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Hydrogen Bond Studies. XV.* The Crystal Structure of Hydrogen Chloride Dihydrate

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The crystal structure of hydrogen chloride dihydrate, $HCl.2H_2O$, has been determined from three-dimensional single-crystal X-ray data obtained at −187°C. Crystals of this compound are monoclinic, space group $P2_1/c$, with four formula units in a cell with the dimensions: $a=3{\cdot}991$, $b=12{\cdot}055$, $c=6{\cdot}698$ Å, $\beta=100{\cdot}58°$. The structure contains puckered layers of Cl^- ions connected by hydrogen bonds from the water molecules (3·04, 3·06, 3·09 and 3·10 Å). The water molecules are held together in pairs by a very short hydrogen bond (2·41 Å), forming $H_5O_2^+$ ions. The formula should accordingly be written as $H_5O_2^+Cl^-$.

Introduction

The melting point diagram of the system hydrogen chloride–water indicates three intermediate compounds, namely, the mono-, di-, and tri-hydrates. The melting points of these have been reported as: $HCl.H_2O$: −15·4°C (Rupert, 1909); $HCl.2H_2O$: −17·4°C (Pickering, 1893) and −17·7°C (Roozeboom, 1883); $HCl.3H_2O$: −24·9°C (Pickering, 1893). The crystal structure of hydrogen chloride monohydrate has been determined earlier by Yoon & Carpenter (1959), and was found to consist of $H_3O^+Cl^-$. The oxonium ion has also been found in $HClO_4.H_2O$ (Lee & Carpenter, 1959; Nordman, 1962).

The present investigation of hydrogen chloride dihydrate was undertaken to study the hydration of the proton in a crystal containing more water than necessary to form an H_3O^+ ion and to investigate the hydrogen bonding pattern of the structure. The structure determination is based on single-crystal X-ray diffraction data recorded at −187°C.

Experimental

The vapour pressure of the dihydrate is very high above its melting point [~25 atm. at −15·6°C, Roozeboom (1883)], and capillaries containing the dihydrate explode a few degrees above this temperature. The samples therefore had to be transferred in solid form to the X-ray camera. They were prepared directly in the capillaries in the following manner: Commercial hydrogen chloride from a gas container was led into a thin-walled glass capillary containing concentrated hydrochloric acid kept at −20 to −22°C. Impurities in the gas were removed by bubbling through liquid mercury. After ½–2 hr crystals were formed in the capillary. The crystals were allowed to melt, and the solution was thoroughly stirred. More hydrogen chloride gas was bubbled through the solution and crystals were again formed. Crystals were melted and reformed until a homogeneous crystal mass was obtained in the capillary. During careful cooling with liquid nitrogen the capillary was melted off to an appropriate size and put into the camera (a modified Weissenberg camera, as described by Olovsson, 1960). Many attempts were made before a capillary could be successfully fixed in the camera without exploding. A single crystal was then grown in the usual way at a temperature of about −20°C.

A cylindrical crystal with a diameter of 0·20 mm and a length of 0·6 mm was used when the intensity data were collected. The crystal was rotated about the *a* axis. The angle between this axis and the cylinder axis was about 10°. Equi-inclination Weissenberg photographs for the four layers $0 \le h \le 3$ were recorded at −187°C by the multiple-film technique (five films) with Cu $K\alpha$ radiation. 577 independent reflexions were recorded, corresponding to about 80% of the reflexions within the copper reflexion sphere. 56 of the recorded reflexions were too weak to be measured. The intensities were estimated visually by comparison with an intensity scale. The intensity range was 1 to 2000. The data were corrected for the Lorentz and polarization effects. No correction for absorption was performed. The linear absorption coefficient for Cu $K\alpha$ radiation is $\mu=86{\cdot}0$ cm^{-1}, $\mu R=0{\cdot}86$.

In addition photographs were recorded at −40°C, but no indication of structural differences could be detected when comparing data recorded at −40°C and −187°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 β angle was determined according to the method of angular lag (Buerger, 1962). The dimensions b and $c \sin \beta$ were fitted to the measured θ values by the method of least squares. The following values of the parameters and their estimated standard deviations were obtained (temperature −186°C):

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* Part XIV, p. 956 of this issue.

