viewed along $[012]_r$. It is seen that it comprises two interpenetrating sets of $\langle 111\rangle$ strings of edge-linked octahedral face-shared dimers, the directions of both strings being different from that in the low-temperature $(121)_r$ precursor phase, Fig. 14(*a*). In transforming to the high-temperature phases, the integrity of the $[1\bar{1}1]_r$ strings is lost, but the $[10\bar{1}]_r$ strings of corner-linked face-shared octahedral pairs persist.

A high-resolution electron-imaging and diffraction study of the transformation mechanism has been carried out and will be reported elsewhere (Bursill & Grey, 1977). This study shows $(121)_r$ and $(\bar{1}2\bar{1})_r$ CS structures intersecting to form $(101)_r$ interfaces containing the $[10\bar{1}]_r$ strings common to both high- and low-temperature structures. These $[10\bar{1}]_r$ structural features (imaged edge-on in Figs. 3 and 4) provide the key to the structural relations and the reaction mechanism. It is interesting to note that the high-temperature structures may be derived mathematically as follows:

$$\text{I}\quad (020)_r = (121)_r + (\bar{1}2\bar{1})_r,$$

$$\text{II}\quad (0kl)_r = p(020)_r + q(011)_r.$$

The element $(011)_r$ represents the same anti-phase component required for swinging in the low-temperature structures.

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Hydrogen Bond Studies.

CXXIX.* An X-ray Determination of the Crystal Structure of Hydrogen Chloride Hexahydrate, $H_9O_4^+Cl^-.2H_2O$

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The structure of hydrogen chloride hexahydrate has been determined by X-ray diffraction at 87 K. The crystal is orthorhombic, space group *Pbcm*, $a = 6{\cdot}3302$ (1), $b = 6{\cdot}4528$ (1), $c = 17{\cdot}8979$ (3) Å, $Z = 4$. The structure contains $H_9O_4^+$ ions and water molecules hydrogen-bonded to each other and to Cl^- ions to form a layer structure. O–H···O hydrogen bonds within the $H_9O_4^+$ complex are 2·514 (1), 2·514 (1) and 2·540 (2) Å. Other O–H···O bonds are 2·753 (1) and 2·805 (1) Å.

Introduction

This report is part of a systematic study of the hydrated proton in solids in progress at this Institute. The study of the hexahydrate of hydrogen chloride is of special interest since its composition gives the possibility of the formation of an $H_{13}O_6^+$ ion.

The freezing-point diagram of the system hydrogen chloride/water (Pickering, 1893; Rupert, 1909) indicates the existence of the mono-, di- and trihydrates of HCl. The existence of the hexahydrate was later shown by Vuillard (1955). $HCl.6H_2O$ melts congruently at −70·0 °C.

The monohydrate (Yoon & Carpenter, 1959) was found to contain the oxonium ion, H_3O^+, whereas crystals of the di- and trihydrates both contain the

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* Part CXXVIII: Loehlin & Kvick (1978).

diaquahydrogen ion, $H_5O_2^+$ (Lundgren & Olovsson, 1967). In other crystalline hydrates of strong acids, the existence of the higher proton hydrates $H_7O_3^+$ and $H_9O_4^+$ has been confirmed (Lundgren, 1974; Lundgren & Olovsson, 1976). The crystal structure of only one compound has been reported in which a complex has been found where the number of water molecules exceeds that in $H_9O_4^+$: $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$-$H_{13}O_6^+Cl^-$ (Bell, Christoph, Fronczek & Marsh, 1975).

The present determination is based on single-crystal data obtained at 87 K.

Crystal data

Hydrogen chloride hexahydrate, $HCl.6H_2O$, FW 144·52, orthorhombic, $a = 6{\cdot}3302\,(1)$,* $b = 6{\cdot}4528\,(1)$, $c = 17{\cdot}8979\,(3)$ Å, $V = 733{\cdot}09$ Å^3, $Z = 4$, $D_x = 1{\cdot}313$ g cm^{-3} at 87 K, μ(Cu $K\alpha$) = 44·83 cm^{-1}, space group *Pbcm* (No. 57; *International Tables for X-ray Crystallography*, 1969).

