that most of the silver formed in these crystals is in the interior at dislocations or internal cracks where only the mechanism involving cation motion can be operative, thus giving only the parallel orientation of silver as observed by X-rays. The electron-diffraction method detects only the silver very near the surface. Since by this method only the orientations suggested by Dankov are observed, one must assume that, although both the mechanism based on cation motion and the mechanism of *F*-center aggregation may be possible at the surface, the latter is favored. This seems to be explained by the calculations of Simpson (1949) which show that the electron trap associated with a vacant anion site is of greater depth than the trap associated with an interstitial positive ion in silver bromide.

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Acta Cryst. (1950). **3**, 222

The Structures of the *n*-Propylammonium Halides at Room Temperature*

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(*Received* 30 *September* 1949)

Structures are found for *n*-propylammonium chloride, bromide and iodide with space group D_{4h}^7–$P4/nmm$, with two molecules of $C_3H_7NH_3X$ per unit cell. These structures are related to the structure of tetragonal PbO, with the *n*-propylammonium ion replacing Pb, and the halide ion replacing O. The cations extend along the fourfold axes; hence they must either rotate or show orientational disorder. Study of the structure factors shows that the cation in the chloride crystal shows configurational isomerism, and an electron-density projection of the chloride crystal shows that a model of the crystal showing free rotation of the cation fits the X-ray data slightly better than a model showing simple orientational disorder. An electron-density projection of the bromide crystal also shows no preferred orientations of the cation, within the limits of error of the determination.

Introduction

Determinations of the structures of *n*-propylammonium chloride, bromide and iodide have been reported by Hendricks (1928*a*). These structures were related to the cesium chloride structure by the substitution of the *n*-propylammonium ion for the cesium ion. The unit cell reported was tetragonal, with the cations extended along fourfold axes with the NH_3^+ ends all pointing in the same direction. According to Pauling (1930), the cations must be considered zigzag in shape, and therefore must rotate if the tetragonal symmetry is to be preserved. However, a structure of this same type was reported for methylammonium chloride by Hendricks (1928*b*), but was subsequently disproved by Hughes & Lipscomb (1946), who established a structure in which the NH_3^+ ends of the cations pointed alternately in opposite directions. The present work was undertaken to find whether the *n*-propylammonium halides also have this type of structure, rather than the structure reported by Hendricks.

Another reason for undertaking this research was to investigate the nature of the rotating group by X-ray diffraction studies. The groups might rotate essentially without hindrance, or might rotate in a potential field, according to the model of the hindered rotator proposed by Pauling (1930), or might show orientational disorder without continuous rotation, according to the model proposed by Frenkel (1935). The *n*-propylammonium halides were thought to afford a fairly favorable case for the study of the rotating group, since the rotating carbon and nitrogen atoms have appreciable scattering power for X-rays, whereas in many crystals, only hydrogen atoms rotate.

Preparation and physical properties of crystals

Crystals of *n*-propylammonium chloride, bromide and iodide were prepared by recrystallization from organic solvents by cooling hot, nearly saturated solutions to room temperature and letting the solutions stand for 2 days. For the chloride, chloroform was used as the solvent; for the bromide, *n*-butyl acetate was used; and

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* This paper is in part material from a thesis submitted by M. V. King to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree.

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for the iodide, either ethyl acetate or *n*-butyl acetate was used.

The *n*-propylammonium halides crystallized as tabular crystals, very soft and brittle, and deliquescent at summer humidities. The crystals of the chloride from chloroform solutions were bounded by the forms {110} and {001}, the indices being given according to the directions of axes found in this work. On the other hand, the crystals of the bromide and iodide were bounded by the forms {100} and {001}. The crystals showed cleavage parallel to (100), the cleavage being distinct in the bromide and iodide, and indistinct in the chloride, which usually showed conchoidal fracture. Samples of the chloride and of the iodide gave negative tests for piezoelectricity in an apparatus similar to that of Stokes (1947).