$a=3{\cdot}991\pm0{\cdot}005$, $b=12{\cdot}055\pm0{\cdot}001$, $c=6{\cdot}698\pm0{\cdot}001$ Å, $\beta=100{\cdot}58\pm0{\cdot}02°$

($a=4{\cdot}913$, $c=5{\cdot}4045$ Å for α quartz at 22°C; λ(Cu $K\alpha_1$) = 1·54051 Å, λ(Cu $K\alpha_2$) = 1·54433 Å).

The density calculated on the basis of a unit cell containing four formula units of $HCl.2H_2O$ is 1·51 g.cm^{-3}. The density given by Roozeboom (1883) is 1·46 g.cm^{-3} at −25°C.

Space group: $P2_1/c$, (no. 14, *International Tables for X-ray Crystallography*, 1952).

Determination of the atomic coordinates

The structure was determined from a three-dimensional Patterson synthesis. The position of the chlorine atom was derived from the Harker vectors and the positions of the oxygen atoms were readily found from the Cl–O vectors. A three-dimensional Fourier synthesis calculated on the basis of the atomic positions derived from the Patterson synthesis showed no peaks of considerable height other than those expected. For the Fourier synthesis a revised version of the Fourier program by A. Zalkin, Berkeley, Calif., U.S.A. was used.

The coordinates and individual isotropic temperature factors for the chlorine and oxygen atoms and the scale factors were refined in a series of least-squares calculations. For these calculations a revised version of the program LALS (A. Zalkin) was used. The original program, called UCLALS1, was written by P.K. Gantzel, R.A. Sparks & K.N. Trueblood, University of California, Los Angeles, Calif., U.S.A. This is a full-matrix program that minimizes 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 of the parameters a and c were 5·0 and 0·02, respectively. Reflexions too weak to be measured were given zero weight in all calculations.

After about five cycles of least-squares refinement the discrepancy index $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ was 0·122 (not including unobserved reflexions). A three-dimensional difference synthesis was calculated at this stage to determine the positions of the hydrogen atoms. Peaks could be found for all the hydrogen atoms at the expected locations. The assignment of the hydrogen atoms to the O···Cl and O···O bonds is discussed below. A few more cycles with the hydrogen atoms included, but not refined, lowered the R value to 0·117. The hydrogen atoms were given an isotropic temperature factor of 3 Å^2, which is about twice as large as the temperature factor of oxygen. The difference synthesis mentioned above showed characteristic dumbbell shaped maxima around the oxygen atoms, indicating anisotropy. Some cycles of least-squares calculations were run to refine the atomic coordinates and anisotropic temperature factors for the chlorine and oxygen atoms together with 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 refined was 28. In the third cycle the shifts of the parameters were less than one tenth of their estimated standard deviations. The R value was 0·097 (0·103 including unobserved reflexions).

Atomic scattering factors for Cl$^-$, neutral O and H were taken from *International Tables for X-ray Crystallography* (1962, p. 202). All calculations were run on a CD 3600 computer.

Atomic coordinates and thermal parameters from the last cycle of refinement together with their standard deviations are listed in Tables 1 and 2. Distances and angles calculated on the basis of these values are found in Table 3. Distances corrected for temperature effects, assuming riding motion or independent motion of the atoms are also found in Table 3. In the following discussion, however, the distances uncorrected for anisotropic thermal motion are used, since no experimental scaling and no absorption correction has been made. Thus part of the anisotropy probably has been accounted for by refining individual scale factors for the separate layers. The program ORFFE (Busing, Martin & Levy, 1964) was used for the distance and angle calculation.

The observed and calculated structure factors are listed in Table 4.

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

	x	y	z
Cl	182 (4)	3277 (1)	1482 (2)
O(1)	5533 (13)	1279 (4)	244 (7)
O(2)	2949 (18)	572 (4)	2974 (8)
H(1)	4300	930	1600
H(2)	3800	1600	−750
H(3)	7300	1900	750
H(4)	1400	−100	2800
H(5)	2200	1100	4100

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

The form of the temperature factor is:

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

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

	Cl	O(1)	O(2)
β_{11}	135 (19)	186 (42)	762 (62)
β_{22}	14 (1)	21 (3)	16 (3)
β_{33}	42 (4)	67 (11)	88 (12)
β_{12}	3 (4)	−23 (16)	−72 (21)
β_{13}	115 (11)	104 (33)	431 (43)
β_{23}	0 (2)	9 (9)	−21 (10)
R_1	53 (10)	88 (14)	74 (12)
R_2	103 (5)	129 (9)	102 (11)
R_3	121 (6)	135 (10)	258 (9)

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

Distances corrected for thermal motion assuming (1) riding and (2) independent motion are given within square brackets. The standard deviations of the distances are × 10³.

