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Hydrogen Bond Studies. XVI*. The Crystal Structure of Hydrogen Chloride Trihydrate

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The crystal structure of hydrogen chloride trihydrate, $HCl.3H_2O$, has been determined from three-dimensional single-crystal X-ray data obtained at −190 °C. Data recorded at −40 °C indicate the same structure. The crystals are monoclinic, space group *Cc*, with four formula units in a unit cell with the dimensions: $a=7{\cdot}584$, $b=10{\cdot}154$, $c=6{\cdot}715$ Å and $\beta=122{\cdot}96°$. The water molecules form chains where two molecules are coupled together by a very short hydrogen bond (2·43 Å), forming $H_5O_2^+$ units. These two molecules have a pyramidal bonding situation while the third water molecule has a normal tetrahedral environment. The O···O distances involved are 2·43, 2·65 and 2·75 Å. The lengths of the O···Cl hydrogen bonds are 3·01, 3·05, 3·07 and 3·13 Å. The structure indicates that the appropriate formulation is $H_5O_2^+Cl^-.H_2O$.

Introduction

The present investigation is part of the systematic studies of the hydrates of the strong acids in progress at this Institute. The structure of $HCl.2H_2O$ was described in the preceding article. In this compound the proton exists as a dihydrate. $H_5O_2^+$. The investigation of $HCl.3H_2O$ is therefore of particular interest as a study of the hydration of the proton in a crystal containing more water than necessary to form H_3O^+ or $H_5O_2^+$.

The present structure determination of $HCl.3H_2O$ is based on single-crystal X-ray diffraction data obtained at −190 °C.

Experimental

The sample was prepared in the way described earlier (Lundgren & Olovsson, 1967). The crystal used for the X-ray work was formed in an accidental way as follows. During the work on the dihydrate (Lundgren & Olovsson, 1967) a crystal of that compound had been grown in a capillary fixed in the camera [a modified Weissenberg camera (Olovsson, 1960)]. However, the crystal melted in spite of the fact that the temperature had not exceeded the melting point of the dihydrate, −17·7 °C (Roozeboom, 1883). Probably the capillary was not quite tight and some hydrogen chloride might have escaped from it, thus altering the composition of the sample. A new crystal was grown at a lower temperature (∼ −28 °C). This crystal proved to be the trihydrate, melting point −24·9 °C (Pickering, 1893).

A cylindrical crystal with a diameter of 0·36 mm and a length of 0·8 mm was used for collection of the intensity data. The crystal was rotated about the crystallographic *c* axis, which coincided with the cylinder axis. Equi-inclination Weissenberg photographs for the seven layers $0 \le l \le 6$ were recorded at −190 °C by the multiple film technique (five films) and Cu $K\alpha$ radiation. The intensities of 414 independent reflexions were estimated visually by comparison with an intensity scale. This number corresponds to about 85% of the reflexions within the copper reflexion sphere. The intensity range was 1 to 700. Only 8 of the recorded reflexions were too weak to be measured and were not included in the refinement. Four strong reflexions with low θ values were rejected during the last cycles of refinement. Their deviations from the calculated F values may depend on secondary extinction effects.

The data were corrected for the Lorentz and polarization effects and, as the crystal was rather thick, also for absorption (cylindrical specimen). These calculations were made on an IBM 7090 computer using the program ERLPA, written by Van den Hende (1962). The absorption coefficient for Cu $K\alpha$ radiation is

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* Part XV: p.966 of this issue.

$\mu = 65{\cdot}7$ cm^{-1}. For a crystal with a radius of 0·018 cm the resulting $\mu R/\cos \beta$ (where β is the inclination angle) lies between 1·18 (layer 0) and 1·61 (layer 6).

In addition photographs were recorded at −40 °C, but no indication of structural differences could be detected when comparing data recorded at −40 and −190 °C, respectively. The refinement was carried out with the data obtained at the lower temperature.

Unit cell and space group

The unit-cell dimensions were determined from quartz-calibrated zero-layer oscillation and rotation photographs. The angle β was determined according to the method of angular lag (Buerger, 1962). The dimensions $a \sin \beta$ and b were fitted to the measured θ values by the method of least squares. The values of the parameters and their estimated standard deviations are, at −184 °C:

$$a = 7{\cdot}584 \pm 0{\cdot}007, \quad b = 10{\cdot}154 \pm 0{\cdot}001, \quad c = 6{\cdot}715 \pm 0{\cdot}005 \text{ Å}, \ \beta = 122{\cdot}96 \pm 0{\cdot}08^\circ$$

$$(a = 4{\cdot}913, \ c = 5{\cdot}4045 \text{ Å for } \alpha\text{-quartz at } 22^\circ\text{C}, \ \lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051 \text{ Å}, \ \lambda(\text{Cu } K\alpha_2) = 1{\cdot}54433 \text{ Å}) .$$

The density calculated on the basis of a cell containing four units of $HCl.3H_2O$ is 1·39 g.cm^{-3}.

