

The Crystal Structure of Ammonium Chlorite at $-35^{\circ}\text{C}.$ *

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The structure of ammonium chlorite has been determined at $-35^{\circ}\text{C}.$ and has been refined by three-dimensional Fourier and least-squares methods. The structure previously published by Levi & Scherillo (1931) is shown to be incorrect. The crystals are tetragonal with space group $P4_2m$, and two molecules in a unit cell of dimensions $a_0 = 6.35$ and $c_0 = 3.78$ Å at $-35^{\circ}\text{C}.$ The Cl–O distance in the chlorite ion is 1.57 ± 0.03 Å, and the O–Cl–O angle is $110.5 \pm 1.4^{\circ}$.

Consideration of the known Cl–O distances indicates that the distance decreases as the oxidation number of chlorine increases.

Single crystals of ammonium chlorite decompose to crystalline ammonium chloride and ammonium chlorate. The new phases formed are precisely oriented with respect to the original ammonium chlorite.

During the past several years, work has been under way in these laboratories to establish the precise structure of the salts of perchloric acid (Prosen, 1955) and chloric acid (Sparks, 1958). The purpose of the present investigation was to extend this program to the establishment of the structure of at least one of the salts of chlorous acid so that the dimensions of the chlorite ion might be determined.

The salts of chlorous acid were first investigated crystallographically by Levi & Scherillo (1931). However, they attempted a structure determination only for one of the salts studied, ammonium chlorite, and because this substance decomposes in a few hours at ordinary temperatures, they had considerable difficulty in the estimation of intensities. The structure which they proposed could only be regarded as tentative and, indeed, has been shown in the present work not to have been correct.

The structure of magnesium chlorite hexahydrate was reported by Ferrari & Colla (1937), but the proposed structure was not confirmed by structure factor calculations. Recently, the structure of silver chlorite has been reported by Curti, Riganti & Locchi (1957).

Experimental

Several salts of chlorous acid were prepared in the hope of finding one suitable for an X-ray investigation. Commercial sodium chlorite (Mathieson Chemical Corporation) was used as the starting material. Silver chlorite was then prepared from the sodium chlorite by adding silver nitrate solution to a hot concentrated

solution of sodium chlorite, filtering off the precipitate arising from impurities, and cooling the filtrate until light yellow flakes of silver chlorite separated. Crystals of other chlorites were obtained by metathesis with the chloride of the corresponding cation and evaporation of the resulting chlorite solution with a stream of air.

Lithium, ammonium, and magnesium chlorites were prepared in this way. The ammonium salt was selected for the structural study because it formed suitable crystals more readily than the others, and because, although these crystals decomposed appreciably even in one hour at room temperature, it was found that they could be kept for several days without appreciable decomposition if they were cooled to $-35^{\circ}\text{C}.$ Hence a simple apparatus was constructed to permit cooling the crystal while X-ray photographs were being taken. A stream of cold dry air, surrounded by a stream of dry air at room temperature to prevent condensation, was passed over the crystal; the cold air had been passed first through a copper tube in a Dry Ice-acetone mixture. It was possible to keep the crystal at $-35^{\circ}\text{C}.$ indefinitely with little attention and no condensation of moisture.

Ammonium chlorite crystallizes in the tetragonal system. The lattice constants are given in Table 1; they apply to the primitive cell, containing two molecules. The density as measured by flotation in benzene-bromoform mixture is 1.817 g.cm.⁻³ at $24^{\circ}\text{C}.$ which corresponds to two (1.98) molecules in the unit cell. Levi & Scherillo (1931) reported the density to be 1.85 g.cm.⁻³.

Two crystals were used for intensity photographs. A needle-shaped crystal with a square cross-section, about 0.1 mm. on a side, was mounted parallel to c . The cold air supply was started after the crystal had been aligned (about one hour after it had been removed from its mother liquor), and multiple-film equi-

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Table 1. *Lattice constants* of ammonium chlorite*

Reference	a_0 (Å)	c_0 (Å)
This work, 24°C .	$6.36_2 \pm 0.005$	$3.82_3 \pm 0.01$
This work, -18°C .	$6.35_3 \pm 0.005$	$3.79_1 \pm 0.01$
This work, -35°C . (extrapolated)	(6.34_9)	(3.77_8)
Levi & Scherillo (1931)	6.33	3.76

* These lattice constants are calculated with

$$\text{Cu } K\alpha \lambda = 1.5418 \text{ \AA} \text{ and } \text{Cu } K\alpha_1 \lambda = 1.5405 \text{ \AA}.$$

inclination Weissenberg photographs were taken for $l=0, 1$, and 2 . A second fragment with cross-section 0.2×0.4 mm. was mounted parallel to $[110]$ and multiple-film equi-inclination Weissenberg photographs were taken for $H=0, 1$, and 2 , where $H=h+k$. Each multiple-film photograph was made with unfiltered copper radiation and three sheets of Eastman no-screen X-ray film. The zero-layer photographs are the most reliable since both crystals showed signs of increasing decomposition on the first- and second-layer photographs.