Bond	Distance (Å)
Cl ····O(1)	3·036 [3·038, 3·043] (5)
···O(1)	3·060 [3·063, 3·068] (5)
···O(2)	3·085 [3·093, 3·099] (5)
···O(2)	3·101 [3·110, 3·117] (6)
O(1)···O(2)	2·414 [2·422, 2·437] (7)

Bonds	Angle (°)
O(1)···Cl ····O(1)	131·5 (0·1)
···O(2)	120·0 (0·2)
···O(2)	115·4 (0·1)

Table 3 (*cont.*)

Bonds	Angle (°)
O(1)···Cl ····O(2)	89·0 (0·2)
···O(2)	104·8 (0·2)
O(2)···Cl ····O(2)	84·0 (0·2)
Cl ····O(1)···Cl	112·6 (0·1)
···O(2)	113·2 (0·2)
Cl ····O(1)···O(2)	111·0 (0·2)
Cl ····O(2)···Cl	95·9 (0·2)
···O(1)	130·1 (0·2)
Cl ····O(2)···O(1)	132·7 (0·2)

Description and discussion of the structure

General

The structure is shown in Figs. 1–3. The chlorine atoms form infinite puckered layers parallel to the *xz*

Table 4. *Observed and calculated structure factors*

Reflexions marked * were too weak to be measured. The F_o values for these are given as $F_{\min}$ for the reflexion in question.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0	0	-8	6.3	6.3
0	1	-8	19.3	20.9
0	2	-8	6.8	6.8
0	3	-8	4.2	3.8
0	4	-8	4.9	5.0
0	5	-8	9.7	13.9
0	1	-7	3.3	3.6
0	2	-7	4.7	2.7
0	3	-7	23.2	21.8
0	4	-7	8.2	6.9
0	5	-7	18.1	16.5
0	6	-7	4.7	3.4
0	7	-7	7.2	7.0
0	0	-6	28.1	26.3
0	1	-6	13.6	12.7
0	2	-6	11.8	9.7
0	3	-6	2.4*	0.4
0	4	-6	12.9	11.0
0	5	-6	2.4*	1.4
0	6	-6	19.6	17.2
0	7	-6	21.9	19.8
0	8	-6	10.5	9.4
0	9	-6	8.5	8.2
0	10	-6	4.4	4.1
0	11	-6	7.8	12.3
0	1	-5	5.0	3.6
0	2	-5	32.4	31.8
0	3	-5	12.5	11.4
0	4	-5	27.7	25.9
0	5	-5	2.3*	2.1
0	6	-5	2.4*	0.2
0	7	-5	12.3	10.3
0	8	-5	18.5	16.9
0	9	-5	8.9	7.9
0	10	-5	19.5	17.9
0	11	-5	1.8*	1.5
0	12	-5	6.2	6.3
0	0	-4	15.0	13.1
0	1	-4	7.5	7.1
0	2	-4	19.8	19.5
0	3	-4	17.0	15.9
0	4	-4	1.8*	0.9
0	5	-4	18.1	17.8
0	6	-4	25.1	24.9
0	7	-4	14.6	12.2
0	8	-4	20.0	19.4
0	9	-4	9.1	7.2
0	10	-4	2.4*	0.3
0	11	-4	6.4	5.1
0	12	-4	20.6	20.2
0	13	-4	16.2	17.7
0	1	-3	41.2	44.7
0	2	-3	10.6	9.9
0	3	-3	38.6	41.3
0	4	-3	1.6*	1.9
0	5	-3	12.8	11.6
0	6	-3	15.0	13.9
0	7	-3	10.7	9.1
0	8	-3	9.1	7.5
0	9	-3	26.6	26.1
0	10	-3	15.5	14.3
0	11	-3	10.3	8.3
0	12	-3	2.3*	0.2
0	13	-3	1.9*	1.8
0	14	-3	2.0	2.5
0	0	-2	12.6	11.9
0	1	-2	42.2	46.7
0	2	-2	10.6	10.2
0	3	-2	12.5	11.5
0	4	-2	18.6	17.6
0	5	-2	38.3	41.4
0	6	-2	1.6*	1.0
0	7	-2	22.7	23.6
0	8	-2	24.2	26.0
0	9	-2	7.5	6.0