The intensity data indicated the space group *Cc* (no. 9) or *C*2/*c* (no. 15, *International Tables for X-ray Crystallography*, 1952). A reasonable structure could only be deduced with the use of *Cc*, and the successful refinement in this space group confirms the choice.

Determination of the atomic coordinates

The coordinates of chlorine were determined from a three-dimensional Patterson synthesis. In *C*2/*c* only the special fourfold position 4(*e*) (*International Tables for X-ray Crystallography*, 1952, p. 101) was found to be possible; in *Cc* the x and z coordinates may be chosen arbitrarily. The oxygen atoms were located in the subsequent three-dimensional F_o synthesis based on chlorine. If the space group is *C*2/*c*, at least one of the water oxygen atoms must be in a special fourfold position. As no such peaks were found, *C*2/*c* must be abandoned and *Cc* used instead. All oxygen peaks were doubled by false symmetry in the above F_o synthesis and the most plausible positions of the oxygen atoms in relation to chlorine and other oxygen atoms were selected. The subsequent F_o synthesis based on all atoms (except hydrogen) showed no extra peaks of considerable height. The Fourier calculations were made on the computer FACIT EDB using programs (STRIX and PROFFS) written by Liminga & Olovsson (1964). Atomic scattering factors for Cl^- and neutral O in these and the following calculations were obtained from *International Tables for X-ray Crystallography* (1962, p. 202).

To refine the atomic coordinates, individual isotropic temperature factors and scale factors a series of least-squares calculations was performed. These calculations were run on FACIT EDB with a program (designated SFLS) written by Åsbrink and Brändén. A block-diagonal approximation is used in this program to minimize the function $\Sigma w(|F_o| - |F_c|)^2$. The weights, w, were calculated according to an expression suggested by Cruickshank: $w = 1/(a + |F_o| + c|F_o|^2)$. The final values used for the parameters a and c were 5·8 and 0·029, respectively. After about ten cycles of least-squares refinements the discrepancy index $R_1 = \Sigma \,||F_o| - |F_c|| / \Sigma \,|F_o|$ was 0·089.

A three-dimensional difference synthesis was calculated at this stage to determine the hydrogen positions. Peaks appeared in the locations predicted for hydrogen from chemical arguments, as described below. The peaks were, however, somewhat diffuse and other peaks also appeared in the maps. Thus the actual location of the hydrogen atoms was not made from these maps.

A series of least-squares calculations was now run on an IBM 7090 computer with a full-matrix program, a local modification of ORFLS, written by Busing, Martin & Levy (1962). The same weighting scheme as above was used. The calculations started with the parameters obtained at the preceding refinements and the same parameters were refined. No significant changes in the parameters or the R value were found. After this two cycles of least-squares refinement were run to refine atomic coordinates, anisotropic temperature factors and an overall scale factor. The inter-layer scale factors were fixed to the values obtained in the last cycle of isotropic refinement. The total number of parameters varied was 35. In the second cycle the shifts in the parameters were, in most cases, less than one tenth of their standard deviations. The R values were

$$R_1 \text{ (as defined above)} = 0{\cdot}086$$
$$R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{\frac{1}{2}} = 0{\cdot}117 .$$

Finally, four reflexions for which F_o was much smaller than F_c were excluded from the data (see above) and the last cycles of refinement were repeated. The R values decreased to 0·081 and 0·111, respectively.

The atomic coordinates and thermal parameters with standard deviations after the final anisotropic least-squares refinement are listed in Tables 1 and 2. Distances and angles calculated from these coordinates are listed in Table 3. The program ORFFE (Busing, Martin & Levy, 1964) was used for the distance and angle calculations. The observed and calculated structure factors are listed in Table 4.

Table 1. *Atomic coordinates with standard deviations* (× 10^4)

	x	y	z
Cl	0	1613 (2)	0
O(1)	7543 (14)	4160 (6)	381 (16)
O(2)	6252 (13)	−49 (7)	1314 (15)
O(3)	7398 (13)	2141 (6)	3015 (16)

In addition to the refinement using data corrected for absorption (case *A*), a complete refinement was also made with data that had not been corrected (case *B*). The results from the two different refinements were coincident as far as the atomic coordinates are concerned. The differences were less than 30% of the standard deviations. The temperature factors were about twice as great in case *A* (~1·5 Å^2 compared to ~0·9 Å^2 for oxygen) and the scale factors applied to F_o were then, of course, smaller. After the anisotropic refinement, distances averaged over thermal motion were calculated in both cases assuming independent motion of the atoms. The increase in bond length as compared to the distance not corrected for thermal motion was 1·7–2·0 times larger in case *A*, but as the increase in bond length was of the order of the standard deviation (see Table 3) the absorption correction did not appreciably change the results of the refinement in this particular case.

