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The Crystal Structure of Hydrogen Chloride Monohydrate

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The crystal structure of $HCl.H_2O$ at about −35 °C. has been determined by X-ray diffraction. The crystal is trigonal, space group $R\bar{3}m$. The rhombohedral cell, of dimensions $a = 4{\cdot}05$ Å and $\alpha = 73° 30'$, contains one formula unit. The actual structure is disordered but is derived from an ordered structure with space group $R3m$. The structure is clearly $H_3O^+Cl^-$. The hydronium ions are flat pyramids with symmetry $3m$. Each hydrogen atom forms a hydrogen bond to the nearest chlorine atom, with $O \cdots Cl = 2{\cdot}95$ Å. The crystal is formed by stacking together the trigonal puckered layers composed of hydrogen-bonded hydronium and chloride ions.

Introduction

The formation of hydronium ions in water has been frequently postulated (Hückel, 1928) to explain the abnormal mobility of protons through water. Evidence of their existence in crystals has been obtained by X-ray diffraction methods (Volmer, 1925; Luzzati, 1953), nuclear magnetic resonance spectra (Richards & Smith, 1951; Kakiuchi, Shono, Komatsu & Kigoshi, 1952) and infrared and Raman spectra (Bethell & Sheppard, 1953; Ferriso & Hornig, 1955; Taylor & Vidale, 1956). From these studies a symmetrical pyramidal configuration for the hydronium ion was deduced. The present study of hydrogen chloride monohydrate was undertaken to obtain additional direct evidence for the existence of the hydronium ion in crystals and to investigate its hydrogen-bonding pattern.

Experimental methods

Single crystals of hydrogen chloride monohydrate were grown in sealed thin-walled Pyrex capillaries from a mixture of hydrogen chloride and water. The hydrogen chloride used was anhydrous commercial hydrogen chloride. Excess hydrogen chloride had to be present since the vapor has a higher proportion of hydrogen chloride than does the liquid phase (the vapor pressure of the monohydrate at its melting point is 17·3 atm. (Rupert, 1909)).

By freezing, melting, and refreezing crystal fragments, satisfactory single crystals were finally obtained. Powder and Weissenberg X-ray photographs were prepared at −35±5 °C. with nickel-filtered Cu $K\alpha$ radiation. (The melting point of the monohydrate is −15·4 °C.) Multiple films were prepared for intensity estimation.

Relative intensities were estimated visually from equi-inclination Weissenberg photographs. An approximate correction was made for angular-dependent absorption in the sample, as for a cylindrical powder rod (Claassen, 1930; Ritter, Harris & Wood, 1951). The relative structure factor magnitudes were then extracted in the usual way. A total of 64 independent reflections were recorded and estimated.

Unit cell and space group

The diffraction pattern was indexed on a rhombohedral lattice (after the initial stages of the structure determination had been carried out in a monoclinic lattice). The cell dimensions were obtained by a least-squares treatment of measurements of spot positions on the equatorial layers of two calibrated rotation photographs. They are $a = 4{\cdot}05 \pm 0{\cdot}01$ Å and $\alpha = 73°30' \pm 30'$. (All errors given in this paper are estimated standard deviations derived from the normal equations in the least-squares treatment.) This unit cell contains only one formula unit since the measured density is 1·48 g.cm.$^{-3}$ (Rupert, 1909) while that calculated on this basis is 1·52 g.cm.$^{-3}$.

Since, then, both chlorine and oxygen atoms must lie in special positions, a Patterson projection onto the plane of a and [111] was computed in order to determine the relation between the special positions. It exhibited chlorine–oxygen vector peaks along [111] with no special relation to the length of this cell diagonal. Since no systematic absences were observed, the probable space group was at this stage taken to be $R3$ or $R3m$. These differ in this case only in the positions available to the hydrogen atoms.

It was later discovered that the structure is actually disordered, as will be described subsequently, so that the true space group is $R\bar{3}m$.

Determination of the structure

Without loss of generality the chlorine atom was placed at 0, 0, 0 and the oxygen atom at x, x, x. An approximate value of x was obtained from the Patterson projection onto the plane of a and [111]. Refinement of the position of the oxygen atom was pursued by means of maps of the electron density in this plane

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until its coordinate ceased changing significantly; a back-shift correction was then applied. Beevers–Lipson strips (Beevers, 1952) were used for all Fourier syntheses.

Next, individual anisotropic temperature factors of the form $\exp[-\alpha(h^2+k^2+l^2)-\beta(hk+kl+lh)]$ were applied. The parameters in this expression were evaluated by a least-squares calculation which minimized $\Sigma(F_o-F_c)^2$.

