

# THE CRYSTAL STRUCTURE OF AMMONIUM PERCHLORATE— $\text{NH}_4\text{ClO}_4$

BY K. VENKATESAN

(Department of Physics, Indian Institute of Science, Bangalore-3)

Received May 10, 1957

(Communicated by Dr. R. S. Krishnan, F.A.Sc.)

## 1. INTRODUCTION

ALTHOUGH the crystal structures of  $\text{NH}_4\text{ClO}_4$ <sup>1</sup> and its isomorph  $\text{KMnO}_4$ <sup>2</sup> have been reported, Wyckoff<sup>3</sup> makes the following remarks in his book *The Structure of Crystals*—"These crystals have units which are almost identical in size and it is probable that their real atomic positions are practically the same. Nevertheless the structures proposed for the permanganate and for the perchlorates show important differences. The potassium permanganate determination rests on photographic spectral data; the observations on potassium perchlorate and ammonium perchlorate are more quantitative spectrometric measurements. It is, however, difficult to be sure of the deductions from the latter results. The published parameters are obviously wrong; they correspond to an impossible grouping." In view of the above remarks, a thorough and accurate study of these crystals has been undertaken. Recently, using the anomalous scattering technique, the structure of  $\text{KMnO}_4$ <sup>4</sup> has been determined to a fair degree of accuracy. The parameters deduced were considerably different from those reported by Mooney.<sup>2</sup> Ammonium perchlorate was next taken up for accurate study. One of the chief objects of the investigation was to determine the positions of the hydrogen atoms and also to find out whether the structure has any hydrogen bonds in it. The results obtained are presented in this paper.

## 2. MORPHOLOGICAL AND OPTICAL DATA

Ammonium perchlorate crystallizes in the form of needles elongated along the *b*-axis. From morphological studies the crystal is known to belong to the orthorhombic bipyramidal class with the axial ratios.

$$a : b : c = 0.7932 : 1 : 1.2808.$$

The *m* planes {110} and the *c* planes {001} are the most prominent. The crystal exhibits a weak positive birefringence, and its refractive indices are  $\alpha = 1.481$ ,  $\beta = 1.483$  and  $\gamma = 1.488$  and  $2V = 68^\circ$ .

## 3. UNIT CELL AND SPACE-GROUP

The unit cell, as determined from Weissenberg photographs, is

$$a = 9.13 \text{ \AA} \quad b = 5.79 \text{ \AA} \quad c = 7.47 \text{ \AA}$$

The axial ratios are thus 1.579:1:1.290. The ratios are in fair agreement with the morphological values given by Barker,<sup>5</sup> if one takes Barker's ( $hkl$ ) as ( $2h, k, l$ ). The space-group is found to be  $Pnma$  in agreement with the results of the previous investigators. The density of the crystal is 1.952 and the number of molecules per unit cell is 4.

$\text{CuK}\alpha$  radiation and the multiple-film technique were employed in taking zero-layer Weissenberg photographs about the  $b$ - and  $c$ -axes. The relative intensities of the reflexions were estimated visually. The values were corrected for Lorentz and Polarization factors and the correction for absorption was made using Bradley's method for cylindrical specimens.

To obtain the correct distribution of the atoms among the available positions in the space-group  $Pnma$ , one could make use of the fact that  $\text{ClO}_4$  and  $\text{NH}_4$  ions are approximate tetrahedra. The asymmetric unit, therefore, consists of one nitrogen, one chlorine, four oxygens and four hydrogens. This leads one to the conclusion that the chlorine, the nitrogen, two hydrogens and two oxygens of the  $\text{ClO}_4$  group must lie on the reflexion planes at  $y = \pm 0.25$  and the other two oxygen atoms of the  $\text{ClO}_4$  group and the two hydrogen atoms of the  $\text{NH}_4$  ion must be equidistant from the mirror plane, one being the mirror image of the other. Hence we find that the  $y$  parameter of all atoms except the two oxygen and two hydrogen atoms which occupy general positions should be  $\pm b/4$ .