Experimental

Single crystals were grown from hydrogen chloride/water solutions (molar ratio 1:6) sealed in thin-walled glass capillaries. The crystals grew preferentially with **b** along the axis of the capillaries. Collection of intensities and measurements of cell dimensions were performed at 87 K with a semi-automatic Stoe–Philips Weissenberg diffractometer (Cu $K\alpha$ radiation monochromatized with a graphite crystal) modified for low-temperature studies. The cell dimensions were determined by least-squares refinement from the 2θ values of 46 reflexions [λ(Cu $K\alpha_1$) = 1·54051 Å] from two different crystals mounted about [100] and [010]. The diffraction symmetry and systematic absences indicated the space groups $Pca2_1$ or *Pbcm*.

Intensities were recorded from two cylindrical crystals with diameters of 0·20 mm rotating about [100] (*A* data) and [010] (*B* data) respectively. The equi-inclination ω-scan mode with a variable scan range was used. Three test reflexions were monitored periodically within each layer. A 7% decrease in intensity was observed for the first three layers of the *B* data for which a correction was later applied. For the *B* data *hkl* and $hk\bar{l}$ reflexions were recorded in layers *h*0*l* to *h*6*l* giving 1450 reflexions. For the *A* data 409 reflexions were recorded in layers 0*kl* to 2*kl*.

Lorentz, polarization and absorption corrections were applied. The range of transmission factors was 0·384 to 0·520. A contribution to the variances arising from errors in the absorption correction was added according to the expression $\sigma^2 = \sigma_c^2 + \mu^2\bar{t}^2\{[\sigma^2(\mu)/\mu^2] + [\sigma^2(\bar{t})/\bar{t}^2]\}F^4$, where σ_c^2 is based on Poisson counting statistics, μ is the absorption coefficient and $\bar{t}$ is the mean path length of the X-ray beam through the crystal. The relative errors in μ and $\bar{t}$ were estimated to be 0·03 and 0·02 respectively.

Relative scale factors for the different layers were calculated from *A* and *B* data where $F^2 > 5\sigma(F^2)$. For polar space groups the interlayer scaling procedure requires that both crystals have the same polarity, *i.e.* if the space group is $Pca2_1$, care must be taken that *hkl* reflexions from one crystal are not compared with $hk\bar{l}$ reflexions from the other. It was observed that $F^2(hkl)$ and $F^2(hk\bar{l})$ differed systematically throughout the data sets. For $F^2 > 5\sigma$, the values of $F^2(hkl)$ were on average 1·3% smaller than those of $F^2(hk\bar{l})$ for the *A* data set. We think this discrepancy is largely due to a variation in the wall thickness of the glass capillary which could not be taken into account in the absorption correction. Anomalous-dispersion effects would be unlikely to affect the intensities in such a systematic way. The scaling procedure was therefore carried out neglecting anomalous-dispersion effects, *i.e.* a non-polar space group was assumed. As a consequence of the successful use of the centrosymmetric space group in the refinements this assumption was justified and reflexions *hkl* and $hk\bar{l}$ were later averaged. The 1450 reflexions of the *B* data set were averaged to give 742 independent reflexions. The agreement between equivalent reflexions was $R = 0{\cdot}010$. Only the *B* data set was used in the subsequent refinement.

Structure determination and refinement

The structure was solved in the noncentrosymmetric space group $Pca2_1$ by Patterson methods. The positions of the non-hydrogen atoms derived from the Patterson synthesis and subsequent Fourier syntheses were also consistent with the centrosymmetric space group *Pbcm*. The structure was later successfully refined in *Pbcm* by full-matrix least-squares techniques minimizing the function $\sum w(F_o^2 - F_c^2)$, where $w^{-1} = \sigma^2(F^2)$. After refinement with anisotropic thermal parameters, the H atom positions were found in a difference synthesis calculated from data with $\sin\theta/\lambda < 0{\cdot}45$ Å^{-1}.

In the final cycles 64 parameters were allowed to vary. These included one overall scale factor, one isotropic extinction parameter, coordinates for all atoms, anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for the H atoms. All parameter shifts were $<0{\cdot}1\sigma$ in the last cycle. The final $R(F^2) = \sum(F_o^2 - F_c^2)/\sum F_o^2 = 0{\cdot}033$, $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2} = 0{\cdot}058$, and $R(F) = 0{\cdot}020$. The refined value of the isotropic extinction parameter g (Coppens & Hamilton, 1970) was 1204 (191). The e.s.d. of an observation of unit weight was $s = [\sum w(F_o^2 - F_c^2)^2/(m - n)]^{1/2} = 1{\cdot}706$, where m is the number of observations and n the

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* E.s.d.'s in the least significant digits are given in parentheses.

number of parameters varied. A δR plot was obtained by plotting $(F_o^2 - F_c^2)/\sigma(F_o^2)$ for all structure factors from the final cycle of refinement *vs* the corresponding values expected for a normal distribution (0,1) (Abrahams & Keve, 1971) (Fig. 1). We believe that the non-linear appearance of the δR plot is partly due to the systematic differences between $F^2(hkl)$ and $F^2(hk\bar{l})$ mentioned above.