0	10	-2	8.1	6.3
0	11	-2	12.0	10.1
0	12	-2	12.8	10.0
0	13	-2	22.8	22.1
0	14	-2	5.0	4.4
0	15	-2	6.4	7.0
0	1	-1	4.9	5.1
0	2	-1	15.4	16.3
0	3	-1	6.3	6.7
0	4	-1	46.9	59.1
0	5	-1	26.6	26.7
0	6	-1	5.6	3.7
0	7	-1	10.1	9.1
0	8	-1	16.3	15.5
0	9	-1	24.0	25.4
0	10	-1	19.7	18.5
0	11	-1	17.9	16.4
0	12	-1	16.2	14.4
0	13	-1	4.6	3.6
0	14	-1	14.4	14.5
0	15	-1	11.7	12.8
0	2	0	11.9	14.0
0	4	0	35.6	43.0
0	6	0	28.3	32.2
0	8	0	22.0	23.5
0	10	0	15.1	14.6
0	12	0	14.8	12.1
0	14	0	14.1	14.3
1	0	-8	14.2	12.7
1	1	-8	15.5	14.8
1	2	-8	3.4	2.3
1	3	-8	2.3	2.2
1	4	-8	1.5*	0.2
1	5	-8	7.7	8.0
1	1	-7	16.0	13.3
1	2	-7	14.5	11.6
1	3	-7	30.3	28.1
1	4	-7	4.4	3.4
1	5	-7	14.4	11.7
1	6	-7	1.9*	1.8
1	7	-7	11.2	9.7
1	8	-7	4.2	3.7
1	9	-7	11.5	15.1
1	0	-6	4.6	2.6
1	1	-6	22.9	20.8
1	2	-6	20.0	17.4
1	3	-6	2.4*	0.0
1	4	-6	2.4*	1.5
1	5	-6	20.9	17.9
1	6	-6	22.0	20.4
1	7	-6	17.0	14.6
1	8	-6	12.4	10.0
1	9	-6	2.7	2.0
1	10	-6	4.5	3.2
1	11	-6	7.0	7.0
1	1	-5	2.0*	1.0
1	2	-5	27.8	27.5
1	3	-5	5.0	3.7
1	4	-5	19.0	16.6
1	5	-5	8.9	7.4
1	6	-5	16.4	16.0
1	7	-5	8.9	6.7
1	8	-5	20.0	18.3
1	9	-5	12.9	9.9
1	10	-5	28.9	26.7
1	11	-5	6.3	5.4
1	12	-5	3.4	4.0
1	0	-4	35.9	34.8
1	1	-4	21.1	19.6
1	2	-4	29.1	27.7
1	3	-4	8.4	7.2
1	4	-4	26.0	25.1
1	5	-4	7.1	5.9
1	6	-4	33.0	31.6
1	7	-4	16.4	14.9
1	8	-4	3.3	2.7
1	9	-4	3.4	2.2
1	10	-4	2.4*	0.6
1	11	-4	10.3	8.5
1	12	-4	15.3	14.0
1	13	-4	4.6	4.1
1	1	-3	12.1	8.9
1	2	-3	25.3	23.1
1	3	-3	28.5	28.2
1	4	-3	8.2	6.8
1	5	-3	30.0	29.4
1	6	-3	8.3	7.5
1	7	-3	7.2	6.1
1	8	-3	11.5	10.6
1	9	-3	22.2	20.0
1	10	-3	14.2	12.4
1	11	-3	27.0	26.5
1	12	-3	2.2*	0.0
1	13	-3	5.2	4.2
1	14	-3	1.3*	1.1
1	0	-2	43.3	45.0
1	1	-2	48.8	51.8
1	2	-2	1.1*	1.0
1	3	-2	13.3	10.7
1	4	-3	21.8	20.5
1	5	-2	15.9	14.1
1	6	-2	7.5	6.6
1	7	-2	35.4	38.1
1	8	-2	5.5	3.6
1	9	-2	10.5	9.4
1	10	-2	5.6	4.5
1	11	-2	21.4	19.8
1	12	-2	3.3	3.2
1	13	-2	16.5	15.0
1	14	-2	1.6*	1.1
1	1	-1	12.9	12.3
1	2	-1	25.1	27.7
1	3	-1	63.1	64.9
1	4	-1	26.8	29.2
1	5	-1	12.5	11.3
1	6	-1	9.6	8.8
1	7	-1	27.4	27.9
1	8	-1	16.0	16.3
1	9	-1	4.1	3.1
1	10	-1	21.3	20.2
1	11	-1	14.1	12.7
1	12	-1	8.9	7.2
1	13	-1	2.2*	1.6
1	14	-1	9.4	8.7
1	15	-1	9.1	10.0
1	0	0	22.1	23.7
1	1	0	11.1	9.1
1	2	0	33.4	33.2
1	3	0	16.8	15.9
1	4	0	5.1	3.6
1	5	0	18.0	16.2
1	6	0	33.4	36.4
1	7	0	13.2	12.4
