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The Crystal Structure of Ammonium Chlorate

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The structure of ammonium chlorate has been determined from powder data and has been refined by least-squares methods. The crystals are rhombohedral with probable space group $R3m$ and one molecule in a unit cell of dimensions $a_0 = 4{\cdot}44_4$ Å and $\alpha = 86{\cdot}4°$. The Cl–O distance in the chlorate ion is $1{\cdot}45 \pm 0{\cdot}03$ Å and the O–Cl–O angle is 106°.

The structure of ammonium chlorate is of interest because it is one of the products arising from the interesting decomposition of ammonium chlorite (Gillespie, Sparks & Trueblood, 1959). Since no structural data for the compound could be found in the literature, its structure has been determined.

Experimental

Ammonium chlorate was obtained by mixing equivalent amounts of solutions of ammonium sulfate and barium chlorate, filtering the resulting precipitate of barium sulfate, and evaporating the filtrate in a stream of air. Only small quantities should be prepared since the compound is unstable and has been known to detonate violently (Davis, 1896; Fairbrother, 1922).

The crystals obtained were dendritic and were not suitable for single-crystal X-ray photographs. Further, since ammonium chlorate is unstable, it was not possible to obtain crystals by slow evaporation. Hence, the structure was determined and refined with powder data alone.

Examination under the polarizing microscope indicated that the crystals were uniaxial. The crystals were markedly pyroelectric, showing that they belong to a polar class. This agrees with early observations (Groth, 1908) suggesting that ammonium chlorate is isomorphous with potassium bromate, which has a rhombohedral unit cell with $a_0 = 4{\cdot}40$ Å and $\alpha = 86°$ (Zachariasen, 1928; Swanson, 1957).

Powder photographs of ammonium chlorate can be indexed on the basis of a rhombohedral unit cell with $a_0 = 4{\cdot}444 \pm 0{\cdot}005$ Å and $\alpha = 86{\cdot}4 \pm 0{\cdot}1°$, calculated with $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å. The density, measured by flotation in bromoform-carbon tetrachloride, is 1·91 g.cm.$^{-3}$; the calculated density corresponding to one molecule in the unit cell is 1·930 g.cm.$^{-3}$.

Intensities were determined by means of multiple-film powder photographs using three strips of Eastman no-screen X-ray film and filtered copper radiation. The intensities on each strip were determined with a microdensitometer and were intercompared in the usual way. Only completely resolved lines were used in the structure determination, and multiplicities were taken into account in converting the intensities to F^2 values.

The form factors used in the refinement were those of Hoerni & Ibers (1954) for nitrogen and oxygen, and Dawson (1960) for chlorine.

Determination of the structure

The space group was assumed to be $R3m$ on the basis of the pyroelectric properties and probable isomorphism with potassium bromate. With the help of standard bond lengths and angles, a reasonable trial structure was calculated to be:

(*a*) Cl at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
(*b*) O at 0·566, 0·566, 0·176
(*c*) N at 0, 0, 0.

The discrepancy index R for this trial structure was found to be 11·5%. Refinement was carried out by a full-matrix least-squares method, with $\sqrt{w} = 1/F_o$; the computer program used was ACA No. 317 (Gantzel, Sparks & Trueblood, unpublished). Because the space group is a polar one, the position parameter of the chlorine could be arbitrarily chosen and was not refined. Individual isotropic temperature factors were assigned and refined with the structure. The final parameters are given in Table 1.

Table 1. *Parameters of ammonium chlorate*

			Position parameter	Temperature parameter
Cl	(*a*)		0·5000	0·4 Å^2
O	(*b*)	x	$0{\cdot}588 \pm 0{\cdot}002$	2·6
		z	$0{\cdot}179 \pm 0{\cdot}002$	
N	(*a*)		$0{\cdot}040 \pm 0{\cdot}006$	2·0

The estimated standard deviations were calculated from the diagonal terms of the matrix of the least-squares normal equations. The observed and calculated structure factors for the final structure are given in Table 2, together with the observed and calculated values of the spacings for the corresponding lines. The final value of R, the discrepancy index, was 6·4%.