Scattering factors for Cl^- and O were from Hanson, Herman, Lea & Skillman (1964). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for H. An anomalous-dispersion correction was included for the non-hydrogen atoms (Cromer & Liberman, 1970). The programs used for all computations with IBM 370/155 and 1800 computers have been described by Lundgren (1976). The final atomic coordinates are given in Table 1.*

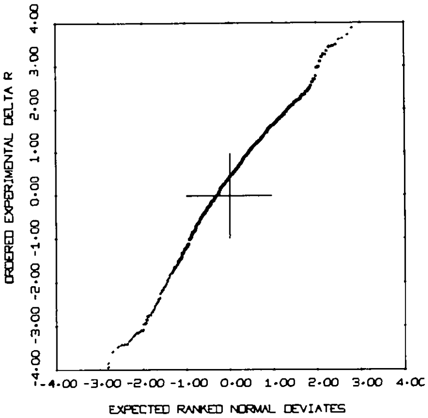

Fig. 1. Normal probability plot comparing observed $(F_o^2 - F_c^2)/\sigma(F_o^2)$ values *vs* the corresponding values expected for a normal distribution (0,1).

Description of the structure

A stereoscopic view of the structure is shown in Fig. 2. The hydrogen-bond distances are included in Fig. 3 and are listed with angles in Table 2. E.s.d.'s of interatomic distances and angles were obtained from the variance–covariance matrix from the final refinement. Effects of the e.s.d.'s of the cell parameters were included.

The crystal structure of $HCl.6H_2O$ is most adequately formulated as $H_9O_4^+Cl^-.2H_2O$. This ionic formulation is based on the positions of the H atoms and on the hydrogen-bond distances between the water molecules.

The $H_9O_4^+$ complex consists of an oxonium ion, $H_3O^+(2)$ (site symmetry *m*), hydrogen-bonded to three other water molecules at 2·514 (1), 2·514 (1) and 2·540 (2) Å in a pyramidal arrangement (Fig. 3). The average O···O(2)···O angle is 113·1°. The outer water molecules of $H_9O_4^+$, $H_2O(1)$ and $H_2O(3)$ also have a pyramidal bonding arrangement. The O—H···O bonds donated by these molecules (2·805 and 2·753 Å) are considerably longer than the bonds within $H_9O_4^+$. These complexes are hydrogen-bonded *via* $H_2O(4)$ molecules to form infinite chains of puckered six-membered rings of water molecules

Table 1. *Atomic coordinates* ($\times 10^5$, *for* H $\times 10^4$)

	x	*y*	*z*
Cl	23250 (5)	25000	0
O(1)	9802 (17)	6179 (18)	25000
O(2)	39791 (15)	32321 (18)	25000
O(3)	40558 (11)	52788 (13)	36951 (4)
O(4)	14616 (12)	86601 (13)	38891 (4)
H(11)	1008 (25)	−99 (26)	2149 (8)
H(21)	2836 (35)	2217 (34)	2500
H(22)	3941 (25)	3978 (27)	2094 (8)
H(31)	6201 (23)	−388 (26)	959 (8)
H(32)	6733 (27)	1290 (28)	1276 (8)
H(41)	9472 (31)	3226 (33)	858 (8)
H(42)	7993 (27)	4539 (31)	917 (9)

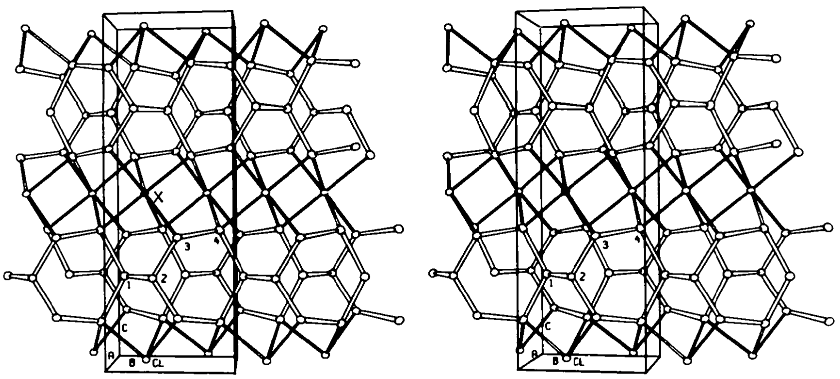

Fig. 2. A stereoscopic drawing of the crystal structure of $H_9O_4^+Cl^-.2H_2O$. The O atoms in the asymmetric unit have been labelled 1–4. The thermal ellipsoids are scaled to enclose 60% probability.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33520 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

The interatomic distances have not been corrected for thermal motion.