Table 2. *Anisotropic thermal parameters with standard deviations* (× 10^4)

The form of the temperature factor is:

$$\exp\left(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl\right).$$

The r.m.s. components (R_i) of thermal displacement of the atoms along the ellipsoid axes are also given (× 10^3 Å).

	Cl	O(1)	O(2)	O(3)
β_{11}	90 (5)	139 (18)	103 (18)	125 (19)
β_{22}	28 (2)	27 (5)	35 (5)	40 (6)
β_{33}	101 (8)	165 (29)	108 (24)	124 (26)
β_{12}	4 (2)	14 (8)	0 (8)	19 (8)
β_{13}	44 (5)	100 (20)	54 (18)	93 (19)
β_{23}	−1 (3)	2 (10)	−6 (9)	5 (9)
R_1	120 (4)	108 (14)	125 (14)	102 (17)
R_2	127 (5)	148 (14)	140 (13)	138 (12)
R_3	146 (4)	175 (12)	149 (12)	173 (12)

Description and discussion of the structure

General

The structure can be described with reference to Figs. 1–3. In Fig. 2, which shows the structure viewed along the *b* axis, it is noted that the chlorine atoms and two water oxygen atoms, O(2) and O(3), are situated in, or very near planes parallel to ($10\bar{1}$). (The equation of the planes is: $x-z=n\cdot\frac{1}{2}$, $n=0, \pm 1, \pm 2, \ldots$). The third water molecule is situated between these planes. Fig. 3 shows the structure seen along the normal to the plane $x-z=0$. The chlorine atoms form zigzag chains, where the distance Cl···Cl is 3·88 Å and the angle Cl–Cl–Cl is 124·6°. The shortest distance between chlorine atoms belonging to different chains is 4·69 Å. These two chains are then not situated in the same plane.

O–H···Cl *bonds*: O(2) is bonded to a chlorine atom in the same plane; the bond length is 3·01 Å. O(3) is bonded to a chlorine atom in an adjacent plane; bond length 3·05 Å. O(1), which is situated between two planes, is bonded to a chlorine atom in each plane; bond lengths 3·07 and 3·13 Å.

O–H···O *bonds*: The water molecules $H_2O(2)$ and $H_2O(3)$ are held together by a very short hydrogen bond (2·43 Å). The bonds O(2)···O(1) and O(3)···O(1) are 2·65 and 2·75 Å, respectively. The water molecules are then bonded to each other in chains.

Table 3. *Interatomic distances and angles with standard deviations*

Distances corrected for thermal motion assuming independent motion are given within square brackets. Distances corrected for riding motion all agree with the uncorrected distances to within 0·002 Å. The standard deviations of the distances are × 10^3.

Bond	Distance (Å)	Increase in bond length (independent motion) Absorption correction applied (Å)	not applied (Å)
O(1)···O(2)	2·652 [2·655] (12)	0·013	0·007
O(1)···O(3)	2·749 [2·764] (10)	0·015	0·008
O(2)···O(3)	2·434 [2·450] (10)	0·016	0·008
Cl ····O(1)	3·132 [3·144] (10)	0·012	0·005
···O(1)	3·074 [3·089] (7)	0·015	0·008
···O(2)	3·012 [3·024] (9)	0·012	0·006
···O(3)	3·053 [3·066] (8)	0·013	0·007

Bonds	Angle (°)
O(2)···O(1)···O(3)	118·8 (0·4)
···Cl	104·9 (0·3)
···Cl	108·1 (0·3)
O(3)···O(1)···Cl	109·9 (0·3)
···Cl	114·5 (0·3)
Cl ····O(1)···Cl	98·2 (0·2)
O(1)···O(2)···O(3)	116·7 (0·4)
···Cl	116·5 (0·3)
O(3)···O(2)···Cl	99·2 (0·3)
O(1)···O(3)···O(2)	120·6 (0·4)
···Cl	102·3 (0·2)
O(2)···O(3)···Cl	116·0 (0·3)

Bonds	Angle (°)
O(1)···Cl···O(1)	74·7 (0·2)
O(1)···Cl···O(2)	84·5 (0·2)
···O(2)	122·0 (0·2)
···O(3)	82·9 (0·2)
···O(3)	117·9 (0·2)
O(2)···Cl···O(3)	112·3 (0·2)

The O···O and O···Cl distances mentioned above indicate seven hydrogen bonds per formula unit of the trihydrate. Other O···O and O···Cl distances are all longer than 3·35 and 3·26 Å, respectively. These facts suggest that all seven hydrogen atoms are involved in hydrogen bonding, with one hydrogen per bond, assuming normal types of bond.

