slightly displaced with respect to Tl^+ or Rb^+ (Fig. 1), whereas the second, K(2), is more displaced, especially along **a** in two opposite directions alternately (see arrows in Fig. 1*c*). In the three compounds the environment of the *A* ion remains rather similar: each *A* ion exhibits three short *A*—O distances (Table 3) corresponding approximately to the sum of the ionic radii (Shannon, 1976). However, the anisotropic displacement of K(2) means that it is characterized by a short K(2)—O(14) distance and two longer K(2)—O(4) distances, unlike K(1) which exhibits three equivalent K(1)—O distances, like rubidium and thallium.

The behaviour of the univalent *A* ions in the oxides $AMo_2P_3O_{12}$ is to be compared with that observed for the oxides $AMo_3P_6Si_2O_{25}$ (Leclaire, Borel, Grandin & Raveau, 1985) which are also characterized by a tunnel structure. In both compounds the size of the *A* ion does not influence the geometry of the host lattice which seems to be rather rigid owing to the presence of SiO_4 and PO_4 tetrahedra. However, the localization of the *A* ions is rather different in the two series of oxides: in $AMo_3P_6Si_2O_{25}$ the thermal agitation of the *A* ion increases drastically as its size decreases, whereas in $AMo_2P_3O_{12}$ the thermal agitation, although rather high ($B_{eq} \sim 3$ Å^2), remains constant, the *A* ion being slightly displaced as its size decreases in order to reach K—O distances compatible with the sum of the ionic radii.

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Structure of Hexaaquahydrogen Tetrachloroferrate(III) at 210 K by X-ray Diffraction

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Abstract. The structure of hexaaquahydrogen tetrachloroferrate(III), $HFeCl_4.6H_2O$, has been determined from single-crystal X-ray diffractometer data collected at 210 K. $[H_{13}O_6]^+.[FeCl_4]^-$, $M_r = 306·76$, orthorhombic, *Pnma*, $a = 12·470\,(2)$, $b = 15·371\,(3)$, $c = 6·286\,(1)$ Å, $V = 1204·9\,(5)$ Å^3, $Z = 4$, $D_x = 1·69\,(1)$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å, $\mu = 2·14$ mm^{-1}, $F(000) = 620$. Refinement based on F^2 including 4781 reflexions gave a final $R(F)$ of 0·020. The structure consists of disordered layers of water–proton complexes interleaved with $FeCl_4^-$ ions. The $FeCl_4^-$ ions are almost regular tetrahedra, which are linked to form chains. The water–proton layers contain four-, five- and six-membered rings of water molecules.

Introduction. This work is part of a project concerned with the structure of hydrated protons. Earlier works describe the geometry of hydrated protons. It is shown that anion properties and water–proton ratios influence the formation of hydrated protons (Lundgren, 1974; Lundgren & Olovsson, 1976; Taesler, 1981). The presence of a highly charged metal ion in a structure can also influence the formation of hydrated protons, either by increasing the number of 'free' protons (Brunton & Johnsson, 1975) or by decreasing the number of water molecules that can take part in the formation of the hydrated proton (Gustafsson, Lundgren & Olovsson, 1977, 1980).

In the present compound, with its unusually large water–proton ratio and its medium-sized univalent anion, one would expect the formation of a large non-isolated water–proton complex.

Experimental. A spherical crystal of $HFeCl_4.6H_2O$ was grown using the technique described in a previous paper (Gustafsson, 1987), radius 0·15 mm, 210 K, cell

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parameters from 22 reflexions ($15 < \theta < 20°$), intensity data out to $(\sin\theta)/\lambda = 0{\cdot}72$ Å^{-1} ($-18 \le h \le 18$, $-22 \le k \le 14$, $0 \le l \le 8$), CAD-4 diffractometer. Ten test reflexions, eight used to scale intensity and its standard deviation (McCandlish, Stout & Andrews, 1975). Lp and absorption corrections, spherical crystal, $\mu R = 0{\cdot}321$, transmission factors 0·62–0·63. Data set of 4781 reflexions, of these 1925 were unique, $R_{\text{int}} = 0{\cdot}014$.