$X\cdots O\cdots Y$	$X\cdots O$	$O\cdots Y$	$\angle X\cdots O\cdots Y$	$H\cdots O\cdots H$	$H\cdots O$	$O\cdots H$	$\angle H\cdots O\cdots H$
O(1)···O(2)···O(3)	2·540 (2)	2·514 (1)	111·31 (3)	H(21)–O(2)–H(22)	0·98 (2)	0·87 (2)	110 (1)
O(3)···O(3)···O(3)	2·514 (1)		116·58 (6)	H(22)–O(2)–H(22)	0·87 (2)		112 (2)
O(4)···O(1)···O(4)	2·805 (1)	2·805 (1)	124·81 (5)	H(11)–O(1)–H(11)	0·78 (2)	0·78 (2)	107 (2)
O(4)···O(1)···O(2)		2·540 (2)	102·59 (3)	H(11)–O(1)···H(21)		1·56 (2)	112 (1)
O(4)···O(3)···O(2)	2·753 (1)	2·514 (1)	120·81 (4)	H(32)–O(3)···H(22)	0·82 (2)	1·64 (2)	116 (1)
O(4)···O(3)···Cl		3·142 (1)	98·66 (3)	H(32)–O(3)–H(31)		0·77 (2)	105 (1)
O(2)···O(3)···Cl	2·514 (1)		109·02 (4)	H(22)···O(3)–H(31)	1·64 (2)		113 (1)
O(1)···O(4)···O(3)	2·805 (1)	2·753 (1)	108·06 (3)	H(11)···O(4)–H(32)	2·04 (1)	1·93 (2)	105 (1)
O(1)···O(4)···Cl		3·203 (1)	125·04 (3)	H(11)···O(4)–H(41)		0·80 (2)	123 (1)
O(1)···O(4)···Cl		3·224 (1)	102·64 (3)	H(11)···O(4)–H(42)		0·75 (2)	101 (1)
O(3)···O(4)···Cl	2·753 (1)	3·203 (1)	109·84 (3)	H(32)···O(4)–H(41)	1·93 (2)	0·80 (2)	104 (2)
O(3)···O(4)···Cl		3·224 (1)	125·87 (3)	H(32)···O(4)–H(42)		0·75 (2)	113 (1)
Cl···O(4)···Cl	3·203 (1)		85·62 (2)	H(41)–O(4)–H(42)	0·80 (2)		110 (2)

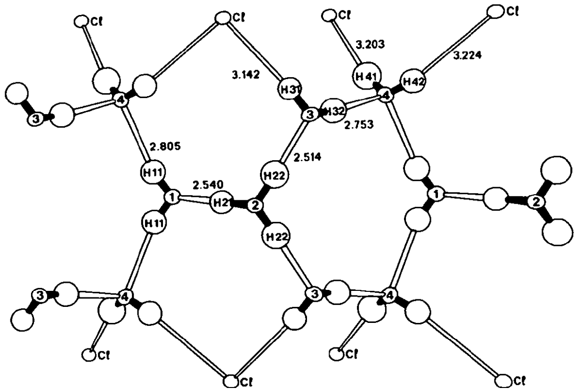

Fig. 3. The bonding situation around the $H_9O_4^+$ complex as obtained from the final refinement. The thermal ellipsoids are scaled to enclose 50% probability.

Table 3. *Angles* (°) *within the* $Cl(H_2O)_6^-$ *octahedron*

For notation see Fig. 4.

O(3)···Cl···O(3)′	139·18 (3)	O(4)···Cl···O(4)″	94·38 (2)
O(3)···Cl···O(4)	70·49 (2)	O(4)···Cl···O(4)‴	83·11 (3)
O(3)···Cl···O(4)′	92·25 (2)	O(4)′···Cl···O(4)″	160·48 (3)
O(3)···Cl···O(4)″	94·53 (2)	O(4)···Cl···O(3)′	148·85 (2)
O(4)···Cl···O(4)′	70·72 (2)		

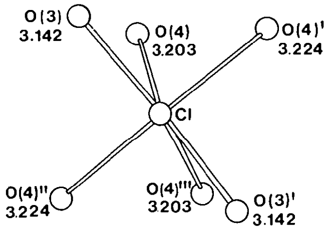

Fig. 4. Hydrogen-bond distances within the $Cl(H_2O)_6^-$ complex marked with an × in Fig. 2.

running along **b**. These chains are, in turn, hydrogen-bonded to Cl^- ions, thus forming layers parallel to the *bc* plane. One such layer is shown in Fig. 2. The shortest interlayer distance is 3·04 Å (between two O atoms).

