in P (u, w) at $(0.02, 0.21)$ and $(-0.02, 0.29)$; which explains the expansion of the maxima A_0 and A_0' and also the irregular form of the maxima A_2 and A_2'.

As a result, the following approximate structure has been obtained:

$$4 \ X^- \ \text{in} \ 4(e) : x \approx 0.24, \quad y \approx 0.18, \quad z \approx 0.395;$$
$$4 \ 'N' \ \text{in} \ 4(e) : x \approx 0.26, \quad y \approx 0.68, \quad z \approx 0.22;$$
$$4 \ 'O' \ \text{in} \ 4(e) : x \approx 0.26, \quad y \approx ?, \quad z \approx 0.105.$$

One sees that all atoms are situated close to the planes $(\frac{1}{4}, y, z)$ and $(\frac{3}{4}, y, z)$ which explains the marked cleavage parallel to (100). If one considers the accessible space in one of these planes, assuming the radius of Cl$^-$ to be 1.8 A., one gets a probable value for $y_{.0}.$ of about 0.88.

Fourier F syntheses

The account is exemplified by the Fourier F syntheses carried out for the chloride.

The above approximate values for the x and z parameters were used for a calculation of the signs of the
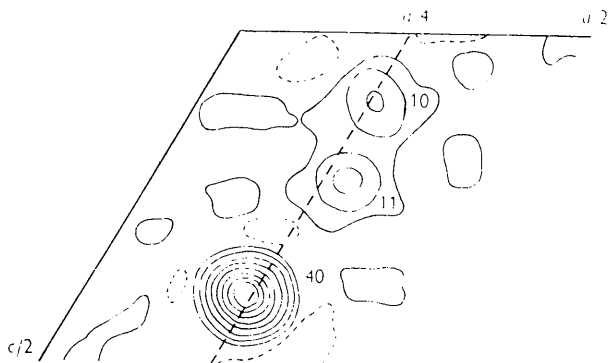

Fig. 3. Relative electron density ρ (x, z) of NH$_3$OHCl. Contour lines as in Fig. 1

F values. A Fourier F synthesis then gave the relative electron density, ρ (x, z), projected on (010) shown in Fig. 3. From this projection the following parameter values were determined:

$$\text{Cl}^- : x = 0.233, \quad z = 0.395;$$
$$'N' : x = 0.283, \quad z = 0.222;$$
$$'O' : x = 0.253, \quad z = 0.106.$$

The signs of the F values were recalculated with these new values. It was found that only one sign had to be changed. This change did not influence the above values, which, consequently, can be regarded as final.

The y parameters could be fixed by means of a calculation of ρ $(\frac{1}{4}, y, z)$. Before that, however, ρ (y, z) was

calculated in order to check the approximate y values. This resulted in the values $y_{\text{Cl}^-} = 0.190$ and $y_{.N.} \approx 0.67$. The y parameter of the 'O' atom could not be obtained in this way as the 'O' maximum was completely covered by the big Cl$^-$ maximum.

For the calculation of

$$\rho \ (\tfrac{1}{4}, y, z) \sim \sum_k \sum_l [C \ (k, l) \cos 2\pi \ (ky + lz)$$
$$\text{where} \qquad\qquad\qquad - S \ (k, l) \sin 2\pi \ (ky + lz)],$$

$$C \ (k, l) = \sum_{h = 2n} (-1)^{h/2} \ F \ (hkl)$$

and

$$S \ (k, l) = \sum_{h = 2n + 1} (-1)^{(h-1)/2} \ F \ (hkl),$$

the signs were calculated in the first approximation exclusively with the use of the Cl$^-$ parameters. The new
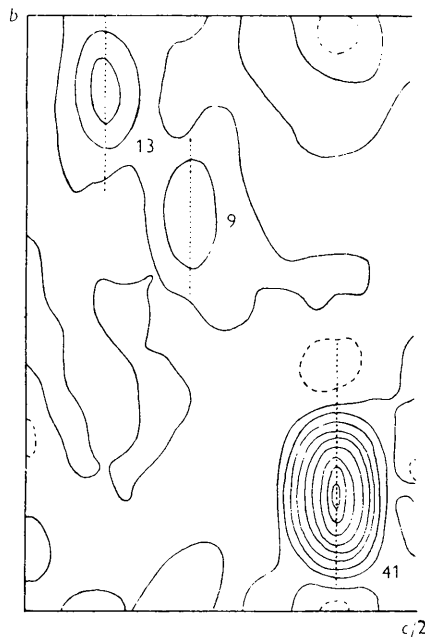