1	8	0	28.0	29.8
1	9	0	7.1	4.7
1	10	0	2.2*	0.5
1	11	0	11.1	8.9
1	12	0	29.1	28.0
1	13	0	2.2*	1.7
1	14	0	18.2	18.0
1	15	0	3.7	3.6
1	1	1	38.1	48.7
1	2	1	47.7	55.8
1	3	1	25.5	29.0
1	4	1	23.8	24.2
1	5	1	2.0	1.4
1	6	1	7.3	6.5
1	7	1	6.4	5.2
1	8	1	19.2	19.8
1	9	1	15.4	15.4
1	10	1	20.5	19.5
1	11	1	3.4	0.6
1	12	1	5.8	4.8
1	13	1	2.1*	1.7
1	14	1	4.2	3.8
1	15	1	1.0*	1.7
1	0	2	18.3	17.6
1	1	2	19.5	22.8
1	2	2	19.5	19.0
1	3	2	19.5	19.9
1	4	2	19.3	19.4
1	5	2	23.3	25.8
1	6	2	18.5	18.2
1	7	2	25.6	27.9
1	8	2	7.1	6.7
1	9	2	10.9	10.0
1	10	2	2.4*	2.0
1	11	2	12.7	11.9
1	12	2	6.4	5.3
1	13	2	22.7	24.4
1	14	2	6.6	5.9
1	1	3	14.6	14.8
1	2	3	9.6	9.5
1	3	3	21.4	23.7
1	4	3	16.0	17.3
1	5	3	20.5	24.0
1	6	3	12.6	13.2
1	7	3	2.1*	1.0
1	8	3	3.2	2.6
1	9	3	26.7	28.5
1	10	3	2.4*	1.7
1	11	3	20.1	19.4
1	12	3	7.0	5.3
1	13	3	4.6	3.7
1	0	4	32.0	38.0
1	1	4	21.0	23.4
1	2	4	5.8	5.7
1	3	4	3.8	3.3
1	4	4	10.9	12.1
1	5	4	18.4	19.6
1	6	4	14.8	16.2
1	7	4	11.4	11.7
1	8	4	14.3	14.6
1	9	4	2.4*	0.8
1	10	4	8.4	7.9
1	11	4	4.9	4.6
1	12	4	8.6	8.6
1	13	4	6.7	8.7
1	2	5	9.4	10.1
1	3	5	5.5	4.6
1	4	5	24.0	28.4
1	5	5	2.4*	1.6
1	6	5	7.5	6.7
1	7	5	3.4	3.2
1	8	5	13.1	12.8
1	9	5	2.1*	1.4
1	10	5	19.3	21.7
1	4	6	5.8	4.5
1	5	6	13.6	15.5
1	6	6	13.5	14.9
1	7	6	6.3	5.9
1	8	6	14.3	16.4
2	0	-8	17.0	19.7
2	1	-8	13.9	16.1
2	2	-8	6.7	6.3
2	3	-8	5.2	5.5
2	4	-8	7.0	8.9
2	1	-7	14.3	14.5
2	2	-7	3.1	2.7
2	3	-7	16.1	16.7
2	4	-7	2.1*	0.2
2	5	-7	16.0	17.1
2	6	-7	2.5	2.0
2	7	-7	2.2	2.7
2	8	-7	1.6	0.6
2	0	-6	24.1	28.0
2	1	-6	15.2	15.2
2	2	-6	8.8	7.5
2	3	-6	11.1	10.4
2	4	-6	13.9	12.9
2	5	-6	21.6	21.3
2	6	-6	14.6	13.8
2	7	-6	16.2	15.3
2	8	-6	6.7	6.6
2	9	-6	5.8	6.2
2	10	-6	3.9	4.5
2	1	-5	18.7	19.0
2	2	-5	19.6	20.1
2	3	-5	13.0	11.7
2	4	-5	27.8	31.5
2	5	-5	2.3*	1.8
2	6	-5	3.3	0.5
2	7	-5	3.4	2.6
2	8	-5	15.9	15.5
2	9	-5	8.6	8.0
2	10	-5	19.1	19.2
2	11	-5	2.2	2.6
2	0	-4	23.1	27.3
2	1	-4	13.6	13.5
2	2	-4	10.0	9.3
2	3	-4	6.4	5.2
2	4	-4	1.9*	1.3
2	5	-4	2.1*	2.5
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2	10	-4	8.9	7.5
2	11	-4	8.8	6.8
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2	10	-3	10.6	9.0
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2	12	-3	10.8	9.8
2	13	-3	2.9	1.9
2	0	-2	24.5	27.0