Determination of the structure of the chloride

Powder pictures of the chloride taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ A.) were successfully indexed on a tetragonal unit cell with $a = 6{\cdot}25$ and $c = 7{\cdot}38$ A. Reflections were found which could not be indexed on Hendricks's structure, which contained one molecule in a tetragonal cell with $a = 4{\cdot}48$ and $c = 7{\cdot}40$ A. Each of these reflections was indexed unambiguously on the new proposed unit cell, the indices being 101, 211, 103 and 302.

Weissenberg pictures were taken by the multiple-film technique of chloride crystals of dimensions $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}1$ mm. with unfiltered Cu K radiation, and of chloride crystals of dimensions $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}1$ mm. and $0{\cdot}7 \times 0{\cdot}7 \times 0{\cdot}2$ mm. with filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ A.). The photographs indicated the point group $4/mmm$. The only systematic absences of reflections were $hk0$ spots with $h+k$ odd. These data indicate uniquely a space group D_{4h}^{7}–$P4/nmm$. The unit-cell parameters were determined from a Weissenberg picture of the zero layer taken with the a axis as rotation axis, on which was superimposed a sodium chloride powder pattern for standardization of the camera radius. The observed values were

$$a = 6{\cdot}220 \pm 0{\cdot}005, \quad c = 7{\cdot}377 \pm 0{\cdot}008 \text{ A.}$$

Since the crystals sink in water, but float in chloroform, the density must be between 1·0 and 1·5 g.cm.$^{-3}$. Hence, there are two molecules of $C_3H_7NH_3Cl$ per unit cell, corresponding to a calculated density of 1·1 g.cm.$^{-3}$. The layer-line spacings of rotation pictures taken with the axes a, c and [110] as rotation axes all agreed with this unit cell.

Possible twofold positions of atoms in the space group found are

$$(2a)\colon\ 0,0,0;\quad \tfrac{1}{2},\tfrac{1}{2},0;\quad (2b)\colon\ 0,0,\tfrac{1}{2};\quad \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};$$
$$\text{and}\qquad (2c)\colon\ 0,\tfrac{1}{2},z;\quad \tfrac{1}{2},0,\bar{z}.$$

Atoms linked together at usual interatomic distances into a group can lie only in positions (2c). However, such a group would be linear if no disorder exists. Therefore we assume that the cation rotates or shows orientational disorder, such that the mean positions of the carbon, nitrogen, and hydrogen atoms lie in (2c) with differing parameters z. Since the cation thus situated occupies the entire height of the unit cell, the anions cannot lie in (2c), but must lie in (2a) or (2b). The choice is immaterial, since it depends only on the choice of origin. The structure thus described is analogous to the structure of methylammonium chloride found by Hughes & Lipscomb (1946).

The intensities of the Cu $K\alpha$ spots on the Weissenberg films were determined by visual comparison with spots of standard intensities, prepared by varying times of exposure of a collimated X-ray beam on a strip of Eastman No-Screen X-Ray Film. With the use of a relative scale factor determined between successive members of the multiple-film pack, the intensities of all reflections were found. From the intensity data, structure-factor data were calculated. The structure factors for spots in different sets of multiple films were then put on a uniform scale such that the best agreement with the calculated values was obtained.

The intensities of the $hk0$ spots were redetermined from the Weissenberg films taken with the use of Mo $K\alpha$ radiation, since difficulties were expected due to absorption and extinction of the Cu $K\alpha$ radiation. The observed structure factors showed some appreciable divergences from the values found by use of Cu $K\alpha$ radiation. The observed structure factors F_{Cl} are given in Tables 1, 2 and 3, the values given for $hk0$ spots being those determined by the use of Mo $K\alpha$ radiation. It should be noted that the hkl spots with $h+k$ odd and $l \neq 0$ are mostly faint, but not all absent. This is to be expected if the assumed structure is correct, since these reflections depend entirely on the difference between the two ends of the *n*-propylammonium ion.