The atoms O(1), O(2), O(3) and Cl′ (Fig. 4) lie almost in plane. Similarly O(2), O(3), O(1) and Cl″ are nearly coplanar, *etc.* The bonds around the water molecules are arranged in an eclipsed way with respect to each other. The dihedral angles between the planes defined by O(1), O(2), O(3) and O(2), O(3), Cl′, *etc.* are shown in Fig. 6. The lone pairs of O(2) and O(3) are also indicated in this Figure.

Assignment of hydrogen

In the water chains water molecules of different kinds can be distinguished. $H_2O(1)$ is involved in four hydrogen bonds; two of them directed towards chlorine and

Table 4. *Observed and calculated structure factors*

h	k	l	$\|F_o\|$	$\|F_c\|$
-8	0	0	25.8	24.4
-8	2	0	3.6	4.0
-7	1	0	8.7	7.1
-7	3	0	21.2	21.6
-7	5	0	11.9	10.3
-6	0	0	13.6	11.3
-6	2	0	13.4	11.7
-6	4	0	14.7	13.5
-6	6	0	24.7	23.7
-6	8	0	5.0	5.1
-5	1	0	20.3	22.0
-5	3	0	19.2	19.9
-5	5	0	13.7	12.7
-5	7	0	22.0	20.7
-5	9	0	15.3	13.5
-4	0	0	39.6	43.4
-4	2	0	29.3	30.9
-4	4	0	28.8	26.4
-4	6	0	7.7	6.0
-4	8	0	16.3	15.4
-4	10	0	14.3	12.6
-3	1	0	36.7	43.5
-3	3	0	31.2	33.1
-3	5	0	22.7	24.2
-3	7	0	21.5	22.2
-3	9	0	17.7	15.7
-3	11	0	13.7	11.5
-2	0	0	29.9	26.8
-2	2	0	21.8	22.7
-2	4	0	29.2	31.5
-2	6	0	45.9	47.3
-2	8	0	9.0	7.9
-2	10	0	27.9	23.9
-2	12	0	17.4	14.6
-1	1	0	9.4	12.5
-1	3	0	55.2**	67.6
-1	5	0	39.3	42.1
-1	7	0	15.4	15.2
-1	9	0	31.2	30.7
-1	11	0	7.5	5.1
0	2	0	8.2	10.9
0	4	0	5.1	5.4
0	6	0	29.0	29.8
0	8	0	4.8	4.3
0	10	0	3.3	2.4
0	12	0	25.3	22.1
-8	2	1	9.2	9.4
-8	4	1	11.2	12.9
-7	1	1	18.8	20.7
-7	3	1	7.7	6.8
-7	5	1	15.7	14.7
-7	7	1	9.9	10.6
-6	2	1	28.6	29.6
-6	4	1	15.6	15.0
-6	6	1	6.4	5.8
-6	8	1	10.5	10.8
-5	1	1	15.5	14.4
-5	3	1	16.8	15.7
-5	5	1	26.2	26.9
-5	7	1	14.4	15.8
-5	9	1	7.7	6.4
-4	2	1	15.2	15.4
-4	4	1	28.9	28.2
-4	6	1	12.1	12.4
-4	8	1	29.5	32.1
-4	10	1	9.4	9.6
-3	1	1	47.3	57.1
-3	3	1	25.5	25.3
-3	5	1	26.8	24.8
-3	7	1	20.8	17.9
-3	9	1	4.9	5.1
-3	11	1	14.9	14.9
-2	2	1	58.5**	71.2
-2	4	1	32.0	30.3
-2	6	1	11.7	10.9
-2	8	1	14.1	13.7
-2	10	1	18.8	19.4
-2	12	1	8.0	8.8
-1	1	1	22.4	26.1
-1	3	1	38.1	36.2
-1	5	1	41.1	42.1
-1	7	1	31.4	26.1
-1	9	1	15.8	15.5
-1	11	1	21.7	21.1
0	2	1	21.7	25.4
0	4	1	47.9	52.8
0	6	1	15.5	16.2
0	8	1	35.5	36.3
0	10	1	13.4	12.1
0	12	1	8.5	8.2
1	1	1	62.0**	72.2
1	3	1	26.9	22.8
1	5	1	25.7	25.1
1	7	1	22.1	20.5
1	9	1	9.9	9.0
1	11	1	17.9	16.7
2	2	1	47.9	53.4
2	4	1	25.3	20.8
2	6	1	11.7	11.1
2	8	1	17.4	16.9
2	10	1	18.6	16.7
2	12	1	4.6	5.5
3	1	1	15.7	13.5
3	3	1	18.1	14.6
3	5	1	32.3	33.1
3	7	1	18.8	16.5
3	9	1	12.4	10.6