The intensities were estimated visually and were converted to relative values of F^2 in the usual way. No correction for absorption was made. This is justified in the case of the photographs taken about the c axis by the smallness of the crystal. Absorption probably has a small effect on the intensities in the photographs taken about $[110]$; furthermore, these photographs were of generally lower quality. Consequently spots on these photographs were given a somewhat lower weight in obtaining the average values of F^2 . Because of the decomposition of the crystals, the intensity data, especially from the upper layers, are not of the quality usually obtainable.

Of the 128 independent reflections allowed by the space group within the copper sphere of reflection, 88 were observed to be present and 10 more were observed to be absent.

Determination and refinement of the structure

The Laue symmetry of ammonium chlorite is $4/mmm$. Since the only systematic absences observed are $h00$ for h odd (and $0k0$ for k odd), the lattice is primitive, and the only symmetry elements involving translation are screw axes parallel to a and b . Only two space groups having Laue symmetry $4/mmm$ give the observed extinctions: $P4_21_2$ and $P\bar{4}2_1m$. The first of these may be eliminated since special positions would be needed for all the atoms, and this would lead to unobserved extinctions. Hence the space group is $P\bar{4}2_1m-D_{2d}^3$. (Levi & Scherillo (1931) arrived at the space group $P4bm-C_{4v}^2$ but had insufficient data to prove the correctness of their assignment. Their structure differs from that reported here chiefly in that it has all the chlorite ions pointing in the same direction along c).

For $P\bar{4}2_1m$, with order 8, the four oxygen atoms must be assigned the coordinates

$$(e) \ x, \frac{1}{2}+x, z; \bar{x}, \frac{1}{2}-x, z; \frac{1}{2}+x, \bar{x}, \bar{z}; \frac{1}{2}-x, x, \bar{z}$$

since the other four-fold positions would yield unobserved extinctions.

The chlorine atoms and ammonium ions could be at the two-fold positions (a), (b), or (c):

$$\begin{aligned} (a) & \ 0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0 \\ (b) & \ 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\ (c) & \ 0, \frac{1}{2}, z; \frac{1}{2}, 0, \bar{z}. \end{aligned}$$

The chlorine atoms must be in position (c) since (a) and (b) are equidistant from all the oxygen atoms, and chemical evidence indicates that each chlorine atom is nearer one pair of oxygen atoms. Preliminary structure factor calculations indicated that the ammonium ions are at (b).

Rough calculations based on approximate bond lengths and angles ($\text{Cl-O}=1.5 \text{ \AA}$, $\angle \text{O-Cl-O}=120^{\circ}$) indicated the x parameter for oxygen to be about 0.35. Two successive Fourier syntheses of the (001) projection were then carried out. These projections gave well resolved peaks, and the second projection gave the x parameter of oxygen as 0.361.

The z parameters were then determined by comparison of observed and calculated structure factors for several trial structures and refinement was effected by three-dimensional Fourier and least-squares methods. These calculations as well as the structure factor calculations were carried out on SWAC (Sparks, Prosen, Kruse & Trueblood, 1956). Individual anisotropic temperature factors were assigned and refined with the structure. There was only a hint of the presence of the hydrogen atom in a late difference map; although it was included at a reasonable position (see Table 2) in the final calculations, its inclusion decreased R by only 0.003, which is certainly not significant.

Table 2. *Position parameters of ammonium chlorite*

			Best Fourier	Best least squares	Final (average of L.S. and Fourier)
Cl	(c)	z	-0.1145	-0.1127	-0.1136 \pm 0.004
O	(e)	x	0.3575	0.3564	0.357 \pm 0.004
		z	0.8756	0.8801	0.878 \pm 0.005
H*	(f)	x	—	—	0.033
		y	—	—	0.100
		z	—	—	0.341

* The hydrogen atom was not located; the position here is the one which corresponds to a tetrahedral ammonium ion with the hydrogen atoms lying approximately along the $2.83 \text{ \AA} \text{ N} \cdots \text{O}$ lines.