The structure-factor data were treated in two ways in the study of the structure of the chloride crystal. Theoretical structure factors of the $hk0$ and $00l$ reflections were calculated from assumed models of the cations for comparison with the observed structure factors. Also, an electron-density map projected on (001) was prepared in order to get a direct view of the rotating group to find whether rotation is hindered or free. A one-dimensional electron-density projection on [001] was also prepared in order to find the z parameters of the C and N atoms. In the calculation of theoretical structure factors, there were so many parameters to be fixed that it was not possible to arrive at a unique model for the cation. However, since the variation of some parameters produced a much larger change in the calculated structure factors than the variation of other parameters, it was possible to arrive at conclusions regarding certain features of the structure.

Structure factors of the $hk0$ reflections were first calculated for a model of the chloride crystal containing the cation in the familiar *trans* (zigzag) form, rotating freely about its principal axis of inertia having the minimum moment of inertia. The $hk0$ reflections were chosen here, since their structure factors are

Table 1. *Observed structure factors of the chloride and bromide**

hkl	F_{Cl}	F_{Br}	*hkl*	F_{Cl}	F_{Br}	*hkl*	F_{Cl}	F_{Br}	*hkl*	F_{Cl}	F_{Br}
101	18	18	631	2	(<5)	442	7	16	503	(<5)	5
111	33	55	641	4	10	502	4	5	603	7	11
201	23	51	651	(<2)	(<3)	512	9	21	703	(<5)	(<4)
211	8	9	701	(<2)	(<5)	522	3	(<5)	104	4	(<4)
221	21	45	711	3	9	532	6	16	204	5	16
301	5	6	721	(<2)	(<5)	542	3	(<5)	304	(<4)	4
311	17	39	731	2	7	552	3	9	404	4	11
321	3	4	801	†	7	602	6	15	504	(<5)	5
331	11	28	811	†	(<3)	612	3	(<5)	604	4	4
401	15	36	821	†	7	622	5	13	105	4	(<5)
411	2	4	102	12	11	632	(<3)	(<5)	205	4	11
421	13	30	112	26	47	642	3	8	305	(<5)	(<5)
431	3	5	202	23	49	652	(<2)	(<3)	405	(<5)	7
441	9	20	212	11	11	702	3	(<5)	505	(<5)	(<5)
501	(<3)	5	222	18	40	712	4	9	605	(<5)	(<4)
511	7	23	302	8	9	722	(<2)	(<5)	106	6	6
521	3	5	312	16	38	732	2	7	206	4	7
531	6	16	322	6	7	802	†	6	306	(<5)	(<5)
541	3	5	332	12	29	812	†	(<3)	406	(<5)	5
551	3	9	402	13	30	103	9	8	506	(<5)	(<4)
601	8	18	412	5	7	203	20	37	606	(<5)	(<4)
611	3	(<5)	422	11	26	303	4	4			
621	7	16	432	3	5	403	10	22			

* See also Tables 2 and 3.

† Not observed because of experimental arrangement.

Table 2. *Observed and calculated hk*0 *structure factors*

	Calculated (for chloride)						Observed	
hkl	F_t	F_g	F_e	F_t^h	F_g^h	F_e^h	F_{Cl}	F_{Br}
110	10	3	8	10	4	8	12	23
200	−52	−43	−45	−54	−42	−46	42	66
220	38	27	29	36	29	28	28	61
310	7	18	9	6	18	8	8	35
330	− 9	−20	− 9	− 9	−19	− 9	9	33
400	28	17	18	29	15	18	18	43
420	−26	−14	−14	−25	−14	−14	15	35
440	20	10	9	22	11	10	8	22
510	−10	−21	− 8	−10	−21	− 8	7	26
530	11	20	7	10	20	7	6	20
550	−11	−17	− 5	− 7	−15	− 4	5	10
600	−19	−10	− 8	−17	− 8	− 7	7	20
620	18	9	7	17	9	6	6	16
640	−16	−11	− 5	−18	−12	− 6	5	11
660	14	12	3	18	14	4	3	†
710	11	17	5	14	19	6	5	11
730	−10	−14	− 4	−10	−14	− 4	3	8
750	9	11	2	6	10	2	3	†
800	15	11	4	11	8	3	4	7
820	−14	−12	− 3	−12	−11	− 3	3	7
840	14	12	3	15	14	3	3	†