3	11	1	17.0	20.0
4	2	1	17.6	17.1
4	4	1	27.1	26.6
4	6	1	9.9	8.2
4	8	1	27.5	24.6
4	10	1	7.8	8.7
5	1	1	24.6	27.6
5	3	1	8.5	6.9
5	5	1	16.1	15.5
5	7	1	14.0	12.7
6	2	1	21.3	20.0
6	4	1	13.1	12.0
6	6	1	6.2	5.1
-9	1	2	8.9	8.5
-8	0	2	18.2	19.2
-8	2	2	10.5	10.0
-8	4	2	13.8	13.5
-8	6	2	10.6	11.8
-7	1	2	13.2	13.2
-7	3	2	13.6	12.5
-7	5	2	10.9	9.7
-7	7	2	20.6	20.9
-6	0	2	14.9	13.0
-6	2	2	26.0	28.4
-6	4	2	16.5	15.7
-6	6	2	18.1	18.4
-6	8	2	9.0	6.8
-6	10	2	12.6	16.3
-5	1	2	31.7	29.3
-5	3	2	30.4	29.2
-5	5	2	20.0	20.3
-5	7	2	17.5	19.3
-5	9	2	9.4	10.0
-4	0	2	48.2	48.8
-4	2	2	3.8*	2.2
-4	4	2	36.2	36.0
-4	6	2	20.8	22.3
-4	8	2	9.4	9.7
-4	10	2	14.2	14.3
-3	1	2	36.3	32.6
-3	3	2	44.2	42.7
-3	5	2	5.7	6.1
-3	7	2	22.9	22.4
-3	9	2	30.3	31.8
-3	11	2	4.9	4.8
-2	0	2	52.2**	72.9
-2	2	2	27.4	28.8
-2	4	2	18.1	15.6
-2	6	2	49.0	51.7
-2	8	2	6.7	5.0
-2	10	2	12.3	10.5
-2	12	2	13.2	13.2
-1	1	2	43.2	48.7
-1	3	2	56.6	66.8
-1	5	2	11.9	11.2
-1	7	2	11.1	8.8
-1	9	2	23.2	24.6
-1	11	2	7.5	6.2
0	0	2	46.5	53.7
0	2	2	38.7	37.2
0	4	2	43.2	40.4
0	6	2	23.7	21.3
0	8	2	13.5	11.6
0	10	2	18.3	16.7
0	12	2	22.1	23.9
1	1	2	29.0	26.9
1	3	2	27.4	26.8
1	5	2	22.3	20.9
1	7	2	40.2	38.5
1	9	2	20.4	19.0
1	11	2	6.5	5.8
2	0	2	21.2	19.9
2	2	2	46.8	44.9
2	4	2	20.4	19.4
2	6	2	23.1	22.4
2	8	2	14.6	11.0
2	10	2	19.7	18.4
3	1	2	25.1	27.2
3	3	2	25.9	25.7
3	5	2	15.1	14.2
3	7	2	18.2	19.3
3	9	2	13.3	12.4
4	0	2	24.3	24.7
4	2	2	4.8*	3.7
4	4	2	19.9	21.4
4	6	2	21.0	18.1
4	8	2	9.3	7.8
5	3	2	24.0	22.8
5	5	2	4.4*	5.4
5	7	2	11.8	11.5
-9	1	3	12.5	13.0
-8	2	3	15.5	14.8
-8	4	3	20.1	20.0
-8	6	3	2.1*	1.8
-7	1	3	19.1	21.0
-7	3	3	8.2	5.7
-7	5	3	18.7	19.2
-7	7	3	11.2	10.2
-6	2	3	25.1	25.2
-6	4	3	8.4	6.6
-6	6	3	12.3	9.7
-6	8	3	19.4	19.2
-6	10	3	13.4	15.5
-5	1	3	27.6	29.7
-5	3	3	7.7	5.7
-5	5	3	25.0	23.8
-5	7	3	20.0	18.3
-5	9	3	11.2	11.8
-5	11	3	12.0	13.5
-4	2	3	27.7	26.3
-4	4	3	39.1	42.3
-4	6	3	4.0*	2.9
-4	8	3	22.5	19.8
-4	10	3	7.5	5.9
-3	1	3	38.7	39.6
-3	3	3	20.8	19.2
-3	5	3	25.9	26.9
-3	7	3	18.7	17.6
-3	9	3	12.1	10.3
-3	11	3	18.5	17.9
-2	2	3	42.3	41.8
-2	4	3	9.1	7.3
-2	6	3	17.7	16.4
-2	8	3	24.1	24.8
-2	10	3	21.7	21.6
-2	12	3	5.8	6.1
-1	1	3	42.5	44.4
-1	3	3	14.4	13.4
-1	5	3	32.3	31.8
-1	7	3	21.9	21.3
-1	9	3	11.4	10.6
-1	11	3	15.3	14.8
0	2	3	31.3	31.0
0	4	3	40.2	39.2
0	6	3	9.3	7.3
0	8	3	22.1	23.8
0	10	3	5.5	4.2
1	1	3	27.0	27.3
1	3	3	16.2	14.7
1	5	3	26.0	26.2
1	7	3	11.8	12.8
1	9	3	7.2	5.7
1	11	3	17.5	20.9
2	2	3	25.9	28.6
2	4	3	9.5	10.0
2	6	3	10.7	10.4
2	8	3	20.5	20.4
2	10	3	12.1	14.9
3	1	3	20.3	24.0
3	3	3	6.8	5.6