Fig. 4. Relative electron density ρ $(\frac{1}{4}, y, z)$ of NH$_3$OHCl. Contour lines as in Fig. 1. Projections on the plane $(\frac{1}{4}, y, z)$ of the z-parameters determined by ρ (x, z) are marked by dotted lines.

values then obtained for the y parameters of Cl$^-$, 'N' and 'O' were used for a new calculation of the signs of the F values. This resulted in changes of the signs of only a few very small F values. A recalculation of ρ $(\frac{1}{4}, y, z)$, illustrated in Fig. 4, showed only a slight displacement of the y parameter of 'N' which did not cause any further changes of signs. The final y parameters were

$$\text{Cl}^- : y = 0.190;$$
$$'N' : y = 0.664;$$
$$'O' : y = 0.870.$$

The final parameters of the bromide were determined in practically the same way.

The parameters

Because of the very similar scattering factors of nitrogen and oxygen it was found impossible to use the electron density data for deciding the nature of the atoms which were temporarily denoted as 'N' and 'O'. The environments discussed below of the two kinds of atoms showed, however, that the kind of atoms denoted as 'N' is nitrogen and the kind denoted as 'O' is oxygen. The final parameters of the hydroxylammonium chloride will then be

4 Cl$^-$ in $4(e)$: $x=0.233$, $y=0.190$, $z=0.395$;

4 N in $4(e)$: $x=0.283$, $y=0.644$, $z=0.222$;

4 O in $4(e)$: $x=0.253$, $y=0.870$, $z=0.106$.

The final parameters of the hydroxylammonium bromide are:

4 Br$^-$ in $4(e)$: $x=0.240$, $y=0.190$, $z=0.397$;

4 N in $4(e)$: $x=0.286$, $y=0.667$, $z=0.226$;

4 O in $4(e)$: $x=0.263$, $y=0.864$, $z=0.116$.

The parameter values are estimated to be correct within the limits ± 0.003.

Discussion of the structure

The discussion is given for the structure of the chloride, and reference is made to Fig. 5.

Each oxygen atom has two closest Cl$^-$ neighbours at the distances O–Cl$_2^-$ = 2.99 A. and O–Cl$_1^-$ = 3.05 A. The

Table 1. NH$_3$OHCl. *Observed and calculated F values for* $(h0l)$, $(hk0)$ *and* $(0kl)$

hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$
100	1	0.5	$\bar{4}$04	12	$\bar{1}4$	$\bar{3}$08	5	$\bar{6}$	012	17	26
200	20	$\bar{3}6$	$\bar{3}$04	11	13	$\bar{2}$08	5	$\bar{5}$	013	2	2
300	0	$\bar{2}$	$\bar{2}$04	12	16	$\bar{1}$08	6	4	014	11	6
400	19	21	$\bar{1}$04	11	$\bar{1}0$	008	8	8	015	0	0
500	0	3	004	13	$\bar{1}5$	110	4	$\bar{6}$	016	9	$\bar{8}$
600	13	$\bar{1}4$	104	8	5	210	6	$\bar{6}$	017	0	2
$\bar{8}$02	8	11	204	15	13	310	7	5	018	16	$\bar{1}2$
$\bar{7}$02	2	0	304	5	$\bar{1}$	410	9	8	021	8	$\bar{9}$
$\bar{6}$02	8	$\bar{1}1$	404	10	$\bar{1}1$	510	11	$\bar{5}$	022	2	$\bar{0}\text{·}5$
$\bar{5}$02	5	$\bar{1}$	$\bar{8}$06	11	$\bar{1}0$	610	9	$\bar{9}$	023	0	0
$\bar{4}$02	10	10	$\bar{7}$06	3	0	710	9	5	024	10	8
$\bar{3}$02	4	2	$\bar{6}$06	12	12	120	0	$\bar{1}$	025	5	$\bar{2}$
$\bar{2}$02	3	$\bar{6}$	$\bar{5}$06	7	4	220	14	15	026	11	7
$\bar{1}$02	6	$\bar{6}$	$\bar{4}$06	16	$\bar{1}4$	320	0	3	027	9	5
002	3	0	$\bar{3}$06	9	$\bar{6}$	420	12	$\bar{1}0$	028	6	$\bar{4}$
102	9	9	$\bar{2}$06	16	14	520	0	$\bar{3}$	031	6	8
202	2	3	$\bar{1}$06	7	8	620	11	7	032	5	$\bar{2}$
302	11	$\bar{1}0$	006	17	$\bar{1}2$	130	7	10	033	8	$\bar{6}$
402	0	$\bar{4}$	106	9	$\bar{9}$	230	0	1	034	3	$\bar{2}$
502	10	10	206	10	10	330	9	$\bar{9}$	035	9	$\bar{5}$
602	0	5	306	8	8	430	0	$\bar{2}$	036	0	2
$\bar{8}$04	6	$\bar{6}$	$\bar{7}$08	5	$\bar{7}$	530	6	6	037	6	$\bar{4}$
$\bar{7}$04	9	12	$\bar{6}$08	0	2	630	0	$\bar{2}$			
$\bar{6}$04	12	10	$\bar{5}$08	4	6	730	5	$\bar{5}$			
$\bar{5}$04	14	$\bar{1}3$	$\bar{4}$08	0	2	011	4	$\bar{2}$			

Calculated and observed F values for $(h0l)$, $(hk0)$ and $(0kl)$ are compared in Table 1. In order to facilitate the comparison, the calculated F values have been divided by the mean quotient $F_{calc.}/F_{obs.}$. The best agreement was obtained by introducing a temperature factor $\exp\left[-B\,(\sin\theta/\lambda)^2\right]$, with $B=1.5\times 10^{-16}$ cm.^{2} The atomic scattering factors, f_0, were taken from the *Internationale Tabellen* ... (1935). The hydrogen atoms were neglected, which may have caused the calculated F values of some observed reflexions ($\bar{7}$02, 002, $\bar{7}$06) to be ≈ 0. The two most intense reflexions (200, 012) are weaker than calculated. This may be caused partially by the difficulty in estimating their high intensity correctly, and partially by extinction.

directions to these Cl$^-$ ions form the angles $97°$ and $180°$ with the O–N bond. Each Cl$^-$ ion has two closest oxygen neighbours at the same distances.

Each nitrogen atom has four closest Cl$^-$ neighbours at the distances N–Cl$_1^-$ = 3.16 A., N–Cl$_2^-$ = 3.21 A., N–Cl$_3^-$ = 3.23 A. and N–Cl$_4^-$ = 3.26 A. The directions to these ions form the following angles with the O–N bond:

$\wedge$ O–N–Cl$_1^-$ = $99°$, $\wedge$ O–N–Cl$_2^-$ = $172°$,

$\wedge$ O–N–Cl$_3^-$ = $90°$, $\wedge$ O–N–Cl$_4^-$ = $95°$.

These values can be compared with the results of Jeffrey (1945) for geranylammonium chloride, where the nitrogen atom has four closest Cl$^-$ neighbours at

the distances 3·17, 3·24, 3·24 and 3·24 A. (These values are probably not expressed in true A. units and must then be multiplied by 1·00202 in order to be exactly comparable with the ones given here for the hydroxyl-ammonium chloride. The same is the case for the distance values quoted below from other papers.) An analysis of the grouping of these four Cl⁻ ions around the nitrogen atom shows that one of them (at the distance 3·24 A.) lies approximately in the extension of the N–C bond, and that the directions from the nitrogen atom to the others form angles with this bond that are slightly larger than 90°.