Attention was then directed to finding the hydrogen atoms. An electron-density difference section in the plane of *a* and [111] was computed with the use of calculated structure factors which contained no hydrogen contributions. A definite but small peak appeared in this section in the expected position. Certain disturbing features elsewhere in this difference map were temporarily ignored.

Since the limit of Fourier refinement appeared to have been essentially reached, refinement was continued by the least-squares method wherein not only the atomic coordinates but also the scale and temperature factor parameters were varied simultaneously. However, a fixed isotropic temperature factor $\exp[-B\sin^2\theta/\lambda^2]$ with $B = 1$ Å^2 was applied to the contribution from the one independent hydrogen atom. The observational equations were weighted by the function $w = N/F_o$, where for each reflection N is the number of independent measurements entering into the average observed value F_o. The second such cycle changed $x(\mathrm{O})$ by only 0·0001 and the hydrogen coordinates by less than 0·001, so the refinement was terminated. The resulting atomic positions and conventional discrepancy are included in Table 1 under the heading '$R3m$'. The conventional discrepancy R is calculated here by ignoring all unobserved reflections and omitting reflections 011 and 01$\bar{1}$ (which appear to suffer from extinction errors).

Table 1. *Atomic coordinates and discrepancies for* $\mathrm{HCl.H_2O}$

Quantity	$R3m$	$R\bar{3}m$
$x(\mathrm{Cl})$	0	0
$x(\mathrm{O})$	0·4388	0·4400
$x(\mathrm{H})$	0·286	0·308
$z(\mathrm{H})$	0·674	0·648
R(%)	5·4	5·3

In order to check the reality of the hydrogen atoms and the general correctness of the structure thus determined (in view of the disturbing features in the difference map calculated earlier), a second difference map in the plane of *a* and [111] was computed, again omitting hydrogen contributions from the calculated structure factors. The expected hydrogen peak did appear, but other aspects of the map were still unsatisfactory. In particular, the map exhibited distortion in the neighborhood of the oxygen atom in such a way as to suggest previously unrecognized scattering matter nearby, but on the other side of the unit-cell center.

At this point it was realized that the postulated structure could easily be subject to disorder, with half an oxygen atom on either side of the cell center, which would thus become a center of symmetry. Accordingly, it was tentatively assumed that the structure really belongs to the centrosymmetric space group $R\bar{3}m$ and contains one chlorine atom in position (*a*) and two half-atoms of oxygen in positions (*c*) with $x(\mathrm{O})$ the same as for the ordered structure. Calculated structure factors showed agreement almost as good as those for the ordered structure, before any adjustment had been made in the parameters.

Refinement of the disordered structure was then carried out by the least-squares method wherein the oxygen coordinate and the scale and temperature factor parameters were varied. Hydrogen contributions were included in calculated structure factors although hydrogen parameters were not varied in the least-squares calculation. Six half-atoms of hydrogen were assumed to lie in positions (*h*) of $R\bar{3}m$ with initially the same values of the coordinates as resulted from the refinement of the ordered model. This assumption was justified by the decrease of the discrepancy when the hydrogen contributions were included.

After the third least-squares cycle, the parameters appeared to have converged; the resulting atomic coordinates for chlorine and oxygen atoms are included in Table 1 under the heading '$R\bar{3}m$'. In calculating the structure factors and thence the discrepancy for this model, the hydrogen coordinates were adjusted to follow the slight movement that took place in the position of the oxygen atom. The parameter in the isotropic temperature factor for hydrogen was changed gradually (by rough inspection) to $B = 3$ Å^2. The final disordered model had a slightly smaller discrepancy than did the best ordered model (see Table 1), but the conventional discrepancy is remarkably insensitive to the difference between these models.

The electron-density in the plane of *a* and [111] (a mirror plane) is shown in Fig. 1(*a*). The chlorine and oxygen atoms appear plainly and a trace of a hydrogen atom may be discerned.

As a further check that the disordered $R\bar{3}m$ structure is correct, and in order to seek further evidence for the hydrogen atom positions, a final difference map in the plane of *a* and [111] was calculated; it is shown in Fig. 1(*b*). Again no hydrogen contributions were included in the calculated structure factors. The objectionable features of the corresponding map for the ordered structure are no longer present, and the near-flatness of this map at the oxygen and chlorine positions demonstrates that they have been correctly located.