3	5	3	19.0	20.2
3	7	3	16.4	15.9
3	9	3	7.4	8.1
4	2	3	16.1	16.8
4	4	3	19.0	20.2
4	6	3	2.7*	2.9
4	8	3	9.1	14.5
-9	1	4	14.5	13.8
-9	3	4	9.9	9.0
-8	0	4	18.3	17.3
-8	2	4	11.6	10.7
-8	4	4	17.5	16.8
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-7	1	4	17.4	16.5
-7	3	4	19.2	20.7
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-7	7	4	13.3	11.8
-7	9	4	5.8	8.8
-6	0	4	31.3	32.1
-6	2	4	16.2	13.3
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-6	6	4	23.6	25.5
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-6	10	4	10.7	14.1
-5	1	4	12.6	9.9
-5	3	4	29.8	28.1
-5	5	4	15.3	14.2
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0	2	4	25.8	24.1
0	4	4	26.8	26.3
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0	8	4	13.9	13.4
0	10	4	14.6	15.3
1	1	4	19.0	18.6
1	3	4	26.1	25.8
1	5	4	22.5	22.6
1	7	4	17.6	16.4
1	9	4	10.9	10.5
2	0	4	24.4	26.5
2	2	4	10.4	9.1
2	4	4	14.5	13.8
2	6	4	20.9	22.3
2	8	4	3.0	2.9
3	1	4	10.7	8.5
3	3	4	18.2	21.0
3	5	4	9.1	8.0
3	7	4	8.1	8.4
4	4	4	6.5	5.7
-9	1	5	13.7	13.7
-9	3	5	6.8	6.8
-8	2	5	13.5	12.1
-8	4	5	11.8	11.6
-8	6	5	6.9	7.1
-7	1	5	18.9	17.2
-7	3	5	13.7	12.6
-7	5	5	16.2	15.0
-7	7	5	9.8	8.9
-6	2	5	28.4	27.2
-6	4	5	18.7	19.5
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-6	8	5	10.8	9.8
-5	1	5	22.4	21.8
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-3	1	5	19.7	26.4
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-3	7	5	12.4	11.2
-3	9	5	2.1	2.2
-2	2	5	34.2	32.8
-2	4	5	22.8	22.7
-2	6	5	4.7	3.7
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-1	3	5	12.8	11.2
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-1	9	5	8.4	7.8
0	2	5	17.5	16.6
0	4	5	15.2	14.2
0	6	5	11.0	8.9
0	8	5	21.0	23.5
1	1	5	21.3	21.7
1	3	5	12.0	10.0
1	5	5	15.2	15.5
1	7	5	10.0	11.1
2	2	5	18.2	20.0
2	4	5	16.1	17.4
2	6	5	2.3*	0.5
-9	1	6	11.1	13.7
-9	3	6	10.6	13.1
-8	0	6	22.9	24.1
-8	2	6	10.6	9.0
-8	4	6	12.0	11.4
-8	6	6	12.0	14.3
-7	1	6	6.1	3.7
-7	3	6	18.6	20.6
-7	5	6	4.7	4.0
-7	7	6	12.1	14.2
-6	0	6	22.2	19.9
-6	2	6	7.9	6.3
-6	4	6	13.7	10.7
-6	6	6	25.1	24.0
-6	8	6	7.3	3.9
-5	1	6	17.7	16.5
-5	3	6	29.1	29.7
-5	5	6	3.1	3.0
-5	7	6	7.2	5.9
-5	9	6	8.5	12.7
-4	2	6	21.2	22.7
-4	4	6	15.3	12.6
-4	6	6	18.4	15.4
-4	8	6	9.3	7.9
-3	1	6	11.3	11.7
-3	3	6	14.2	11.6
-3	5	6	15.6	14.7
-3	7	6	25.7	25.4
-3	9	6	11.3	15.4
-2	0	6	14.3	10.4
-2	2	6	19.2	17.7
-2	4	6	20.0	20.9
-2	6	6	17.5	14.6
-2	8	6	7.7	7.4
-1	1	6	22.9	21.7
-1	3	6	22.1	20.9
-1	5	6	13.5	12.0
-1	7	6	8.5	6.9
0	2	6	10.4	8.7
0	4	6	14.0	13.6
0	6	6	16.8	17.9
1	3	6	18.3	18.6

