Les résultats structuraux obtenus pour $KGdNb_6Cl_{18}$ montrent que la cohésion de la structure est assurée essentiellement par l'intermédiaire des atomes de Gd, les sites du K n'étant occupés que pour moitié. Ces sites pourraient devenir vacants sans destruction de l'édifice structural. Ceci nous a conduit à isoler une nouvelle famille de composés $RENb_6Cl_{18}$ à motifs $(Nb_6Cl_{12})^{3+}$, isotypes de $KGdNb_6Cl_{18}$. Les résultats structuraux récemment obtenus pour $LuNb_6Cl_{18}$ sont compatibles avec la présence de groupements $(Nb_6Cl_{12})^{3+}$ et montrent que le site occupé par le potassium dans $KGdNb_6Cl_{18}$ est alors ici effectivement vacant (Ihmaïne, Perrin & Sergent, 1986).

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Structure of Triaquaoxonium Tetrachloroferrate(III) at 215 K by X-ray Diffraction*

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Abstract. $[H_9O_4]^+.[FeCl_4]^-$, structure determined from single-crystal X-ray diffractometer data collected at 215 K. $M_r = 270.73$, monoclinic, $P2_1/c$, $a = 6.355$ (1), $b = 11.738$ (2), $c = 13.004$ (2) Å, $\beta = 97.03$ (1)°, $V = 962.8$ (5) Å^3, $Z = 4$, $D_x = 1.87$ (1) Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 2.64$ mm^{-1}, $F(000) = 540$. Refinement based on F^2 including 1932 reflexions gave a final $R(F)$ of 0.020. The structure consists of $H_9O_4^+$ ions and tetrahedral $FeCl_4^-$ ions. The central oxonium ion in the $H_9O_4^+$ complex is disordered. The $H_9O_4^+$ ions form a hydrogen-bonded two-dimensional three-coordinated network parallel to the *ab* plane. Each water molecule also forms hydrogen bonds with the Cl ions.

Introduction. This work is part of a larger project to study the structures of water–proton complexes.

* Hydrogen Bond Studies. 151.

Lundgren (1974) and Lundgren & Olovsson (1976) described the different types of water–proton complexes found in acid hydrates. Taesler (1981) showed that the type of complex formed in a compound is dependent on the water/proton ratio and on the anion properties. The influence of metal ions on the complex formed can also be of importance. The effective water/proton ratio is lowered when water molecules are bonded to the metal ion in such a way that they cannot participate in the formation of a water–proton complex. The effective water/proton ratio is also lowered when a weak acid is deprotonated by the influence of a metal ion. In the present compound there are four water molecules per proton, which ideally would lead to the formation of an $H_9O_4^+$ complex. However, if one or more of the water molecules are coordinated by the Fe ion, we can expect the formation of a water–proton complex with lower water content.

Experimental. A solution with stoichiometric composition $FeCl_3.HCl.4H_2O$ was made from anhydrous $FeCl_3$, concentrated hydrochloric acid and water. A capillary (Fig. 1) made from Pyrex glass was filled with a few mm^3 of the solution and sealed off. A single crystal was formed in the spherical capillary tip by repeated crystallization with a nitrogen gas-flow cooling device mounted on a CAD-4 diffractometer. The melting interval was 270–272 K.

Crystal diameter 0·21 mm, cell parameters from 22 reflexions $(17 < \theta < 20°)$, intensity data to $(\sin\theta)/\lambda = 0·62 \text{ Å}^{-1}$ $(-7 \le h \le 7, -8 \le k \le 14, 0 \le l \le 14)$ at 215 K. Ten test reflexions, all decreased during first 260 h, corrections applied to intensities and their standard deviations (McCandlish, Stout & Andrews, 1975). Lp and absorption correction, spherical crystal, $\mu R = 0·278$, transmission factors 0·66–0·67. Data set of 1932 reflexions, of these 1560 unique, $R_{int} = 0·016$.