There are, consequently, three known structures in which Cl⁻ ions, as in the hydroxylammonium chloride, surround a NH₃ group where the nitrogen atom has the formal charge +1. If the choice between the nitrogen and oxygen atoms of the hydroxylammonium chloride is that which has been reported above, the nitrogen atom obtains the same number of closest Cl⁻ neighbours as in these three known cases. Furthermore, the magnitude of the distances from nitrogen to Cl⁻ will be nearly the same. The directions nitrogen to Cl⁻ will be practically the same as in the geranylammonium chloride and similar to those in the hydrazinium di-
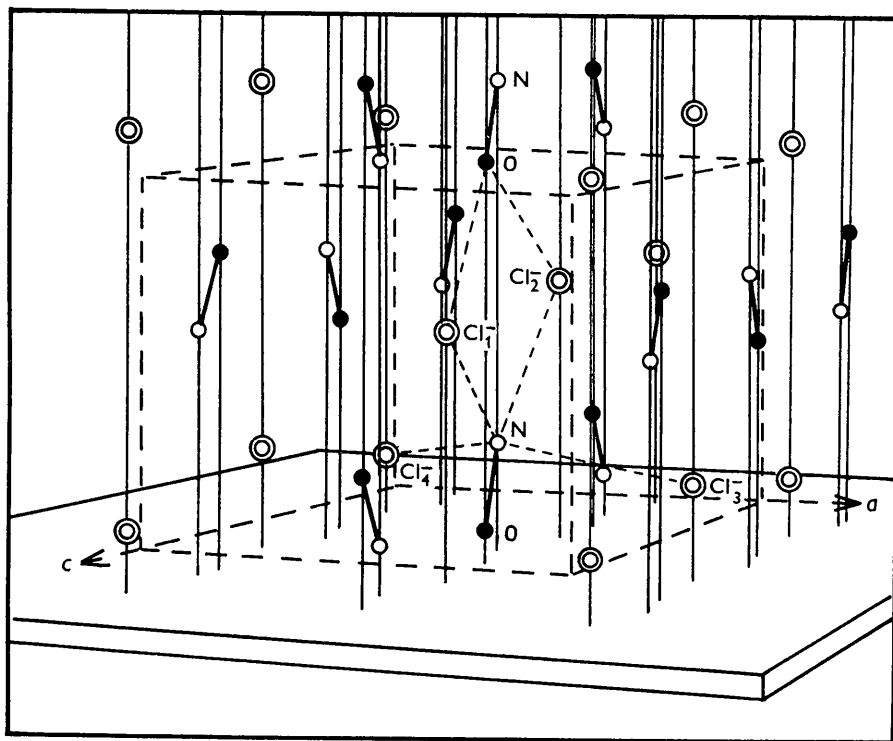

Fig. 5. Schematic drawing of the structure of NH₃OHCl. The outline of a unit cell is marked. Hydrogen atoms not shown. The N and O atoms of the same group [NH₃OH]⁺ are connected with a thick line. ○ = N, ● = O, ◎ = Cl⁻.

A similar but more regular grouping of Cl⁻ about a nitrogen atom was found by Donohue & Lipscomb (1947) for hydrazinium dichloride where the nitrogen atom is surrounded by four Cl⁻, all at a distance of 3·10 A. One of the Cl⁻ ions is situated in the extension of the N–N bond. The directions from the nitrogen atom to the others form angles of about 100° with this bond.

In methylammonium chloride, the structure of which has been studied recently by Hughes & Lipscomb (1946), the nitrogen atom also has four closest Cl⁻ neighbours. These are situated at a distance of 3·18 A. from the nitrogen atom, but the directions N–Cl⁻ constitute the edges of a regular tetragonal pyramid. These edges form equal obtuse angles with the N–C bond.

chloride. These facts are considered to give very strong support to the choice in question.

For the neighbouring NH₃OH⁺ groups the shortest N–O distances are 3·15 and 3·30 A. Each Cl⁻ has three closest Cl⁻ neighbours in the distance 3·92 A.