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2	3	-2	6.0	6.3
2	4	-3	10.7	10.3
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2	7	-2	29.2	29.7
2	8	-2	2.2*	1.5
2	9	-2	12.9	11.0
2	10	-2	9.5	7.8
2	11	-2	17.5	16.5
2	12	-2	9.3	8.6
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2	14	-2	3.8	3.7
2	1	-1	6.0	5.9
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2	5	-1	24.8	24.0
2	6	-1	8.9	7.1
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2	13	0	5.1	4.1
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2	1	1	11.7	8.7
2	2	1	22.3	22.0
2	3	1	11.8	10.3
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2	6	1	17.6	17.3
2	7	1	2.8	2.1
2	8	1	16.9	16.4
2	9	1	9.3	7.9
2	10	1	27.4	28.2
2	11	1	14.3	13.4
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2	5	3	16.0	15.5
2	6	3	9.0	8.0
2	7	3	13.6	12.9
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2	9	3	14.6	14.6
2	10	3	6.8	6.4
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2	8	4	12.0	11.4
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2	10	4	1.8*	1.0
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3	8	-6	13.4	17.5
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3	9	-4	3.8	3.1
3	10	-4	7.0	6.0
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3	1	-3	14.9	11.9
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3	10	-2	2.3	2.3
3	11	-2	8.0	7.5
3	12	-2	5.2	5.6
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3	4	-1	19.7	17.8
3	5	-1	11.2	9.4
3	6	-1	7.3	6.5
3	7	-1	8.2	6.3
3	8	-1	8.6	7.3
3	9	-1	18.2	19.7
3	10	-1	15.1	16.0
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3	12	-1	5.6	6.4
3	0	0	29.8	26.2
3	1	0	2.0	1.2
3	2	0	14.5	11.7
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3	6	1	6.7	5.5
3	7	1	7.4	5.6
3	8	1	14.8	14.2
3	9	1	3.4	3.3
3	10	1	12.4	13.0
3	11	1	3.2	3.0
3	12	1	5.2	8.2
3	0	2	20.4	21.2
3	1	2	13.4	12.4
3	2	2	6.1	5.5
3	3	2	7.7	6.8
3	4	2	8.4	7.0
3	5	2	10.2	8.7
3	6	2	11.4	11.3
3	7	2	19.2	20.3
3	8	2	10.0	10.1
3	9	2	9.7	9.8
3	10	2	4.7	4.6
3	11	2	9.6	11.7
3	1	3	11.3	10.8
3	2	3	9.9	9.2
3	3	3	20.4	21.1
3	4	3	2.5	2.4
3	5	3	13.9	14.0
3	6	3	4.9	3.6
3	7	3	6.2	4.8
3	8	3	3.0	1.2
3	9	3	14.9	17.7
3	10	3	3.1	3.2
3	4	4	5.3	4.1
3	5	4	14.6	16.6
3	6	4	12.8	12.0
3	7	4	10.3	10.1
3	8	4	6.1	6.0