At the position where a half-atom of hydrogen is believed to be located, a small circular peak of height about 0·5 e.Å^{-3} appears on this map. However, another peak of about the same height also appears on

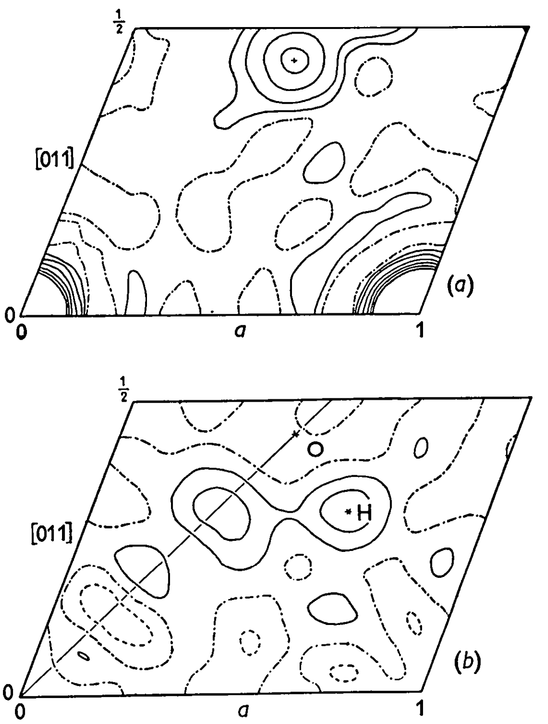

Fig. 1. Hydronium chloride. (*a*) The electron-density in a mirror plane. The contours are drawn at 0 (chain line), 1, 2, 4, 6, 8, and 10 e.Å^{-3}. (*b*) The difference map in a mirror plane. The contours are drawn at −0·2 (dashed line), 0 (chain line), 0·2, and 0·4 e.Å^{-3}. The centers of the oxygen and hydrogen atoms are indicated by stars. The light diagonal line through the origin is the three-fold axis.

the three-fold axis. Calculations according to the method of Cruickshank & Rollett (1953) show that the standard deviation expected in the electron-density amounts to about 0·13 e.Å^{-3} in the general area of this map and to about 0·23 e.Å^{-3} on the three-fold axis. Consequently a peak of height 0·5 e.Å^{-3} is significantly above the expected background fluctuation in the position of the expected hydrogen atom, but is not significant on the three-fold axis. In view of the fact that it is only half of a hydrogen atom which appears here in the presence of an atom as large as chlorine, it is surprising that even this slight indication is observed. The final hydrogen coordinates recorded in Table 1 are taken from the position on this difference map of the peak which is attributed to hydrogen.

It is interesting to note how little an effect on the oxygen and hydrogen positions is produced by changing from the ordered to the disordered model. The standard deviation in the oxygen coordinate in the incorrect ordered structure was computed from the normal equations of the least-squares refinement (Whittaker & Robinson, 1940); it was 0·006 Å. The actual change of the oxygen coordinate from the ordered to the disordered structure was only 0·005 Å. The standard deviation in either hydrogen coordinate is much larger, about 0·075 Å. The standard deviations were not recomputed for the final ordered structure but, from the similarity in the normal equations in the two cases, the standard deviations should be very similar to those for the ordered structure.

The final parameters in the individual anisotropic temperature factors are: $\alpha(\text{Cl})=0{\cdot}036$, $\beta(\text{Cl})=-0{\cdot}007$, $\alpha(\text{O})=0{\cdot}041$, and $\beta(\text{O})=-0{\cdot}016$ and the parameter for the isotropic temperature factor for hydrogen is $B=3$ Å.

Table 2. *Observed and calculated structure factors* (×10) *for hydronium chloride*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	66	65	$12\bar{2}$	39	38	$1\bar{1}4$	38	36
011	125	162	$01\bar{3}$	63	63	$01\bar{4}$	34	32
111	100	86	$1\bar{1}3$	46	44	$2\bar{2}3$	34	32
$01\bar{1}$	115	149	133	50	54	334	26	18
$11\bar{1}$	49	52	233	24	26	034	36	37
112	80	82	$11\bar{3}$	38	35	$\bar{1}24$	33	34
002	98	105	$\bar{1}23$	49	45	$22\bar{3}$	25	26
012	67	66	$22\bar{2}$	58	56	$11\bar{4}$	37	38
122	80	79	033	33	33	244	16	17
$01\bar{2}$	49	48	114	35	33	$03\bar{3}$	41	39
022	69	72	124	42	48	115	31	33
$1\bar{1}2$	84	89	333	50	44	144	32	30
222	45	41	224	23	24	225	28	30
$11\bar{2}$	88	89	014	44	44	125	16	18
113	62	66	$02\bar{3}$	30	32	$13\bar{3}$	22	23
013	60	58	004	43	40	344	27	23
003	53	51	$1\bar{2}3$	53	49	$\bar{2}33$	26	28
$\bar{1}22$	47	48	024	30	30	015	—	21
123	41	40	$12\bar{3}$	54	50	$02\bar{4}$	33	34
$02\bar{2}$	72	76	234	40	38	$1\bar{2}4$	23	25
223	69	64	134	19	22	$\bar{1}34$	21	21
023	53	55	$\bar{1}33$	38	38			

Observed and calculated structure factors for the final disordered structure are presented in Table 2. Reflections are arranged in order of increasing Bragg angle. One unrecorded reflection within the range of angle included is denoted by a dash. The atom form factors of Viervoll & Ögrim (1949) were used.