The parameters resulting from the final three-dimensional Fourier summations and the least-squares refinement are given in Table 2. The final parameters were taken as the average of these two and are given in the last column of Table 2. The estimated standard deviations were calculated from the diagonal terms of the matrix of the least-squares normal equations. The

Table 3. *Structure factors for ammonium chlorite*

All values have been multiplied by 10 for convenience. A minus sign next to F_o means that the reflection was not observed and that the F_o listed is the approximate minimum value that could have been seen

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
200	266	327	270	24	10	161	47	51	442	17	29
400	100	89	370	13	39	261	47	56	152	53	38
600	138	149	001	257	246	361	59	65	252	92	80
800	55	83	101	50	54	461	71	34	352	-40	27
110	205	232	201	39	35	561	43	52	452	73	64
120	187	179	301	187	196	171	54	78	552	25	5
220	309	291	401	-20	2	271	43	50	003	125	120
130	35	27	501	79	81	371	36	43	103	53	49
230	49	67	601	67	73	002	90	83	203	55	64
330	203	199	701	27	28	102	71	70	113	58	46
140	51	30	111	322	364	202	104	64	123	68	82
240	217	194	121	207	186	302	172	209	223	99	74
340	21	1	221	123	117	402	43	40	133	-30	9
440	186	173	131	177	129	502	108	100	233	55	58
150	84	88	231	97	92	602	35	24	333	38	36
250	74	51	331	177	188	112	78	79	243	-40	58
350	106	99	141	165	132	122	122	149	343	-30	35
450	23	35	241	84	87	222	114	103	443	75	52
550	67	69	341	44	38	132	61	30	004	94	60
160	30	21	441	87	87	232	90	99	104	-20	13
260	104	105	151	103	109	332	-40	10	204	-40	24
360	-20	7	251	82	70	142	139	133	114	78	75
460	58	71	351	97	101	242	75	48	224	47	31
560	-30	39	451	59	58	342	47	51	334	66	62
170	83	87	551	71	66						

observed and calculated structure factors for the final structure are given in Table 3; the final value of R , the usual discrepancy index, was 0.149. The anisotropic temperature parameters are given in Table 4

Table 4. *Temperature parameters for ammonium chlorite* (\AA^2)*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N	3.6 (1.4)	3.6 (1.4)	2.3 (0.9)			
Cl	1.8 (0.3)	1.8 (0.3)	3.5 (0.5)	1.1 (0.5)		
O	3.0 (0.8)	3.0 (0.8)	4.5 (1.3)	0.8 (1.2)	0.0 (2.5)	0.0 (2.5)

* The values in parentheses are estimated standard deviations. In the final calculations, the B_{ii} for hydrogen were assumed to be equal to those for nitrogen.

and the parameters of the corresponding vibration ellipsoids, calculated by the methods of Rollett &

Table 5. *Vibration ellipsoid parameters for ammonium chlorite*

	Root mean-square displacement	Direction cosine with respect to		
		a	b	c
Cl	0.18 \AA	0.707	-0.707	0.000
	0.14	0.707	0.707	0.000
	0.18	0.000	0.000	1.000
O	0.21	0.707	-0.706	-0.033
	0.18	0.706	0.708	-0.033
	0.24	0.047	-0.003	0.999
N	0.22	1.000	0.000	0.000
	0.22	0.000	1.000	0.000
	0.18	0.000	0.000	1.000

Davies (1955), in Table 5. The estimated standard deviations of these vibration parameters are so large that no great significance can be placed on them; however, they indicate, as might be expected, that vibrations are greatest perpendicular to the plane of the ClO_2^- ion and least in the direction of the Cl-O bond.

Discussion

Fig. 1 is a view of the structure down the c axis. Each ammonium ion is surrounded by four oxygen

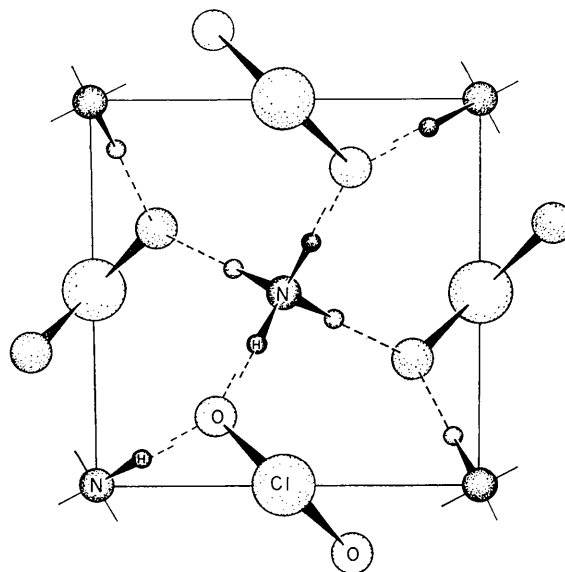


Fig. 1. View of the structure down the c axis. The ammonium ion has been represented as ordered; however, the hydrogen atoms were not located (see text).