† Not observed because of experimental arrangement.

independent of the vertical parameters of the atoms of the cation. The formula used in the calculation was

$$F_{hk0}=2f_{\mathrm{Cl}^-}\cos[\pi(h+k)/2] +2\cos[\pi(h-k)/2]\sum_i f_i J_0[2\pi v_i(h^2+k^2)^{\frac{1}{2}}],$$

where the summation is over all of the atoms in the cation and $v_i=r_i/a$, r_i being the radius of rotation of the ith atom.* The structure factors calculated for this model are given in Table 2 as F_t; they reproduce the observed structure factors F_{Cl} very poorly, thus indicating that other models are required.

A model was then chosen by analogy with the case of *n*-butane, for which Szasz, Sheppard & Rank (1948) showed the presence of two configurational isomers in equilibrium. These were postulated to be the *trans* isomer mentioned above, and the *gauche* (twisted) isomer, derived from the *trans* isomer by rotation by 120° about the central C–C bond. Structure factors calculated under the assumption that the cations are in the *gauche* form as a free rotator are given in Table 2 as F_g. It is seen that the agreement of the observed structure factors with the F_g's is even worse than with the F_t's. However, it was possible to fit the values of F_{Cl} with a set of linear combinations of the F_t's and F_g's, to which a temperature factor had been applied, according to the equation

$$F_e=[(2F_t+F_g)/3]\exp[-3{\cdot}13(\sin\theta/\lambda)^2].$$

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* The scattering factors of H, C and Cl^- were taken from the *Internationale Tabellen zur Bestimmung von Kristallstrukturen*. The scattering factors of N^+ were interpolated between values given for N and N^{+3}.

The values of F_e, given in Table 2 for the $hk0$ reflections, agree well with the values of F_{Cl} except for the reflection 110.

It was noted that the calculated value of F_{110} is the difference between two much larger quantities, since the contribution of scattering from the cations is slightly larger in magnitude than the contribution from the anions, and is opposite in phase. Therefore, this value is very sensitive to small variations in the model of the cation, even, we found, to the positions of the H atoms. A search was made for variations in the model of the cation which would increase the calculated structure factor of 110 over the value of F_e. Structure factors were calculated for models in which the cations do not rotate, but may occupy equivalent positions with the atoms of the cations lying as near as possible to the $\{110\}$ planes; these models may be considered as the extreme example of hindrance of rotation. The calculated structure factors are given in Table 2 as F_t^h for the model containing *trans* cations, F_g^h for the model containing *gauche* cations, and F_e^h calculated analogously to F_e. The values differed somewhat from the values calculated for free rotation, the largest discrepancies being between F_t and F_t^h for reflections of high indices. However, the discrepancy in F_{110} could not be explained on the assumption of orientational disorder without rotation, and the degree of hindrance could not be estimated by interpolation of observed structure factors between values calculated for free rotation and for orientational disorder, because of the interference of the variation of other parameters, whose effect on the structure factors could not be sufficiently well determined.

The fact that the scattering from the hydrogen atoms made an appreciable contribution to F_{110} suggested that the distortion of electron clouds around C–H bonds and N–H bonds might be of importance. It was found that F_{110} is increased relative to the other structure factors if the electrons associated with the hydrogen atoms are moved, as one would expect, closer to the carbon and nitrogen atoms. A correction of the structure factors for this distortion was found to account for this discrepancy without introducing any appreciable new discrepancies. No other type of correction was found which would increase F_{110} to an extent comparable to the correction for distortion of electron clouds. The model of the cation thus described is not necessarily to be considered as a correct model, because of the arbitrary manner in which the corrections were made, and because of the many features still undetermined, such as the character of the rotation. Nevertheless, the existence of configurational isomerism has been proved, since the structure factors could not be accounted for except by the assumption of this feature.