4. THE  $b$ -AXIS FOURIER PROJECTION

When the Patterson projection on (010) was made it was found that due to lack of resolution of the peaks it was possible to get the approximate ( $x, z$ ) co-ordinates of the chlorine and nitrogen atoms only. Consequently, the structure factors of ammonium perchlorate were calculated using the parameters of the corresponding atoms of the isomorph  $\text{KMnO}_4$ .<sup>4</sup> The parameters used are given in Table I.

The signs of about 30 strong reflexions out of the total of about 90 reflexions of the type ( $hol$ ) could be determined unambiguously. These reflexions were used to compute the first Fourier synthesis using the relevant electron density expression<sup>6</sup> for the (010) projection for the space-group  $Pnma$ . The

Fourier summation was performed using the Beevers-Lipson strips at intervals of  $6^\circ$ . The atomic co-ordinates were refined by the iterative process of

TABLE I

Atom	x	z
Cl (Mn)	0.438	0.192
N (K)	0.183	0.158
O <sub>1</sub>	0.321	0.038
O <sub>2</sub>	0.594	0.106
O <sub>3</sub>	0.417	0.317
O <sub>4</sub>	0.417	0.317

Fourier syntheses. At each stage of the refinement the scale and temperature factors were obtained from the graph plotted between  $\log_e \Sigma |F_c| / \Sigma |F_o|$  and  $\sin^2 \theta$ . After the final projection, Booth's back correction method was used to eliminate the errors due to the termination of the Fourier series and the magnitude of these errors were of the order of  $0.06 \text{ \AA}$ . The discrepancy factor at this stage was 0.231.

#### 5. DETERMINATION OF THE $y$ CO-ORDINATE

As mentioned earlier, the space-group demands that all atoms except the two oxygen atoms of the  $\text{ClO}_4$  group should lie on the mirror planes at  $y = \pm 0.25$ . Since there were only 35 ( $hko$ ) reflexions, the least squares method was considered to be more suitable than the Fourier method. The approximate  $y$  co-ordinate of the oxygen atoms  $\text{O}_3$  and  $\text{O}_4$  off the mirror plane was calculated as follows:—The projection of the  $\text{Cl}-\text{O}$  (<sub>3</sub>) distance on the (010) plane was found from the  $b$ -axis Fourier projection to be  $0.817 \text{ \AA}$ . Assuming the angle of  $\text{O}_3\text{ClO}_4$  to be the tetrahedral angle, the distance of the oxygen from the mirror plane was calculated to be 0.192 in fractional co-ordinate. The  $y$  co-ordinate was changed by trial so as to attain better agreement between the calculated and observed structure amplitudes for the ( $oko$ ) reflexions. The value of  $y$  thus obtained was 0.050. The scale and temperature factors were respectively 1.6 and  $2.7 \times 10^{-16}$ . The discrepancy factor was as low as 0.131. In evaluating the discrepancy factors given in this paper a few reflexions with very weak intensities have been omitted,

## 6. REFINEMENT OF ATOMIC PARAMETERS

The approximate  $y$  parameter of the oxygen atom in the general position was refined by the method of least squares.<sup>7</sup> Neglecting, to a first approximation, the off-diagonal terms of the normal equations, we get

$$\Delta y_n \sum w \left( \frac{\partial F_c}{\partial y_n} \right)^2 = \sum w (F_o - F_c) \frac{\partial F_c}{\partial y_n} \quad (1)$$

where  $w$  the weight to be given to each reflexion was taken to be equal to unity. Such of those reflexions which are believed to have been affected by extinction were given zero weight. Three cycles of the least squares treatment gave  $y = 0.044$ , the next cycle giving a negligible value for  $\Delta y$ . The final discrepancy factor for this zone came out of the order of 0.128.

The  $(xz)$  co-ordinates were further refined by a succession of  $(F_o - F_c)$  syntheses. These indicated slight movements of the oxygen atoms and also that the temperature factor on the oxygens had to be increased. When these changes were made it was noticed that the calculated amplitudes were very much higher than the observed ones in some of the strongest reflexions. The values for  $I_c/I_o$  plotted against  $I_c$  for these reflexions lay very nearly on a straight line. When the effect of extinction was taken into account the value of the discrepancy factor came out to be 0.151.