atoms at a distance of 2.83 ± 0.03 Å. The oxygen atoms are arranged almost tetrahedrally about the ammonium ions, the two unique O–N–O angles being $119^{\circ}20'$ and $105^{\circ}20'$. The N \cdots O distance is characteristic of that in many crystals containing N–H \cdots O bonds (Donohue, 1952). The hydrogen atoms of the ammonium ions have been assumed above to be approximately on the lines joining the nitrogen and oxygen atoms. However, there was no unequivocal evidence for the hydrogen atoms in the final difference map from which their contribution was omitted. Because the intensity data are not of high quality, this does not necessarily imply that the ammonium ion is disordered, but such disorder is a possibility. Each ammonium ion is also surrounded by eight chlorine atoms, four at a distance of 4.62 Å and four at 5.28 Å. There are two short non-bonded Cl–O contacts, one of 3.21 Å essentially parallel to [110] (see Fig. 1) and the other of 3.16 Å between the oxygens of a given chlorite ion and the chlorine atom of the chlorite ion directly below in the next unit cell along *c*. These distances agree well with the sum of the usual van der Waals radii (Pauling, 1940) for oxygen and chlorine, about 1.40 and 1.80 Å respectively.

The Cl–O distance in the chlorite ion is 1.57 ± 0.03 Å at -35°C . This includes an oscillation correction of 0.007 Å (Cruickshank, 1956; Leung & Marsh, 1958). The O–Cl–O angle is $110.5^{\circ} \pm 1.4^{\circ}$. (If one assumes that the position parameters are independent of temperature and uses the lattice constants determined at 24°C ., the Cl–O distance is found to be 1.58 Å and the angle 110.1° .) These values might be compared with the Cl–O distance of 1.59 ± 0.05 Å and O–Cl–O angle of $114 \pm 5^{\circ}$ calculated for AgClO_2 from the listed parameters of Curti, Riganti & Locchi (1957). (They give these values as 1.62 ± 0.05 Å and $116 \pm 5^{\circ}$ respectively.) Silver chlorite is probably not typical of the other chlorites if it has, as reported, a molecular rather than an ionic structure.

Ferrari & Colla (1937) arrived at the rough value of 110° for the O–Cl–O angle in magnesium chlorite hexahydrate, merely by analogy with another isomorphous compound.

The Cl–O bond in ammonium chlorite is significantly longer than the Cl–O bonds in the chlorates and perchlorates. Table 6 gives some representative values. Although an average value 1.57 Å has been reported by Kartha (1952) for barium chlorate monohydrate, recalculation with his parameters gives an average of 1.53 (individual values 1.50, 1.51 and 1.58 Å).

The increased length of the Cl–O bond in the chlorites suggests that this bond has more single bond character than do the bonds in the chlorates and perchlorates. Siebert (1954), by use of Raman data and his 'Product Rule', states that the bond order is 1.5 in the perchlorate ion, 1.3 in the chlorate ion, and 1.0 (or single) in the chlorite ion. Other Raman spectral studies have also been interpreted to indicate that the

Table 6. Cl–O distances in perchlorates and chlorates

Compound	Average ClO distance (Å)	Method*	Reference
$\text{LiClO}_4 \cdot 3 \text{H}_2\text{O}$	1.46 ± 0.02	3D	Prosen (1955)
LiClO_4	1.44 ± 0.01	3D	Prosen (1955)
KClO_4	1.43 ± 0.01	3D	Prosen (1955)
	1.46 ± 0.05	2D	Mani (1957)
H_3OClO_4	1.42 ± 0.01	3D	Lee & Carpenter (1959)
NH_4ClO_4	1.46 ± 0.03	2D	Venkatesan (1957)
$\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$	1.48 ± 0.03	3D	Smith & Rundle (1958)
KClO_3	1.46 ± 0.01	3D	Sparks (1958)
	1.48 ± 0.04	2D	Aravindakshan (1958)
NaClO_3	1.46 ± 0.02	3D	Bower, Sparks & Trueblood (1957)
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	1.53†	2D	Kartha (1952)

* All studies were by X-ray diffraction; 2D, two dimensional; 3D, three-dimensional.