Description and discussion of the structure

The general features of the structure are not affected by the existence of disorder in the crystal, so the following description refers mainly to the idealized structure in which no disorder is present.

Two views of the idealized structure are shown in Fig. 2: (*a*) shows a view along the [111] direction and (*b*) shows a view perpendicular to the first, along the [121] direction. Atoms are drawn with van der Waals radii (Pauling, 1945). Around each oxygen atom there are three nearest chlorine atoms which form the base of a flat trigonal pyramid having the oxygen atom at its apex. The oxygen atoms surround each chlorine atom in a similar way. The O · · · Cl distance is 2·95±0·01 Å and the Cl · · · O · · · Cl angle is 110·4±0·2°. Each oxygen atom lies on a site with $3m$ point symmetry. Even without consideration of the hydrogen atoms revealed by the difference map, the most natural inference from this arrangement is that the oxygen atom represents a hydronium ion, H_3O^+,

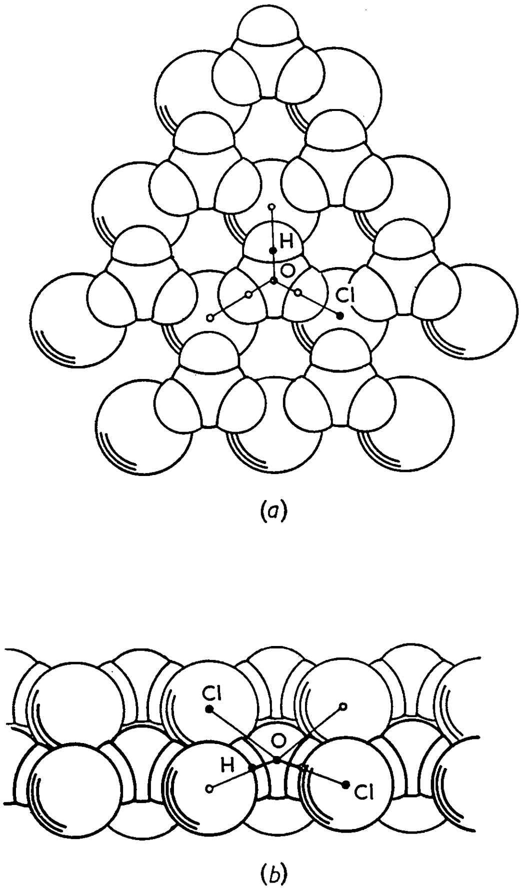

Fig. 2. The idealized ordered structure of hydronium chloride. Atoms are drawn with van der Waals radii. (*a*) A view along [111] showing a single layer of hydrogen bonded ions. (*b*) A view along $[1\bar{2}1]$ showing how layers are stacked.

and that the O · · · Cl distance represents a hydrogen bond. The substance is then more properly called hydronium chloride.

This interpretation is supported by the positions determined directly but approximately for the hydrogen atoms. The O · · · H distance is 0·96±0·08 Å and the H · · · O · · · H angle is approximately 117.° Furthermore each hydrogen atom lies only 0·10 Å distant from the line joining the oxygen atom to the corresponding chlorine atom.

The existence and structure of the hydronium ion in this crystal is consistent with the conclusions from other lines of evidence. The infrared absorption of the hydrogen halides (Ferriso & Hornig, 1955) showed in each case the four fundamental frequencies expected for the hydronium ion. The nuclear magnetic resonance studies of Richards & Smith (1951) led to the conclusion that the H · · · H distance in the hydronium ion is 1·70 Å. That calculated from the present X-ray determination is 1·65 Å.

The length of the O–H · · · Cl hydrogen bond in hydronium chloride is comparable with others involving a chloride ion: 2·99 Å in hydroxylammonium chloride (Jerslev, 1948) and 2·91 and 2·99 Å in tropolone hydrochloride (Sasada, Osaki & Nitta, 1954). The oxygen atoms and chloride ions are bound by these hydrogen bonds into infinite puckered layers perpendicular to the [111] direction as shown in Fig. 2. The crystal is formed by the packing together of these layers. The minimum distance from an oxygen atom in one layer to a chloride ion in an adjacent layer is 3·43 Å, which exceeds the sum of the van der Waals radii of the neutral atoms by 0·2 Å. In the idealized ordered structure the adjacent layers are not joined by hydrogen bonds. In the actual disordered structure the identities of the layers are partly lost; adjacent planes of chloride ions are separated by interleaving hydronium ions which form hydrogen bonds to one or the other plane of chloride ions at random.

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