## 7. HYDROGEN POSITIONS

A further difference projection with reflexions affected by extinction removed was prepared and it was found from it that the nitrogen was surrounded by three electron density maxima, giving an indication of the probable hydrogen positions. In fact one can discern the positions of two hydrogens even in the final electron density projection, the third being swamped out by the nearness of the oxygen atom. Figure 3 represents the difference map which shows three peaks surrounding the nitrogen atom. These peaks are at distances less than 1 Å from the nitrogen atom. Making use of the assumption that the N-H distance is 1 Å and the fact that the hydrogens surround the nitrogen tetrahedrally, positions were assigned to the hydrogen atoms. When the structure factors were calculated with the contributions of the hydrogen taken into consideration the agreement between the calculated and observed structure amplitudes of low angle reflexions improved considerably and, in fact, the discrepancy factor was 0.136. Perhaps it is worth mentioning that the co-ordinates assigned to the hydrogen atoms are far less accurate than those of the other atoms. The present data, however, do not warrant an attempt at refining the hydrogen position. Due to overlap the  $y$  co-ordinate of the hydrogen atom in the general position could not be

found in the (*hko*) projection. But an approximate value for *y* was obtained assuming the N-H distance to be 1 Å and it was found that the H-N-H angle came to be very nearly the tetrahedral angle. The final (*xyz*) parameters (in fractional co-ordinates) of the atoms in the crystal are tabulated in Table II.

TABLE II

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cl	0.433	0.250	0.192
N	0.183	-0.250	0.167
O <sub>1</sub>	0.321	0.250	0.054
O <sub>2</sub>	0.575	0.250	0.096
O <sub>3</sub>	0.421	0.044	0.300
O <sub>4</sub>	0.421	0.456	0.300
H <sub>1</sub>	0.242	-0.250	0.075
H <sub>2</sub>	0.225	-0.250	0.275
H <sub>3</sub>	0.117	0.896	0.183
H <sub>4</sub>	0.117	0.604	0.183

The final electron density projection along the *b*-axis is shown in Fig. 1 together with its key diagram in Fig. 2.

#### 8. ACCURACY

To get an idea of the accuracy of the atomic co-ordinates the value of  $R_2$  in the expression<sup>8</sup>

$$R_2 = \frac{\sum_{h0l} (|F_o| - |F_c|)^2}{\sum_{h0l} |F_o|^2} \quad (2)$$

was calculated. The R.M.S. error was found to be 0.0028 Å which, in the opinion of the author, appears to be too low an estimate of the actual errors that exist in the present work. This is probably because the equation (2) is strictly applicable to the case where there is no overlap and reflexions are numerous. It was found that the oxygen movements of the order of 0.01