Reflexions marked * were too weak to be measured. The F_o values for these are given as $F_{\min}$ for the reflexion in question. Reflexions marked ** were omitted in the last cycles of least-squares refinement.

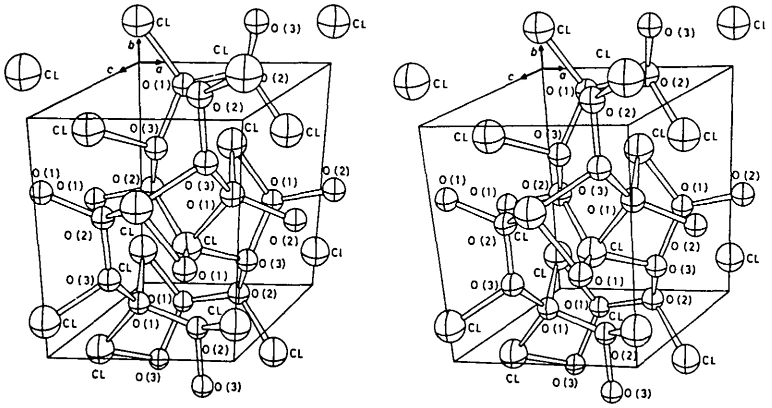

Fig. 1. A stereoscopic illustration of the structure showing the hydrogen bonding pattern. The Figure has been drawn with use of the program ORTEP (Johnson, 1965).

two of them directed towards other oxygen atoms. $H_2O(2)$ and $H_2O(3)$ are each involved in three hydrogen bonds; one towards chlorine and two towards other oxygen atoms.

From the above it is clear that the hydrogen atoms of $H_2O(1)$ are both directed towards Cl. In the bonds O(2)···O(1) and O(3)···O(1) the hydrogen atoms are thus donated by $H_2O(2)$ and $H_2O(3)$, respectively. The angles between the bonds around O(1) are roughly tetrahedral (*cf.* Fig. 5). If the bond lengths around O(1) are compared with other distances in the structure we find that the proton originating from HCl cannot belong to O(1), as the bonds around O(1) should then be shorter than other O···Cl and O···O bonds. $H_2O(1)$ is accordingly a normal water molecule.

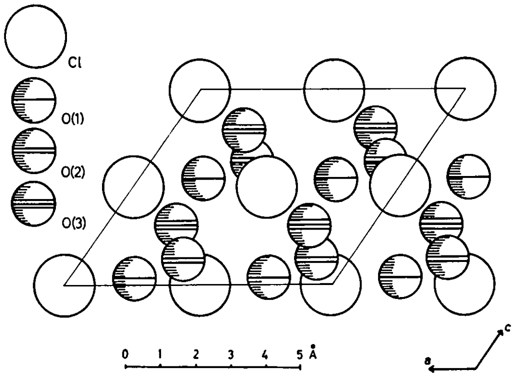

Fig. 2. The structure viewed along the *b* axis.

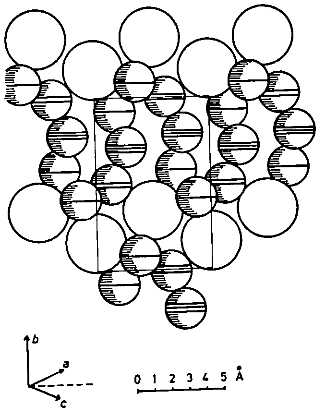

Fig. 3. The structure viewed along the normal to the plane $x-z=0$. For notation see Fig. 2.

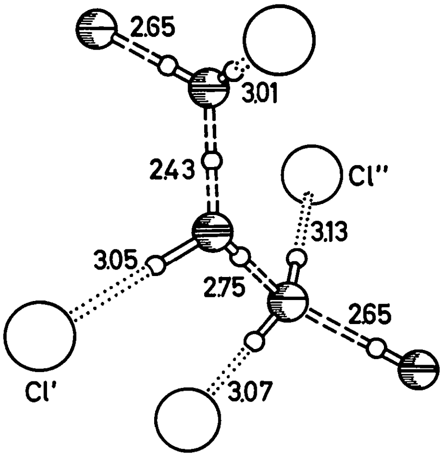

Fig. 4. Bond distances. The Figure also shows the assignment of hydrogen as discussed in the text. For notation see Fig. 2.