Space-group extinctions indicate *Pnma* or $Pn2_1a$. Centrosymmetry assumed, structure solved with Patterson methods and refined for non-H atoms. The $\Delta\rho$ map showed large variation close to Cl atoms indicating a poor model for Cl-atom displacement. The maps also indicated disordered positions for all H atoms. Inclusion of the disordered H atoms and γ tensors for Cl-atom displacements improved the model. The *R*-value test (Hamilton, 1964) shows that in all steps of expansion of the model the irrelevance of the new parameters can be rejected at the 0·005 significance level (Table 1). In the final cycle of refinement, 1 scale factor, 1 extinction factor, 54 positional parameters and 70 displacement parameters were refined, all shifts $< 0{\cdot}1\sigma$. All 4781 reflexions measured gave a final $wR(F^2) = 0{\cdot}037$, $R(F) = 0{\cdot}020$ and $S = 1{\cdot}50$. The $\Delta\rho$ map calculated from an averaged data set including 1680 reflexions $> 3\sigma$ gave $\Delta\rho_{\min} = -0{\cdot}14$ and $\Delta\rho_{\max} = 0{\cdot}20$ e Å^{-3}. The isotropic type-I extinction factor was 1460 (30), largest correction of 1·85 for $F^2(400)$ (Becker & Coppens, 1974, 1975). Refinements on F^2, weights $w = \sigma(F^2)^{-2}$, f, f' and f'' from *International Tables for X-ray Crystallography* (1974). All computer programs described by Lundgren (1982). Final atomic parameters are given in Table 2.*

Discussion. The compound forms a layer structure involving two types of layer. One is composed of $FeCl_4^-$ ions and the other of the hydrated protons. The layers are held together by Coulomb interactions and hydrogen bonds (Fig. 1).

$FeCl_4^-$ *ion.* The $FeCl_4^-$ ion is an almost regular tetrahedron (Fig. 2). The internal distances and angles agree well with corresponding values in $[H_9O_4]^+.[FeCl_4]^-$ (Gustafsson, 1987) and $FeCl_3.2{\cdot}5H_2O$ (Szymanski, 1979). The tetrahedra are linked to form chains so that Cl(3) in one tetrahedron points at the face defined by Cl(1), Cl(1′) and Cl(2) in the next. Each chain has two neighbouring chains running antiparallel to it, thus forming a layer. A similar arrangement is found in $[H_9O_4]^+.[FeCl_4]^-$ where such layers are stacked to form a three-dimensional structure. Cl(2) and Cl(3) each accept two weak bifurcated hydrogen bonds. This is consistent with the elongation of their distances to the Fe ion compared to the Fe—Cl(1) distance. All Cl ions have large displacement parameters. γ tensors were included in the model for the Cl ions to obtain a better fit.

Table 1. *Results for different models used in the refinement*

Refined models

I	Anisotropic displacement factors for Fe, Cl and O. No H atoms
II	I + γ tensors for Cl-atoms
III	I + isotropic H atoms
IV	II + isotropic H atoms

	NPAR	NREF	$R(F)$	$wR(F^2)$	S	$\Delta\rho_{\min}$	$\Delta\rho_{\max}$
I	56	4781	0·039	0·133	5·30	−0·54	0·68
II	78	4781	0·036	0·127	5·07	−0·43	0·59
III	104	4781	0·024	0·050	2·00	−0·32	0·48
IV	126	4781	0·020	0·037	1·50	−0·14	0·20

NPAR is the number of parameters refined
NREF is the number of reflexions in the refinement

Hamilton *R*-value test

Ration of weighted *R*-values

	I	II	III
II	1·05		
III	2·66	2·54	
IV	3·59	3·43	1·35

Corresponding significance points

$\mathscr{R}_{22,4655,0.005} < 1{\cdot}005$
$\mathscr{R}_{48,4655,0.005} < 1{\cdot}010\ \mathscr{R}_{26,4655,0.005} < 1{\cdot}006$
$\mathscr{R}_{70,4655,0.005} < 1{\cdot}016\ \mathscr{R}_{45,4655,0.005} < 1{\cdot}010\ \mathscr{R}_{22,4655,0.005} < 1{\cdot}005$

Table 2. *Positional* ($\times 10^5$; *for* H $\times 10^3$) *and displacement* ($\times 10^2$) *parameters and* H-*atom occupancy factors* (G)

U_{eq} is calculated from u_i, the r.m.s. displacement along the principal axis, with the formula $U_{\text{eq}} = (u_1u_2u_3)^{2/3}$.