plane. Within these layers the Cl···Cl distances are 3·84, 3·84, 3·99 and 3·99 Å. The layers are puckered along the *c* axis and the angle Cl–Cl–Cl in this direction is 122°. The shortest distance between chlorine atoms belonging to different layers is 4·60 Å. The *y* coordinates of the middle of the layers are 0·25 and 0·75, respectively. The layer at $y=0·75$ is displaced in relation to the layer at $y=0·25$ in the *a* and *c* directions as is shown in Figs. 1 and 2.

The water molecules are bonded to each other in pairs by a very short bond (2·41 Å). These pairs connect the chlorine layers by hydrogen bonds; one end, O(1), is bonded to two chlorine atoms belonging to the same layer (bond lengths 3·04 and 3·06 Å) and the other end, O(2), is connected to chlorine atoms in different layers (bond lengths 3·09 and 3·10 Å). Each oxygen atom is accordingly surrounded by three neighbours. O(1) is surrounded by three atoms which are pyramidally arranged. The distance from O(1) to the plane defined by the three neighbouring atoms is 0·80 Å. The arrangement around O(2) is considerably flatter, and the corresponding distance is only 0·18 Å. The bond distances and angles around the oxygen atoms are shown in Fig. 5.

The O···Cl distances found in this structure are all somewhat longer than the O–H···Cl distance found in oxonium chloride (2·95 Å) (Yoon & Carpenter, 1959).

The hydrogen positions

The difference Fourier synthesis calculated before the anisotropic refinement was used to locate the hydrogen atoms.

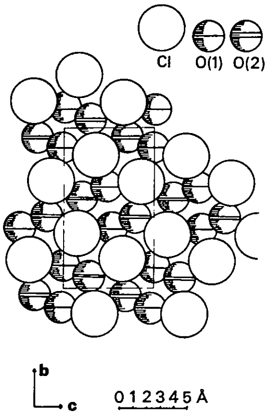

Fig. 2. The structure viewed along the *a* axis. The *x* coordinates of the atoms are: Cl 0·02, −0·02; O(1) 0·45, 0·55; O(2) 0·29, 0·71.

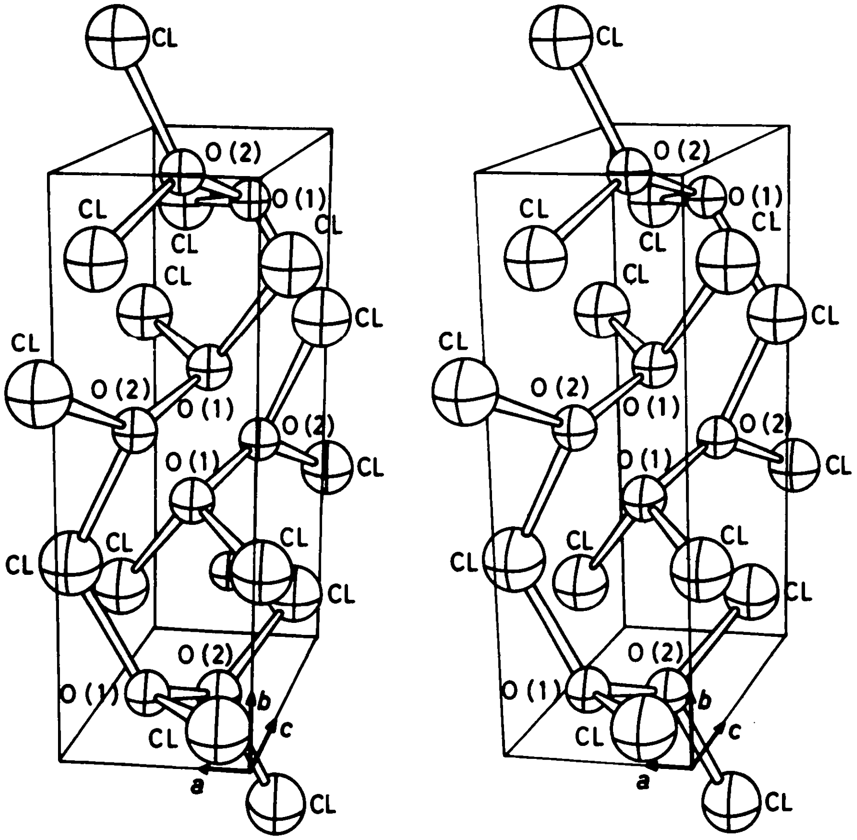

Fig. 1. A stereoscopic illustration of the structure showing the hydrogen bonding pattern. The figure has been drawn with use of the program ORTEP (Johnson, 1965).