Theoretical structure factors were calculated for the $00l$ reflections. It was not possible to determine accurately the vertical parameter z of the center of gravity of the cation from the structure factors, but this parameter was estimated to be 0·34 for the *trans* configuration, and 0·28 for the *gauche* configuration, if the N–Cl distance is assumed to be the same as in methylammonium chloride. With this assumption concerning the parameter z, values of F_t and F_g were calculated. Values of structure factors F_a were also calculated for a model containing two-thirds of the cations in the *trans* configuration, and one-third in the *gauche* configuration, with a temperature factor $\exp[-4(\sin\theta/\lambda)^2]$ for the *trans* cations, and $\exp[-8(\sin\theta/\lambda)^2]$ for the *gauche* cations and anions. The several temperature factors were suggested by the case of methylammonium chloride, and may be justified in that the *trans* cations are held firmly in the vertical direction by their abutting ends, while neither the *gauche* cations nor the anions are thus held. The agreement between values of F_a and F_{Cl} (Table 3) is fairly good, and we did not consider it worthwhile to introduce any additional correction factors.

Table 3. *Observed and calculated* $00l$ *structure factors*

	Calculated (for chloride)			Observed	
hkl	F_t	F_g	F_a	F_{Cl}	F_{Br}
001	22	26	22	21	54
002	31	39	29	26	57
003	31	13	19	32	51
004	14	15	7	3	16
005	18	17	7	5	13
006	3	16	0	(< 5)	7

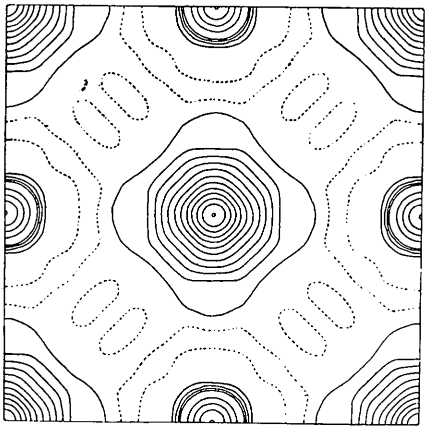

Fig. 1. Electron-density projection of the chloride on (001)

An electron-density projection of the chloride crystal in (001) was prepared from the values of F_{Cl} and is shown in Fig. 1. The signs of the terms were fixed on the assumption that the signs of the F_e's are correct. The map is drawn with a contour spacing of 1 e.A.$^{-2}$, except in the region in the chloride ion above the 5-electron contour, where the contour spacing is 5 e.A.$^{-2}$ The 1-electron contour is dotted. The map shows nearly circular contours around the cation, the departure from circularity being within the limits of error estimated from the false detail shown by the 1-electron and 2-electron contours. This map was compared with similar maps prepared from the values of F_e and F_e^h $(=(2F_t^h+F_g^h)/3)$ for the $hk0$ reflections and showed more similarity to the map prepared from the F_e's. The map prepared from the $F_e^{h'}$'s showed quite appreciable bulging of the contours about the cation in the [110] directions.* This would indicate that the model of the cation as a free rotator is in better accord with the X-ray evidence than the model showing only orientational disorder. This does not necessarily mean, however, that the cation rotates freely in the true sense of the term, but that the cation must be free, at least, to occupy a sufficient number of different orientations that the projected electron density appears not to depend on the orientation angle of the cation. The actual motion of the cations in the chloride crystal is probably quite complicated, involving both changes in the internal configuration of the cations and dynamic orientational disorder of the cations as a whole, and it is doubtful whether all of the characteristics of this motion could be discovered by X-ray means alone.

A one-dimensional electron-density projection on [001] was prepared, with the signs of all the F_{00l}'s taken positive. The C and N atoms were not resolved, but maximum electron densities were found at $z=0$, 0·37, 0·63. Since, in the assumed model, most of the C and N atoms cluster near these planes, the assumed model is corroborated.