Fe and Cl atoms were located in a Patterson synthesis. O and H atoms were subsequently found after successive least-squares refinements and $\Delta\rho$-map calculations. After conventional refinement, the $\Delta\rho$ map contained two areas of residual electron density. The maximum peak was situated close to O(1) and there were several peaks in the vicinity of the Fe and Cl atoms. Two modifications to the structure model were introduced: (I) disorder of O(1); (II) Hirshfeld deformation functions on Fe and Cl atoms. Details of these modifications are given in the *Discussion*.

The different models refined are summarized in Table 1. In the final refinement (I+II), 1 scale factor, 1 isotropic extinction coefficient, 57 positional parameters, 54 anisotropic and 10 isotropic [H atoms and O(1A)] thermal parameters, 1 occupancy factor and 27 deformation parameters were refined. No shifts were larger than 0·1σ. Two parameters defining the radial dependence of the deformation functions were fixed.

All refinements were based on F^2 and each reflexion was given the weight $w = \sigma(F^2)^{-2}$. Values of f, f' and f'' were taken from *International Tables for X-ray Crystallography*, (1974). All computer programs used are described by Lundgren (1982). Final positional parameters are given in Table 2.* Details of the geometry of the $H_9O_4^+$ complex are given in Table 3.

Discussion. The structure can be described as a distorted hexagonal close packing of Cl ions with the close-packed layers parallel to the ab plane (Fig. 2). Alternate layers contain only one third of the possible

number of Cl ions. This arrangement gives rise to chains of trigonal bipyramids running in the c direction, with each of the bipyramids containing two tetrahedral holes. The Fe ions occupy only one of these holes such that each chain can be considered to run either in the + or − direction. The chains pack such that each chain is surrounded by four other chains, two parallel and two antiparallel.
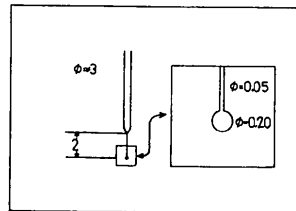

Fig. 1. Shape and size (mm) of the capillary used for sample preparation.

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

N_{par} is the number of parameters refined for each model. G_1 is the type 1 isotropic extinction coefficient (Becker & Coppens 1974, 1975).

I: Alternative positions O(1) and O(1A).
II: Deformation functions on Fe and Cl.

Refinement type	R (%)	wR(F²) (%)	S	$\Delta\rho_{min}$ (e Å⁻³)	$\Delta\rho_{max}$ (e Å⁻³)	N_{par}	G_1 (×10³)
Conventional	2·29	5·07	1·83	−0·24	0·28	119	5·6 (2)
I	2·19	4·75	1·72	−0·24	0·24	129	5·6 (2)
II	2·08	4·51	1·64	−0·19	0·30	143	6·1 (2)
I+II	2·01	4·20	1·53	−0·17	0·18	151+2	6·2 (2)

Table 2. *Positional* $(\times 10^5)$ *and thermal* $(\times 10^2)$ *parameters for non-hydrogen atoms*

U_{eq} is calculated from u_i, the r.m.s. displacement along the principal axis, with the formula $U_{eq} = (u_1 u_2 u_3)^{2/3}$.

	x	y	z	$U_{eq}(\text{Å}^2)$
Fe(1)	92053 (3)	74254 (1)	38 (1)	2·4
Cl(11)	23993 (6)	73824 (2)	−5030 (3)	3·3
Cl(12)	96399 (5)	74612 (2)	17016 (3)	2·9
Cl(13)	74822 (5)	58809 (3)	−5424 (3)	4·0
Cl(14)	75828 (5)	89799 (3)	−5791 (3)	3·9
O(1)	46970 (25)	62724 (13)	68601 (24)	3·3
O(1A)	50312 (223)	85924 (111)	22714 (137)	2·2
O(2)	21481 (15)	51518 (9)	30855 (11)	3·7
O(3)	21554 (17)	52339 (8)	79024 (10)	3·2
O(4)	47087 (16)	65452 (8)	18365 (9)	3·3

Table 3. *Geometry of the* $H_9O_4^+$ *complex*

Mean values of distances and angles are given.