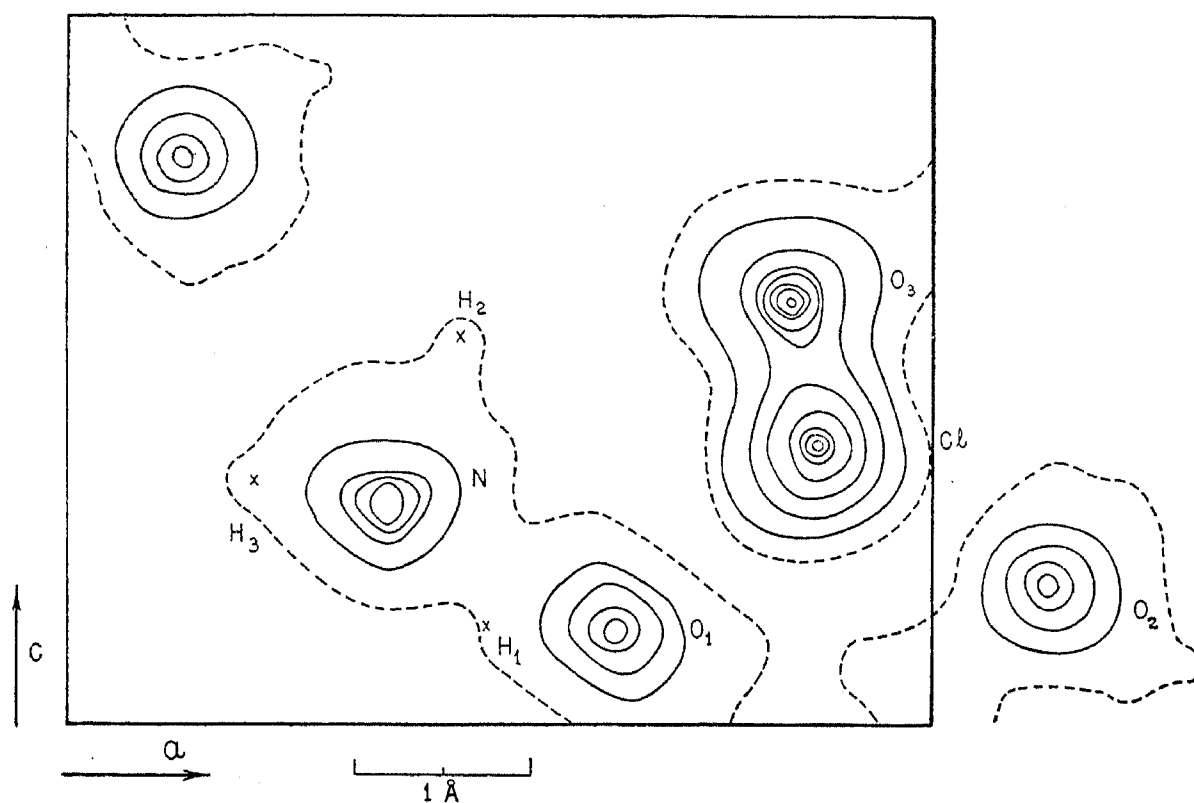


FIG. 1. The final electron density projection of  $\text{NH}_4\text{ClO}_4$  on (010). Contour scale arbitrary.

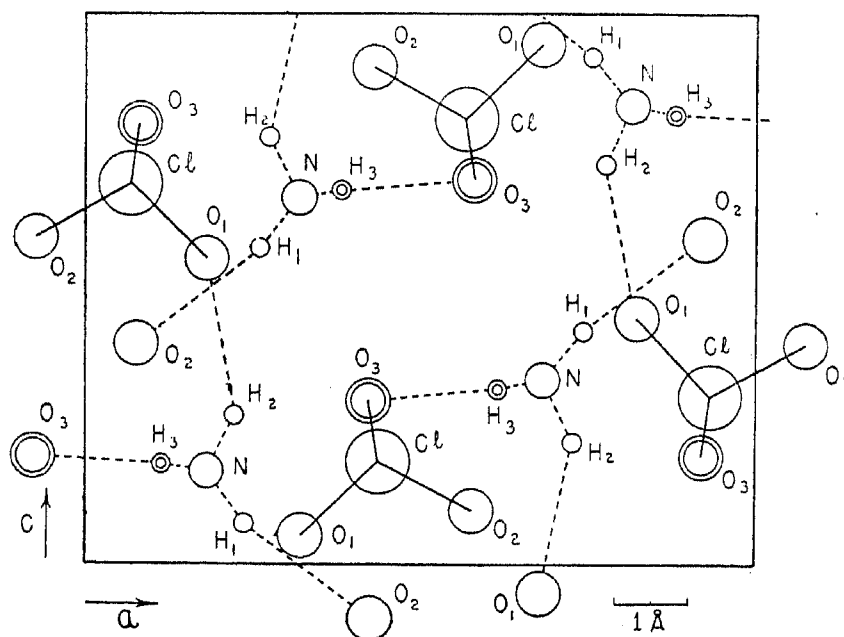


FIG. 2. A projection of the structure along  $b$ -axis of the crystal. Dotted lines represent hydrogen bonds.

to 0.02 Å from the present position had practically no effect on the discrepancy factor. It is, therefore, estimated that the errors in the co-ordinates of the different atoms would not exceed 0.02 Å. The observed structure amplitudes and those calculated using the final atomic co-ordinates are not given here for want of space but could be made available to anyone interested.