Determination of the structure of the bromide

Powder photographs of the bromide taken with Cu $K\alpha$ radiation were successfully indexed on a tetragonal unit cell with $a=6{\cdot}48$ and $c=7{\cdot}38$ A. One reflection was found which could not be indexed on the unit cell proposed by Hendricks, which has $a=4{\cdot}57$ and $c=7{\cdot}36$ A., but was indexed as 101 on the new proposed unit cell.

Weissenberg photographs were taken of bromide crystals of dimensions $0{\cdot}3\times0{\cdot}3\times0{\cdot}1$ mm. with unfiltered Cu K radiation by the multiple-film technique. The photographs indicated uniquely a space group D_{4h}^7–$P4/nmm$. The unit-cell parameters of the bromide crystal were determined from a Weissenberg picture of the zero layer taken with the a axis as rotation axis, on which a sodium chloride powder pattern was superimposed. The observed values were

$$a=6{\cdot}497\pm0{\cdot}005;\quad c=7{\cdot}380\pm0{\cdot}006\text{ A.}$$

The argument used in the case of the chloride concerning the positions of the atoms applies also in the case of the bromide. Consequently, a structure entirely analogous to that of the chloride is proposed. As one should expect, the value of a is increased over the value found for the chloride by twice the difference of r_{Cl^-} and r_{Br^-}, because of the packing of the anions together with the ends of the cations in the plane of the a axes. On the other hand, the value of c is scarcely changed, since the packing in the c direction is determined entirely by the lengths of the cations.

The intensities of the spots on the Weissenberg films were determined by comparison with the spots of standard intensities. From the intensity data, structure factors were calculated. Now, the hkl reflections with $h+k$ odd depend entirely on the cations, and therefore should show comparable structure factors to those shown for the chloride if the crystals have comparable structures. In fact, it was possible to determine a scale factor by least-squares treatment to put the structure factors for the bromide on a scale such that excellent agreement was obtained between the data for the chloride and the bromide for this set of reflections. The other reflections have, in general, greater structure factors for the bromide, because of the greater scattering power of bromide ion than that of chloride ion. The observed structure factors for the bromide crystal on the described scale are given in Tables 1, 2 and 3 as F_{Br}.

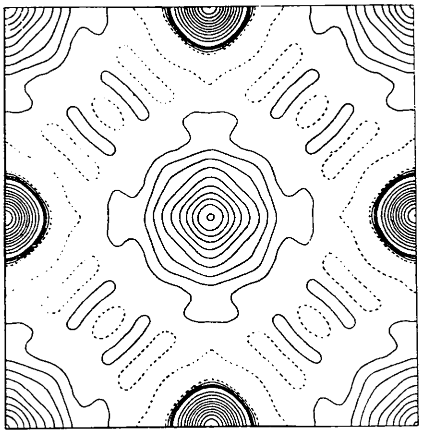

Fig. 2. Electron-density projection of the bromide on (001).

The successive orders of 200 for the bromide show approximately a normal decline, as one would expect from the arrangement of the cations and anions in the (200) planes. The successive orders of 001 vary somewhat from a normal decline, the discrepancies being in the same direction as the discrepancies from normal decline of the $00l$ structure factors for the chloride. The more rapid decline of the $00l$ structure factors than of the $h00$ structure factors indicated that the amplitude of heat motion is greater parallel to the c axis than perpendicular to it.

No theoretical structure factors were calculated for the bromide crystal, since the scattering from the bromide ions predominates for all $hk0$ reflections, and therefore, the structure factors are relatively insensitive to variations in the parameters of the cation. However, an electron-density projection on (001) was prepared, and is shown in Fig. 2. The map is drawn with a contour spacing of 1 e.A.$^{-2}$, except in the region of the bromide ion above the 5-electron contour, where the contour spacing is 5 e.A.$^{-2}$. The 1-electron contour is dotted. Not shown in the map are zero and negative electron

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* It is interesting to note that the electron-density projections prepared from the F_e's and $F_e^{h'}$'s differed considerably although individual values of F_e and $F_e^{h'}$ differed little. The reason why this is possible is the fact that the small discrepancies generally occurred in such a direction that they added systematically in the Fourier summation to produce an appreciable bulge in the contours.

densities going down to $-1{\cdot}4\,\text{e.A.}^{-2}$ in the diffraction ring immediately surrounding the bromide ion. The error in the determination of the shape of the cation was considerably greater than in the case of the chloride crystal, because the scattering from the cation was a smaller fraction of the total. Thus, the shapes of the contours around the cation are inconsistent with one another, but the contours around the bromide ion are practically circular. Since no direction of preferred orientation of the cation is shown, we may say that the cation behaves as a free rotator, within the limits of error of the measurements.