The distance between nitrogen and oxygen within the same NH₃OH⁺ group is 1·45 A. This value was found for both the chloride and the bromide. If one uses the covalent radii of nitrogen (0·74 A.) and oxygen (0·74 A.), given by Schomaker & Stevenson (1941), one gets the sum 1·48 A. This sum, however, ought to be corrected for the effect of ionic character of the bond. According to Schomaker & Stevenson (1941) the correction should be $-\beta \mid x_A - x_B \mid$, where β is a constant and x the electronegativity of an atom. The correction gives the

best general accordance with observed bond lengths for a value of the constant $\beta = 0.09$. Using this value and the electronegativity values $x_O = 3.5$ and $x_N = 3.0$, one obtains the correction -0.045 A. The above distance of 1·48 A. then decreases to 1·435 A.

More recently Giguère & Schomaker (1943), by electron diffraction, have determined the distances N–N and O–O in hydrazine and hydrogen peroxide respectively. Both distances are found to be 1.47 ± 0.02 A. The expected bond length in the hydroxylammonium ion would then be 1.47 ± 0.02 A. if no correction for ionic character is introduced. With the same correction as above one obtains the value 1.425 ± 0.02 A.

As a consequence one can say that the bond length in the hydroxylammonium ion, which has now been found, is in good accordance with the assumption that the bond is covalent.

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Synthese und Kristallstruktur des Eukryptits, LiAlSiO₄

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Crystals of the mineral eucryptite, LiAlSiO₄, have been prepared synthetically as hexagonal bipyramids up to 5 mm. long, having weak negative birefringence and strong optical activity. The space group is $C6_22$ (or its enantiomorph $C6_42$) and the cell dimensions are $a = 5.27$ A., $c = 11.25$ A. The atomic co-ordinates have been determined and show the structure to be closely related to that of high quartz. The Al and Si ions occupy the sites of the Si ions in quartz, and the small Li ions are accommodated in the channels in the structure.

Aus dem Mineralreich sind uns einige Alkali-Alumosilikate gleichen chemischen Formeltyps bekannt, die sich nur durch die Art des Alkalis unterscheiden. Es sind dieses: NaAlSiO₄, der Nephelin; KAlSiO₄, welches in zwei Modifikationen als Kaliophilit und als Kalsilit bekannt ist, und schliesslich das sehr seltene LiAlSiO₄, der Eukryptit. Diese Silikate können unter dem Namen 'Nephelin-Gruppe' zusammengefasst werden, weil der Nephelin das häufigste Mineral unter ihnen ist. Der Eukryptit ist nur als hexagonale, skelettförmige Verwachsung mit Albit bekannt, welche sich bei der Zersetzung des Spodumens von Branchville, Connecticut, bildet (Brush & Dana, 1881). Erst bei starker Vergrösserung konnte die Selbständigkeit der beiden Gemengteile erkannt werden. Man hat daher dem LiAlSiO₄ den Namen Eukryptit von $\epsilon\dot{v}\kappa\rho\upsilon\pi\tau\acute{o}\varsigma$ = wohlverborgen gegeben. Da eine mechanische Trennung des Minerals von dem umgebenden Albit nicht möglich war, ist es nur

sehr unvollständig einer kristallographischen Untersuchung zugänglich gewesen. Als ich nun im Verlaufe der Synthese des Natriumnephelins auch den hexagonalen Lithiumnephelin in Einzelkristallen herstellen konnte, schien es mir angebracht, eine genauere Kenntniss von diesem Mineral zu erlangen. Insbesondere schien mir das interessant zu sein im Hinblick auf einen Vergleich mit dem Na- und K-Nephelin; denn alle drei Nepheline unterscheiden sich ja chemisch nur durch die Alkalien.

Synthese des Eukryptits

Im Rahmen von Untersuchungen über die Synthese des Na-Nephelins wurde das Zustandsdiagramm NaAlSiO₄-LiF mit Hilfe der statischen Abschreckmethode ermittelt. Das Diagramm ist in Fig. 1 wiedergegeben; es stellt keinen Schnitt durch ein quasi-binäres System, sondern durch ein komplizierteres polynäres System dar.