	x	y	z	G	$U_{\text{eq}}/U_{\text{iso}}$(Å^2)
Fe	34309 (1)	$\frac{3}{4}$	4741 (1)		2·7
Cl(1)	41733 (2)	63129 (1)	16694 (5)		4·1
Cl(2)	17335 (3)	$\frac{3}{4}$	14224 (7)		4·4
Cl(3)	35443 (3)	$\frac{3}{4}$	69857 (6)		4·2
O(1)	30904 (5)	41599 (3)	1651 (9)		3·9
O(2)	13514 (4)	49794 (4)	16541 (9)		4·2
O(3)	44710 (5)	40543 (4)	33836 (9)		4·2
H(11)	299 (1)	364 (1)	−24 (2)	0·75	8·5 (3)
H(12)	353 (1)	413 (1)	98 (2)	0·75	4·9 (3)
H(13)	163 (1)	560 (1)	423 (3)	0·50	5·4 (4)
H(14)	261 (1)	433 (1)	58 (2)	0·50	4·7 (4)
H(21)	116 (1)	537 (1)	78 (3)	0·50	4·9 (4)
H(22)	84 (1)	471 (1)	182 (2)	0·50	3·1 (3)
H(23)	143 (1)	530 (1)	272 (3)	0·50	5·2 (4)
H(24)	183 (1)	473 (1)	123 (2)	0·50	3·2 (3)
H(31)	4 (1)	426 (1)	177 (2)	0·50	5·2 (4)
H(32)	419 (1)	428 (1)	429 (3)	0·50	4·3 (4)
H(33)	458 (1)	357 (1)	365 (3)	0·75	5·7 (3)
H(34)	404 (2)	413 (1)	219 (5)	0·25	3·7 (6)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44433 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Water–proton complex. The water–proton complexes are linked together to form layers which contain four-, five- and six-membered rings of water molecules (Fig. 3). The Schläfli symbol is 456, 5^26, 45^26. Atoms O(1) and O(3) are bonded to three water molecules and O(2) to four. The O···O distances are in the range 2·661 (1) to 2·742 (1) Å; there is therefore no indication of the formation of a discrete water–proton complex. In the centrosymmetric space group chosen, there are 6·5 H atoms in the asymmetric unit, and five O···O distances corresponding to possible hydrogen bonds. There are also four O···Cl distances less than 3·5 Å which may indicate hydrogen bonds. In the $\Delta\rho$ maps calculated after the refinement of the non-H-atom structure, there are twelve peaks corresponding to possible H-atom positions. Each O atom is tetrahedrally surrounded by four peaks. In all five possible O···O hydrogen bonds, there are two H peaks, one close to each O atom. The two remaining peaks, which are the two highest, correspond to bifurcated O···Cl hydrogen bonds. This distribution of H peaks in the $\Delta\rho$ map can either be caused by an error in the choice of cell or space group or by a disorder in the hydrogen-bond system. Several attempts were made to refine the structure in the non-centrosymmetric space group $Pn2_1a$. None lead to any improved agreement compared to the refinement in space group $Pnma$. It was decided to carry out the final refinement in the centrosymmetric space group with a disordered model for the H atoms. The occupancy factors for the H atoms were chosen in the interval 0·25–0·75 to correspond to the peak heights in the $\Delta\rho$ map, to give 6·5 H atoms in the asymmetric unit and not more than a total of 1·0 H atoms in each hydrogen bond (Table 1). All twelve partial H atoms refine to reasonable positions. The O—H distances are in the interval 0·70 (2)–0·93 (3) Å, and the O—H···O angles are larger than 161 (1)°. The disorder in the H-atom positions is also reflected in the refined O-atom positions. There are several different possible *local* arrangements of H atoms around each of the three O atoms. The 'true' O-atom position will be different for all these local arrangements. The refined O-atom position is then the mean value in time and space over all 'true' positions. The displacement parameters for the O atoms describe both the thermal motion and the distribution of 'true' positions. This is possibly the reason for an unexpectedly large anisotropy in the displacement parameters for O(2) perpendicular to the water–proton layer (Fig. 1).

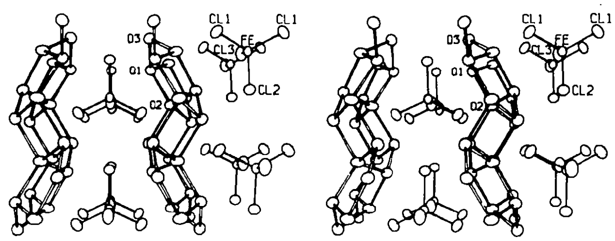

Fig. 1. Stereoscopic view of the structure. Hydrogen bonds are open, Fe—Cl bonds are single lines. Ellipsoids are drawn to include 50% probability. The viewing direction is parallel to **c**.

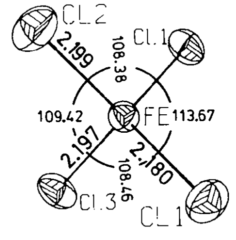

Fig. 2. The geometry of the tetrahedral $FeCl_4^-$ complex. Standard deviations of distances and angles are less than 0·001 Å and 0·02°, respectively.

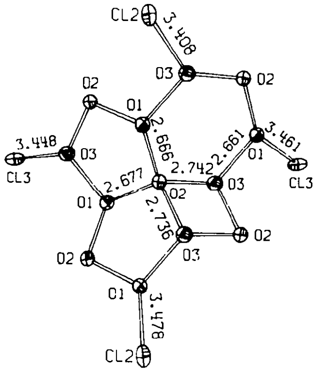

Fig. 3. Part of the hydrated proton layer view along **b**. Hydrogen bonds to Cl ions are included. Standard deviations are less than 0·001 Å.