### 9. DISCUSSION OF THE STRUCTURE

The general arrangement of the atoms in the unit cell is shown in Fig. 4. Each chlorine is surrounded by four oxygens at a mean distance of 1.46 Å and the four oxygens lie at the corners of a nearly regular tetrahedron. The average oxygen-to-oxygen distance in the tetrahedron is 2.37 Å. The distances between oxygens belonging to different ClO<sub>4</sub> tetrahedra are all larger than 3.24 Å. The distances inside the ClO<sub>4</sub> group are given in Table III.

TABLE III

	Cl-O	O-O
Distance in Å	1.45	2.34
	1.48	2.39
	1.45	2.37
	1.45	2.38
Mean ..	1.46 Å	2.37 Å

Each ammonium ion is surrounded by twelve oxygen atoms, the observed distances being 2.89, 2.93 (2×), 2.95 (2×), 2.95, 3.26 (2×), 3.39 (2×) and 3.15 Å (2×). It may be observed that six of these twelve oxygens are at a distance of about 2.95 Å which strongly suggest the presence of weak hydrogen bonds N-H ··· O. Such bonds have been reported in a few cases in the literature.<sup>9, 10, 11</sup> On the face of it there is a slight difficulty to say which of the four oxygen atoms out of the six are linked to the nitrogen by the N-H ··· O bonds, as there are two pairs of oxygen atoms which are at distances of 2.93 and 2.95 Å. But this difficulty is resolved if one assumes (i) that hydrogens satisfy the space group requirements, (ii) that they surround the nitrogen to form an approximate tetrahedron and (iii) that all the four oxygen atoms form hydrogen bonds. The four oxygens which could then be chosen uniquely as forming N-H ··· O bridges are those at distances of 2.89, 2.95

and  $2.95 \text{ \AA}$  ( $2\times$ ). Such a choice is in accord with the disposition of the electron density maxima in the difference map.

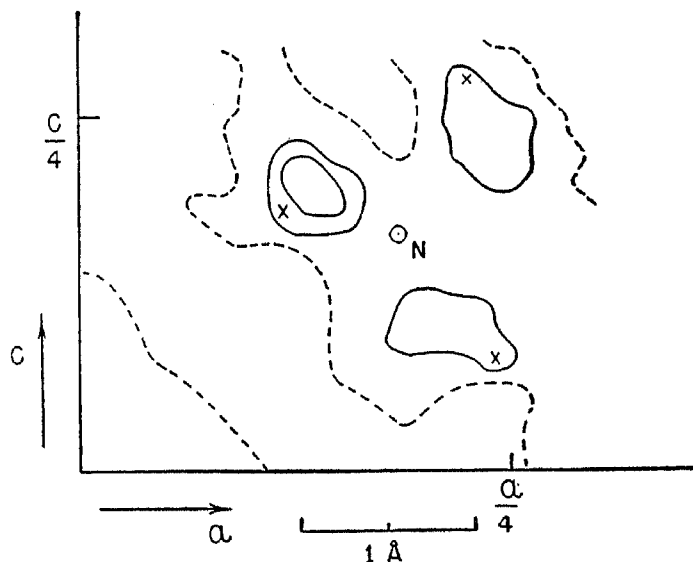


FIG. 3. (010) Difference map indicating approximate hydrogen positions. Contour scale arbitrary.