† Kartha did not estimate his precision; it seems doubtful that it is better than 0.05 Å.

Cl–O bond in ClO_2^- is a single bond (Duchesne & Burnelle, 1953). However, if one interprets the bond in the chlorite ion as a single Cl–O bond, then it might seem necessary to regard the bond in Cl_2O (Dunitz & Hedberg, 1950), which is about 1.70 Å in length and has heretofore been considered the prototype single Cl–O bond, as something *less* than a single bond. This does not seem plausible; the alternatives are to regard the bond in chlorite ion as still retaining a degree of multiple-bond character, or to regard the nature of the bonding in chlorine compounds in which chlorine has a coordination number of unity as sufficiently distinctive that direct comparison with compounds in which it has a higher coordination number is not meaningful without some compensation for the change.

The relatively precise measurements of Cl–O bond distances which have been made in recent years reveal an interesting correlation with the oxidation number of the chlorine atom. Table 7 is a list of the average values for measurements of the independent bonds and angles in the different species; only the three-dimensional studies of Table 6 have been included. There seems to be a definite decrease in Cl–O distance with increasing oxidation number of the chlorine atom. The correlation with the O–Cl–O angle is less obvious, although some rationalization of the variations is possible with the principles summarized by Gillespie & Nyholm (1957).

The variation of Cl–O distance manifested in Table 7 seems to be another instance of the decrease in radius brought about by increasing substitution of electronegative atoms about a central atom. This effect has been cited by Trefonas & Lipscomb (1958) in their

Table 7. Average Cl-O distance and O-Cl-O angle in different Cl-O species

	Oxidation number of Cl	Cl-O Distance (Å)	O-Cl-O Angle (°)
ClO ₄ ⁻	+7	1.44 Å	109.5
ClO ₃ ⁻	+5	1.46	108
ClO ₂ [*]	+4	1.49	116.5
ClO ₂ [†]	+3	1.57	110.5
Cl ₂ O [*]	(+1?)	1.70	

* Dunitz & Hedberg (1950). † At -35 °C.

study of B₂F₄ and in the results of precise studies of the fluorosilanes; it is also manifest in the results of precise studies of the fluoromethanes and some other compounds. However, it cannot be generalized too broadly without further analysis; for example, it is well established (Abrahams, 1956) that the S-O distance in many sulphur-oxygen compounds, including SO₂, SO₃, and some sulfoxides and some sulfones, is about 1.43 Å, appreciably less than that reported (about 1.51 Å) in several recent studies of the sulphate ion. The only reported structural study of a sulphite is the early investigation of sodium sulphite by Zachariassen & Buckley (1931); they reported the S-O distance to be only 1.39 Å which would indicate an effect of just the opposite sort to that in Table 7. This structure is currently being reinvestigated in these laboratories. A recent careful study of the S₂O₅⁻ ion, which has an S-S bond joining a SO₃⁻ group to a SO₂⁻ group (Lindquist & Mortsell, 1957) indicated that the S-O bond length averaged 1.45 Å in the former group and 1.50 Å in the latter, in agreement with studies of S₂O₆⁻ (average S-O distance 1.44 Å) and S₂O₄⁻ (average 1.51 Å). Thus, here the effects are similar to that indicated in Table 7

Decomposition of ammonium chlorite

Weissenberg photographs taken of ammonium chlorite at room temperature show, in addition to the spots due to ammonium chlorite, systems of sharp and elongated spots. These extra spots are caused by the

Table 8. Interpretation of photograph*, † showing decomposition of ammonium chlorite

Set A	<i>d</i>	Interpretation
Elongated	4.43 Å	100 of NH ₄ ClO ₃
Sharp ₁	3.87	100 of NH ₄ Cl
Sharp ₂	4.51	110 of NH ₄ ClO ₂
Set B (45° from A)	<i>d</i>	Interpretation
Elongated ₁	3.24 Å	110 of NH ₄ ClO ₃
Elongated ₂	3.04	10 $\bar{1}$ of NH ₄ ClO ₃
Sharp ₁	2.74	110 of NH ₄ Cl
Sharp ₂	3.18	200 of NH ₄ ClO ₂

* NH₄ClO₃ is indexed here on rhombohedral axes (Gillespie & Trueblood, 1959).