The distances O···O (2·41 Å) and O···Cl (3·04, 3·06, 3·09 and 3·10 Å) indicate five hydrogen bonds. The other distances O···O and O···Cl are longer than 3·11 and 3·40 Å, respectively. All the hydrogen atoms available should thus be involved in hydrogen bonding. The water molecules then have hydrogen bonds in three directions.

A very well resolved peak appeared on the short O···O bond. The maximum of the peak was situated 1·19 Å from O(1) and 1·23 Å from O(2) and very near the connecting line. These distances and the hydrogen positions discussed below are of course not very precise. The peak was slightly elongated in the direction of the bond.

The assignment of hydrogen atoms to the O···Cl bonds could be uniquely determined from the difference maps in which fairly well resolved peaks appeared on, or somewhat off (<0·30 Å) the connecting lines. The O–H distances as obtained from the Fourier maps range between 0·95 and 1·07 Å. The angles H–O(1)–H are 107, 109 and 111°, thus somewhat smaller than the angles Cl–O(1)–Cl and Cl–O(1)–O(2). The angles H–O(2)–H are 108, 122 and 123° (*cf.* Table 3). In Fig. 4 the hydrogen positions as obtained from the difference maps are shown.

As mentioned earlier, hydrogen atom H(1) (Fig. 4) seems to be situated very near the middle of the bond O(1)···O(2). From the present data it cannot of course be decided whether the bond is a symmetrical bond with a single or symmetrical doubly distributed peak or an asymmetric bond. However, as the bond is extremely short, the conditions for a symmetric single maximum distribution might be fulfilled. If this is the case, the proton between the two water molecules belongs to each of them to the same extent.

As shown above, the bonding situation around O(2) is flatter than that around O(1). The atoms Cl, Cl, O(2) and O(1) are almost coplanar. This planar arrangement is still valid for O(1), O(2), H(1), H(4) and H(5). However, the positions of the hydrogen atoms are not accurately determined from the present data. The bonds O(2)···Cl could, for example, be more bent, giving a pyramidal arrangement around O(2). In $HClO_4.2H_2O$ (Olovsson, 1967) there is a crystallographic centre of symmetry in the middle of the short hydrogen bond. In that case the arrangement around each water oxygen is equal by symmetry (pyramidal arrangement) and the situation is thus not quite comparable to this case.

The X-ray study of $HCl.H_2O$ (Yoon & Carpenter, 1959) has shown that the monohydrate consists of oxonium chloride, $H_3O^+Cl^-$. Similarly the dihydrate should be written as $H_5O_2^+Cl^-$.

The authors are indebted to Mr H. Karlsson for his skilful assistance in the preparation of crystals and in the preliminary X-ray work. The authors also wish to thank the people mentioned in the text for the use of their crystallographic programs.

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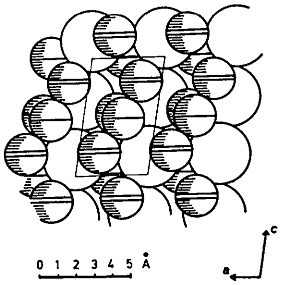

Fig. 3. The structure viewed along the *b* axis. Only the chlorine layer at $y=0·25$ is shown. For notation see Fig. 2.

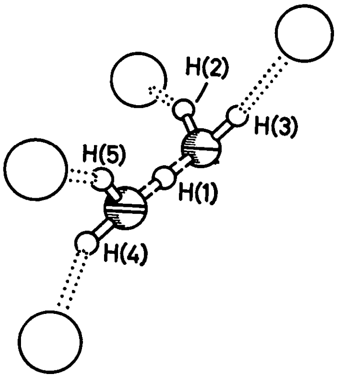

Fig. 4. The bonding situation around the $H_5O_2^+$ ion. The positions of the hydrogen atoms are taken from the difference synthesis. For notation see Fig. 2.

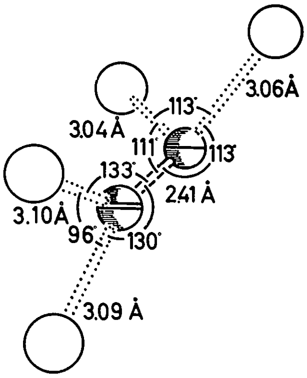

Fig. 5. Bond distances and angles around the oxygen atoms. For notation see Fig. 2.

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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.