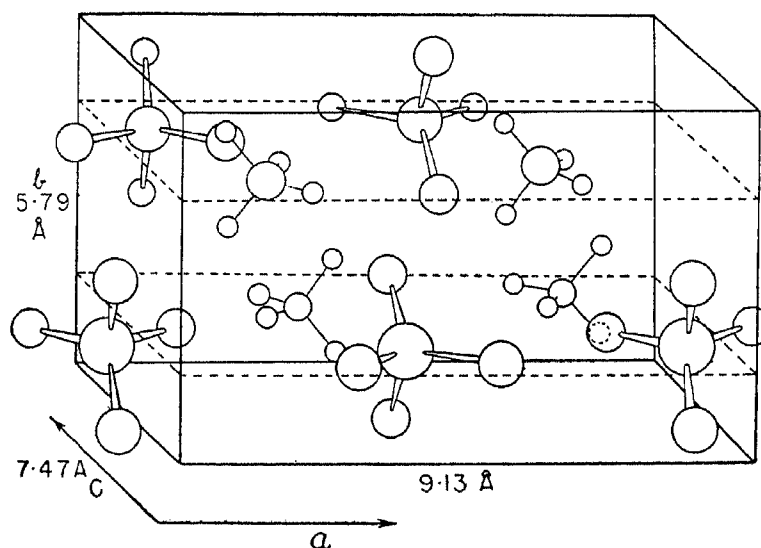


FIG. 4. The atomic arrangement in the crystal. The unit cell is outlined, and the stereoscopic effect is gained by assigning to an atom a diameter depending upon its Z co-ordinate.

In conclusion, it may be mentioned that the positions of the chlorine, oxygen and nitrogen atoms as determined by Gottfried and Schusterius (*loc. cit.*) are not far from those reported here. However, in the case of  $\text{KMnO}_4$ , contrary to the previous determination, the atomic co-ordinates are very close to those of  $\text{NH}_4\text{ClO}_4$ .



The author's grateful thanks are due to Professor R. S. Krishnan for his kind encouragement and continued interest, and to Dr. S. Ramaseshan for guidance and help throughout this investigation.

#### SUMMARY

The crystal structure of ammonium perchlorate has been redetermined. The orthorhombic cell with space-group *Pnma* has four molecules in a unit cell of dimensions  $a = 9.13 \text{ \AA}$ ,  $b = 5.79 \text{ \AA}$  and  $c = 7.47 \text{ \AA}$ . The values of the atomic co-ordinates have been refined by double Fourier-series methods and the final atomic positions determined are accurate to  $0.02 \text{ \AA}$ . The positions of the hydrogen atoms have been obtained by the use of difference projection along the *b*-axis. In the structure each chlorine is surrounded tetrahedrally by four oxygen atoms at a mean distance of  $1.46 \text{ \AA}$ . Each ammonium ion is surrounded by twelve oxygen atoms at distances varying from  $2.89$  to  $3.39 \text{ \AA}$ . The four hydrogens surrounding each nitrogen form weak N-H...O bridges with the nearest oxygen atoms. Tables are given for various atomic co-ordinates and interatomic distances.

#### REFERENCES

1. Gottfried, C. and Schusterius, C. *Zeit. Krist.*, 1933, **84**, 65.
2. Mooney, R. C. L. .. *Phys. Rev.*, 1931, **37**, 1306.
3. Wyckoff, R. W. G. .. *The Structure of Crystals*, 1935, Reinhold.
4. Ramaseshan, S., Venkatesan, K. and Mani, N. V. *Proc. Ind. Acad. Sci.*, 1957, **46 A**, 95.
5. Barker, Th. V. .. *Zeit. Krist.*, 1907, **43**, 533.
6. Henry, N. F. M. and Lonsdale, K. *International Tables for X-Ray Crystallography*, 1952, **1**, 408.
7. Hughes, E. W. .. *J. Am. Chem. Soc.*, 1941, **63**, 1737.
8. Booth, A. D. .. *Phil. Mag.*, 1945, **36**, 609.
9. Romers, C., Ketelaar, J. A. A. and MacGillavry, C. H. *Acta Cryst.*, 1951, **4**, 114.
10. Van Niekerk, J. N. and Schoening, F. R. L. *Ibid.*, 1952, **5**, 475.
11. Duke, J. R. C. and Llewellyn, F. J. *Ibid.*, 1950, **3**, 305.