Water–proton complexes are linked to form layers by hydrogen bonds. The layers are disordered in the cell and space group chosen. It is thus not possible to draw any conclusions about the internal geometry in the complex.

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Structure of $(Ni,Mg)_{10}Ge_3O_{16}$

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Abstract. $(Ni_{0.45}Mg_{0.55})_{10}Ge_3O_{16}$, $M_r = 871{\cdot}7$, trigonal, $R\bar{3}$, $r = 10{\cdot}1250\ (5)$ Å, $\alpha = 33{\cdot}790\ (1)°$ [$a = 5{\cdot}8850\ (4)$, $c = 28{\cdot}6135\ (12)$ Å, hexagonal cell], $V = 286{\cdot}1$ Å^3, $Z = 1$, $D_x = 5{\cdot}060$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 152{\cdot}39$ cm^{-1}, $F(000) = 416$, room temperature, final $R = 0{\cdot}014$ for 1572 unique reflections. The structure consists of alternate {111} layers of spinel-like and rock-salt-like structures stacked in the ratio 3:1 in the direction of c_{hex}. Structural accommodation between the two structural units is made in the layer of O(3) atoms. Otherwise, coordination polyhedra are fairly regular and cation–oxygen distances correspond to ideal values. Ni is weakly partitioned into the rock-salt-like layers.

Introduction. The compound $(Ni_xMg_{1-x})_{10}Ge_3O_{16}$, $x \simeq 0{\cdot}4$–$0{\cdot}5$, was recently synthesized under dry conditions at atmospheric pressure by Barbier (1987*a*) and identified as a new phase in the NiO–MgO–GeO$_2$ system. Investigation by X-ray powder diffraction and transmission electron microscopy suggested a structure in space group $R3m$ formed of alternate triple and single {111} layers of spinel-like and rock-salt-like structures, which gave $R = 0{\cdot}15$ for ideal atomic positions and 41 powder lines. The present single-crystal study confirms this structure and reports on details of the Ni,Mg site ordering and stereochemistry.

Experimental. $(Ni,Mg)_{10}Ge_3O_{16}$ was prepared by crystallization from a flux of PbO composition. 1 g of nutrient and 4 g of flux in a platinum crucible with a well-fitting lid were cooled from 1573 to 1173 K at 4 K h^{-1}. The nutrient had the composition $(Ni_{0.50}Mg_{0.50})_{10}Ge_3O_{16}$ and was prepared by heating high-purity oxides under dry conditions at 1473 K. The product was recovered by dissolution of the flux in dilute HCl and hot water, and characterized as $(Ni_xMg_{1-x})_{10}Ge_3O_{16}$, $x < 0{\cdot}5$, with excess of a NiO-rich rock-salt-structure phase. Electron microprobe analysis using a JEOL JXA-8600 Superprobe with crystalline Mg_2GeO_4 and Ni_2GeO_4 standards yielded a composition of $(Ni_{0.41}Mg_{0.59})_{10}Ge_3O_{16}$ for the fine-grained matrix. However, the structure refinement indicated a composition of $(Ni_{0.45}Mg_{0.55})_{10}Ge_3O_{16}$ for the larger single crystals, which is assumed throughout this study. The crystal was rectangular in shape with approximate dimensions $0{\cdot}075 \times 0{\cdot}083 \times 0{\cdot}105$ mm and a calculated volume of $0{\cdot}65 \times 10^{-3}$ mm^3. It was trimmed from a 0·5 mm diameter composite crystal, and size reduced with 600 abrasive paper. X-ray precession study revealed that the Laue class was $\bar{3}$ and not $\bar{3}m$ (Barbier, 1987*a*), and restricted the possible space groups to $R3$ and $R\bar{3}$. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 20 reflections in 2θ range 53·0–65·3° for cell parameters. Data collected by θ–2θ scan; scan angle $(2\theta) = 2{\cdot}4°$, with dispersion correction. 4740 hkl, $-h-kl$ reflections (hexagonal indices) permitted by space group $R\bar{3}$ out to $2\theta = 90°$; $-11 \le h \le 11$, $-11 \le k \le 11$, $0 \le l \le 57$. Standard reflections 220, $\bar{2}40$, $0\bar{2}8$; $R_{\text{int}} = 0{\cdot}01$, no significant decline in intensity. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a $12 \times 12 \times 12$ grid) varied from 0·276 for $\bar{1},0,17$ to 0·403 for $3,\bar{5},50$. 1572 unique reflections. 589 reflections considered unobserved [$I < 3\sigma(I)$].

Atomic positions in [$R3m$] (Barbier, 1987*a*) and $R\bar{3}$ are related in the following manner: [M(1)]M(1); [M(2)]M(2); [M(3),M(4)]M(3); [Ge(1)]Ge(1);

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