† See text for details.

decomposition products of ammonium chlorite; the sharp spots are due to ammonium chloride and the elongated spots to ammonium chlorate. Furthermore, the crystallographic axes of the three substances present are oriented with respect to each other in a remarkably precise manner. Table 8 gives the data from a zero-layer Weissenberg photograph taken about the *c* axis of an ammonium chlorite crystal which had been kept about five hr. at 24 °C. It appears that the decomposition products form tiny crystals which grow in or on the remaining ammonium chlorite in a precisely oriented manner. A similar effect has been observed on a macroscopic scale by Bunn (1933) who described the oriented overgrowth of ammonium chloride on urea and potassium permanganate on potassium chlorate. He states that the condition for overgrowth is similarity of lattice structure and interatomic distances in specified planes. This similarity in the case of ammonium chlorite, chlorate, and chloride is illustrated in Fig. 2 which shows schematic projections of the three cells, oriented as indicated in Table 8. (Since the position parameters of the ammonium chlorate structure (Gillespie & Trueblood, 1959) have not yet been determined precisely, the chlorine and oxygen

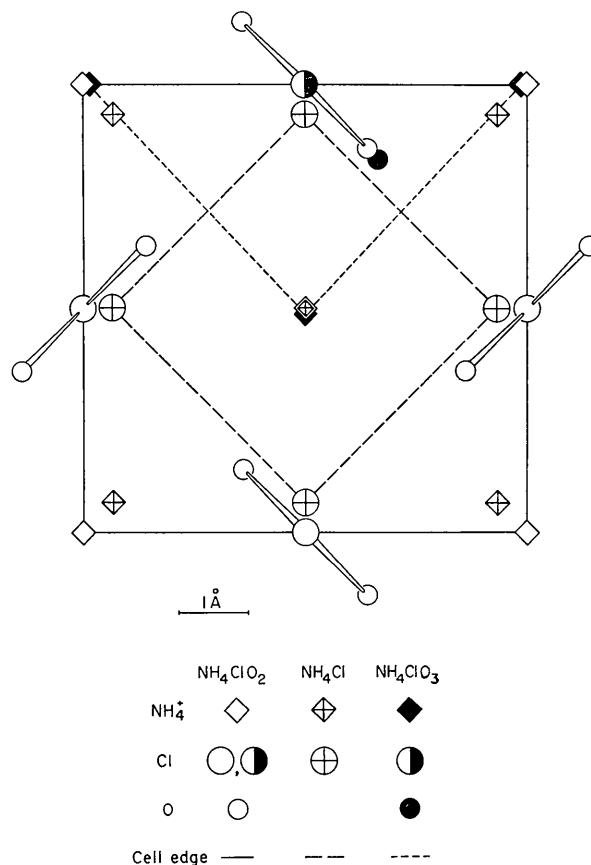


Fig. 2. Schematic projection of portions of the unit cells of ammonium chlorite, ammonium chloride, and ammonium chlorate.

positions for NH_4ClO_3 in this projection can be considered only approximate.)

The problem here appears more complex than in the examples cited by Bunn, inasmuch as here the entire process takes place in the solid state, and two distinct new phases appear together with the original one. The volume of each new phase must be sufficiently large that it gives sharp diffraction maxima. The only disorder appears to be in the NH_4ClO_3 phase; this is not surprising since it belongs to a non-orthogonal crystal system, in contrast to NH_4Cl and NH_4ClO_2 .

The mechanism by which the process of atomic rearrangement occurs is still completely obscure. However, it appears that it must involve the migration of oxygen atoms through distances of at least the order of 10^1 to 10^2 unit cells. Further study of the phenomenon appears worthwhile.

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The Crystal Structure of the *trans* Isomer of β -Ionylidene Crotonic Acid

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The crystal structure of a β -ionylidene crotonic acid, prepared by Arens & Van Dorp (1946), has been determined and refined three-dimensionally. The conjugated side chain is all-*trans*; since this acid was a step in the vitamin *A* synthesis by Arens & Van Dorp, it can be assumed that the corresponding part of the vitamin *A* molecule is also all-*trans*.

Introduction

Preliminary investigations relating to the structure to be described in detail here, were published eight years ago (MacGillavry, Kreuger & Eichhorn, 1951). The

conformation and the more detailed bond distances and angles of this C-17 acid, obtained by Arens & Van Dorp in their vitamin *A* synthesis (Arens & Van Dorp, 1946) were thought to be of much interest in view of the biochemical importance of vitamin *A*. This acid moreover comprises most features found generally in the important group of natural pigments

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