Table 2. *Structure factors for ammonium chlorate**

hkl	d_o	d_c	$10F_o$	$10F_c$
100	4·422 Å	4·428 Å	175	191
110	3·221	3·227	204	220
$10\bar{1}$	3·038	3·044	157	153
111	2·715	2·720	221	229
$11\bar{1}$	2·508	2·508	94	84
200	2·211	2·214	205	214
210	2·026	2·028	71	73
$20\bar{1}$	1·933	1·936	88	82
211	1·900	1·903	137	129
$21\bar{1}$	1·789	1·791	62	62
$2\bar{1}\bar{1}$	1·753	1·757	117	111
220	1·612	1·613	75	77
$20\bar{2}$	1·522	1·522	150	141
300	1·475	1·476	147	124
310	1·426	1·426	133	138
311	1·388	1·388	126	131
$30\bar{1}$	1·375	1·376	134	119
$31\bar{1}$	1·328	1·328	80	81
321	1·243	1·242	84	88
$30\bar{2}$	1·197	1·196	100	101
$31\bar{2}$	1·160	1·160	100	117
$21\bar{3}$	1·150	1·150	100	90

* d_o and d_c are the observed and calculated spacings, $\lambda/2 \sin\theta$.

Discussion

The Cl–O distance is 1·45 ± 0·03 Å, including a small correction (0·01 Å) for libration (Cruickshank, 1956, 1961); the O–Cl–O angle is about 106 ± 2°. These values agree within the limits of error (2σ) with the much more precise values for the chlorate ion in sodium chlorate (Burke, Bower & Trueblood, unpublished), about 1·500 ± 0·007 Å and 106·8 ± 0·4° respectively.

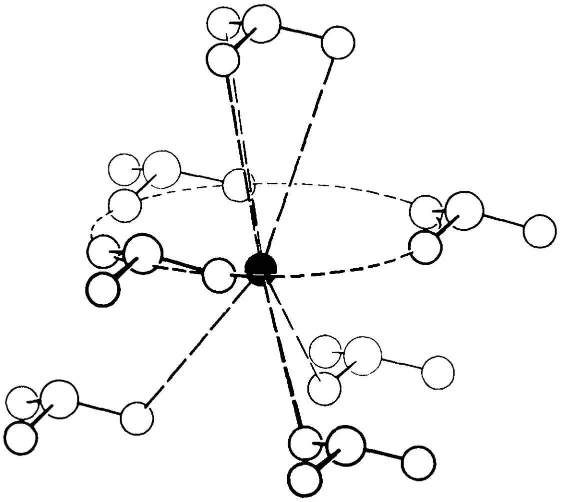

Fig. 1. The environment of an ammonium ion (solid circle) in the structure of NH_4ClO_3.

Each ammonium ion is surrounded by twelve oxygen atoms from seven chlorate ions, as illustrated in Fig. 1. These oxygens are of three kinds: (*a*) three at 3·46 Å, all in a neighboring chlorate ion above along the 3-fold axis; (*b*) six at 3·11 Å, from three different chlorate ions—these six lie in a plane just 0·48 Å above the nitrogen atom along the unique axis; (*c*) three at 3·13 Å, from 3 different chlorate ions, in a plane 2·24 Å below along the 3-fold axis. These latter 3 are staggered 60° with respect to the three above.

The N · · · O distances are sufficiently great and their symmetry is such that it seems doubtful that there are any hydrogen bonds in the structure. If the ammonium ions are ordered, one N–H bond must be directed along the 3-fold axis. If this pointed down, the other three hydrogens would lie about 10° above lines from the N to the six oxygens in the plane just above the NH_4^+, and each bond would presumably be bifurcated. If the unique N–H bond were directed upwards, toward the three oxygens at 3·46 Å in the chlorate ion above, each of the other three hydrogens would lie at least 27° from a line between the N and one of the three oxygens at 3·13 Å in the plane 2·24 Å below. In any event, the present data are, of course, inadequate for locating the hydrogen atoms, even if they are ordered.

There are rather short non-bonded O · · · Cl contacts of 3·07 Å from the oxygens of one chlorate ion to the chlorines of the chlorate ions below on neighboring 3-fold axes. This distance is more than 0·1 Å shorter than the sum of the usual van der Waals radii (Pauling, 1960) and is undoubtedly significant in determining the packing in the crystal. The shortest interionic O · · · O distance is 3·32 Å.

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