One hydrogen atom in both $H_2O(2)$ and $H_2O(3)$ is directed towards O(1) as stated above. The remaining hydrogen atoms in these molecules must be directed towards Cl. For the proton originating from HCl there is accordingly only one place left, namely somewhere on the very short bond O(2)···O(3) (2·43 Å).

The assignment of the hydrogen atoms is clear so far. The final question is where to put the hydrogen atom between O(2) and O(3). The following three cases are then considered.

Case I. H is placed near O(2). The water chains are then built up from the units $H_3O^+(2)$, $H_2O(1)$ and $H_2O(3)$. One would here expect about equal distances O(2)···O(1) and O(2)···O(3). However, the actual distances are 2·65 and 2·43 Å, respectively. It seems very improbable that an ion $H_3O^+(2)$ would bind two similar water molecules with such different strengths. This alternative is accordingly very unlikely.

Case II. H is placed near O(3). This is completely analogous to case I and this alternative is ruled out for similar reasons.

Case III. H is placed near the middle of the bond O(2)···O(3). The water chains are then built up from $H_5O_2^+$ ions $(H_2O\cdots H\cdots OH_2)^+$ and $H_2O(1)$ molecules.

Let us consider case III in more detail. The situation is here very much like the situation in the dihydrate (Lundgren & Olovsson, 1967) with two water molecules coupled together by a very short hydrogen bond. Ideally, both ends of $H_5O_2^+$ should have about the same distances to its neighbours. The distance O(2)···O(1) (2·65 Å) is shorter than O(3)···O(1) (2·75 Å), but the

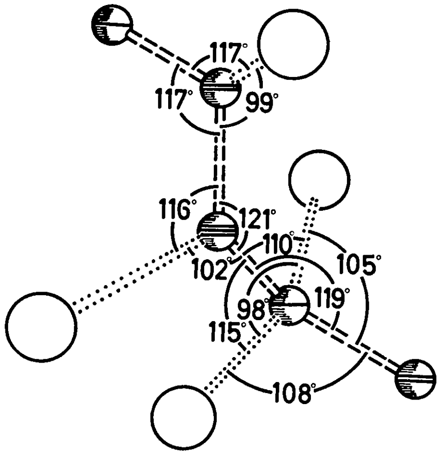

Fig. 5. Angles at the water molecules. For notation see Fig. 2.

difference is much smaller here than the difference in bond lengths around the hypothetical $H_3O^+(2)$ ion (case I). This might indicate that the positive charge of $H_5O_2^+$ is not quite uniformly distributed over the ion, but somewhat displaced towards the O(2) end. Furthermore, the distance O(2)···Cl (3·01 Å) is somewhat shorter than O(3)···Cl (3·05 Å) which indicates the same conclusion.

The water molecules $H_2O(2)$ and $H_2O(3)$ have both a pyramidal bonding arrangement (Fig. 5). The situation is accordingly not exactly the same as in $HCl.2H_2O$, where the bonding arrangement around one end of the $H_5O_2^+$ ion was almost planar and pyramidal around the other.

The bonding situation in and around the water chain thus demonstrates quite clearly that case III applies and that the structure should be described as built up from Cl^- and $H_5O_2^+$ ions and H_2O molecules.

Support for the above assignment of hydrogen to the bonds was obtained from the difference synthesis where peaks could be found corresponding to all hydrogen atoms except for those between O(1)···O(2) and O(2)···O(3).

Fig. 4 shows the bonding situation around the water chain. The hydrogen atoms have been assigned to the oxygen atoms according to the above discussion. In the Figure the hydrogens are schematically placed on the connecting lines.

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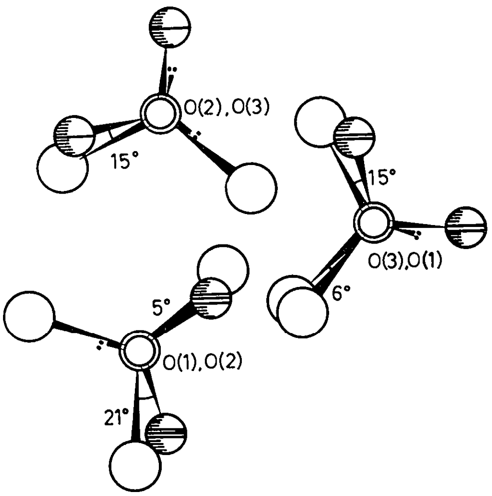

Fig. 6. Dihedral angles in $HCl.3H_2O$. The lone pairs are placed on the bisector of the angle between the bonds from the atom. For notation see Fig. 2.

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