Preliminary determination of the structure of the iodide

The centrosymmetric point group of the iodide was established as D_{4h}–$4/mmm$ by Laue pictures taken along the a and c axes of an iodide crystal. In these pictures a few anomalies of intensity appeared, presumably because of the absorption of the longer wave-lengths, but almost all of the spots showed entirely normal symmetry. The unit-cell parameters for the iodide were found from a Weissenberg photograph of the zero layer with [110] as rotation axis, on which was superimposed a sodium chloride powder pattern. Under the assumption that the structure is analogous to those of the chloride and bromide, the observed parameters are

$$a=6{\cdot}931\pm 0{\cdot}003; \quad c=7{\cdot}332\pm 0{\cdot}003\ \text{A}.$$

Here we find that the expansion of the unit cell on replacing chloride ion by iodide ion takes place only in the plane of the a axes, just as on replacing chloride ion by bromide ion.

Since X-ray diffraction pictures of the iodide with Cu $K\alpha$ radiation had shown strong absorption effects, Weissenberg pictures were taken with Mo $K\alpha$ radiation. Zero- and first-layer pictures were taken with the a axis as rotation axis of an iodide crystal of dimensions $0{\cdot}2\times 0{\cdot}2\times 0{\cdot}1$ mm. The Mo $K\alpha$ spots on both layers showed symmetry C_{2l}, without any anomalies of intensity, thus corroborating the existence of a two-fold axis. An additional Weissenberg picture of the first layer, taken with a short range of oscillation and a long exposure, showed the presence of faint spots which were indexed 103 and $10\bar{3}$. The existence of these spots clearly ruled out the structure proposed by Hendricks. No $hk0$ spots with $h+k$ odd were observed, however. Therefore, we conclude that the structures of the iodide, chloride, and bromide are, in all probability, analogous.

Whereas the decline of the intensities was about the same for the chloride and the bromide, it was much faster for the iodide. The interpretation is apparently that the amplitude of thermal vibration was much greater in the iodide crystal.

Appreciation is expressed to the donors of the Minnesota Mining and Manufacturing Co. Fellowship in Chemistry for 1947–8 to M. V. King.

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Acta Cryst. (1950). **3**, 227

The Low-Temperature Modification of *n*-Propylammonium Chloride[*]

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(*Received* 30 *September* 1949)

The room-temperature structure of n-propylammonium chloride, which shows rotation of the cations, goes over in a second-order transition into a low-temperature form with fixed positions of the cations. In this process, the crystal of the room-temperature form breaks up reversibly into many domains of the low-temperature form, the domains having differing orientations. The space group of the low-temperature form is C^3_{2h}–$C2/m$. The transition is produced by the fixing of the positions of the cations in the $(1\bar{1}0)$ planes of the room-temperature structure in a centrosymmetric arrangement, with the result that the angle between the a axes is contracted, and the c axis is tipped in the direction of the axis [110]. The amount of these distortions varies with the temperature. Approximate positions of the atoms in the low-temperature form are given.

Introduction

Since a study of the room-temperature structures of the n-propylammonium halides by the present authors (1950) had shown the probable existence of rotation of the n-propylammonium ion, the study of the behavior of this rotating group at lower temperatures was of interest. Since a transition at low temperatures to a crystal structure having long-range order in the orientations of the cations was expected, it was therefore of interest to find which orientations the cations take,

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[*] This paper is in part material from a thesis submitted by M. V. King to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree.

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