The $H_9O_4^+$ complex in $HCl.6H_2O$ has a symmetric conformation in contrast to the same complex in $HBr.4H_2O$ (Lundgren & Olovsson, 1968), where the O—H···O distances differ by up to 0·09 Å and where only one of the outer water molecules has a pyramidal coordination while the other two have a tetrahedral environment. Apart from $HBr.4H_2O$ the crystal structures of $HClO_4.2\frac{1}{2}H_2O$ (Almlöf, Lundgren & Olovsson, 1971) and $HClO_4.3\frac{1}{2}H_2O$ (Almlöf, 1973) can be interpreted as containing $H_9O_4^+$ ions, but these complexes are not well defined.

The water molecule $H_2O(4)$ is approximately tetrahedrally hydrogen-bonded to two Cl^- ions and two water molecules [$H_2O(1)$ and $H_2O(3)$] belonging to two different $H_9O_4^+$ complexes. The O(4)···Cl distances are significantly longer than O(3)···Cl, which can be related to the fact that O(4) is a poorer hydrogen-bond donor than O(3).

The Cl^- ion situated on a twofold axis is hydrogen-bonded to six water molecules so as to form a distorted $Cl(H_2O)_6^-$ octahedron. The different octahedra are linked along **b** by sharing edges (Fig. 2). Hydrogen-bond distances and angles within one octahedron are given in Fig. 4 and Table 3 respectively. The average O···Cl distance is 3·190 Å. In $MgCl_2.12H_2O$ (Sasvári & Jeffrey, 1966), which also contains distorted $Cl(H_2O)_6^-$ octahedra, the mean O···Cl distance is also 3·19 Å.

The refined H atoms give O—H distances in the range 0·77–0·98 Å (Table 2). The O—H···*X* angles vary between 155 and 179°.

Although $HCl.6H_2O$ contains six water molecules per proton, which would make it possible for discrete $H_{13}O_6^+$ ions to be formed upon crystallization, this formation does not occur. Bell, Christoph, Fronczek & Marsh (1975) have found $H_{13}O_6^+$ to exist, however, as a discrete complex in $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-H_{13}O_6^+Cl^-$. This can presumably be explained by the presence of the large cation.

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Hydrogen Bond Studies. CXXX. The Crystal Structure of Trifluoromethanesulphonic Acid Tetrahydrate, $H_9O_4^+CF_3SO_3^-$

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The structure of $CF_3SO_3H.4H_2O$ has been determined by X-ray diffraction at 95 K. The crystals are monoclinic, space group $P2_1/c$, with $a = 7\cdot6200\ (4)$, $b = 8\cdot6804\ (3)$, $c = 12\cdot8297\ (2)$ Å, $\beta = 91\cdot940\ (2)°$, $Z = 4$. The structure contains triaquaoxonium ions, $H_9O_4^+$, hydrogen-bonded to $CF_3SO_3^-$ ions. O–H···O hydrogen bonds within the $H_9O_4^+$ complex are 2·502 (2), 2·532 (2) and 2·572 (2) Å. $H_9O_4^+$ ions are linked together by weak hydrogen bonds, 2·967 (2) Å, to form chains.

Introduction

This report is a continuation of a systematic investigation of the structures of the hydrates of trifluoromethanesulphonic acid. Earlier papers in this series report the crystal structures of the hemi-, mono- and dihydrates (Spencer & Lundgren, 1973; Delaplane, Lundgren & Olovsson, 1975*a,b*). The composition of the present compound presents the possibility of the formation of the triaquaoxonium ion, $H_9O_4^+$. Hydrated oxonium ions have, in a few earlier cases, been described in terms of $H_9O_4^+$ ions: $HBr.4H_2O$ (Lundgren & Olovsson, 1968), $HClO_4.2\frac{1}{2}H_2O$ (Almlöf, Lundgren & Olovsson, 1971), $HClO_4.3\frac{1}{2}H_2O$ (Almlöf,