	O(1)	O(1A)
$H_3O^+\cdots H_2O$ (Å)	2·57 (3)	2·54 (9)
$H_2O\cdots H_3O^+\cdots H_2O$ (°)	117 (14)	120 (16)
$H_2O\cdots O$ (Å)	2·91 (3)	2·91 (3)
$H{-}O [H_3O^+]$ (Å)	0·94 (12)	0·96 (5)
$H{-}O [H_2O]$ (Å)	0·75 (3)	0·75 (3)

* Lists of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43669 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

FeCl$_4^-$ ion. Each Fe ion is surrounded by four Cl ions at the corners of a tetrahedron (Fig. 3). The same coordination has been found, for example, in FeCl$_3$.2$\frac{1}{2}$H$_2$O (Szymanski, 1979) and CsFeCl$_4$ (Meyer, 1977). The Fe—Cl distances here fall in the range 2·185 (1)–2·210 (1) Å and the Cl—Fe—Cl angles in the range 107·08 (2)–112·50 (2)° compared to 2·169 (4)–2·220 (4) Å and 106·6 (1)–110·7 (1)° in FeCl$_3$.2$\frac{1}{2}$H$_2$O.

Deformation functions (Hirshfeld, 1971) were introduced in an attempt to describe the bonding electron density in the FeCl$_4^-$ group. Neutral atoms were used as the reference state. Up to hexadecapolar functions were used for Fe. A mirror plane defined by Fe(1), Cl(12) and Cl(13) was introduced to reduce the number of parameters and improved the convergence. Up to quadrupolar functions were used for the Cl atoms. To reduce the number of parameters, all four Cl atoms were given the same deformation functions. Any coefficient refining to a value less than 1σ was fixed to zero in all subsequent cycles of refinement. The thermally smeared deformation electron density map shows a minimum of −0·13 e Å^{-3} at the Fe site and maxima of 0·08–0·13 e Å^{-3} at ~0·75 Å from the Cl atoms in the direction towards the Fe atom. The

difference Fourier map after the deformation refinement still contained residual electron density in the Fe—Cl bond regions but the peaks were 0·01–0·10 e Å^{-3} lower than before.

No significant shifts in the positional and thermal parameters were noted when deformation parameters were introduced, and all correlation coefficients between deformation and other parameters were in the interval ±0·5.

The water–proton complex. The four water molecules and the excess proton form an H$_9$O$_4^+$ ion of the H$_3$O$^+$(H$_2$O)$_3$ type. Each of the three outer water molecules donates one hydrogen bond to a water molecule in another H$_9$O$_4^+$ ion. It also accepts one hydrogen bond from a water molecule. The H$_9$O$_4^+$ ions are linked *via* these hydrogen bonds to form a two-dimensional three-coordinated network with the Schläfli symbol 8^{2}4. These layers are parallel to the *ab* plane (Fig. 4).

Each of the water molecules also donates a hydrogen bond to a Cl ion. Cl(11) accepts the hydrogen bonds donated by O(3) and O(4). The bond from O(2) is bifurcated and accepted by both Cl(11) and Cl(14). The principal hydrogen-bond acceptor, Cl(11), has an Fe—Cl distance ~0·02 Å longer than that for the other Cl ions.

The Δρ map after the conventional refinement contains a peak of 0·27 e Å^{-3} close to O(1). This indicated a disorder with two alternative sites, O(1) and O(1*A*), for the central O atom in the H$_9$O$_4^+$ ion. The position, temperature and occupancy parameters for O(1) and O(1*A*) were refined. O(1) and O(1*A*) are situated on either side of the plane through O(2), O(3) and O(4). The distance from the plane is 0·433 (3) Å for O(1) and 0·14 (2) Å for O(1*A*). The separation of the two sites is 0·57 (2) Å; the occupancies are 0·90 (1) for O(1) and 0·10(1) for O(1*A*). The parameters of
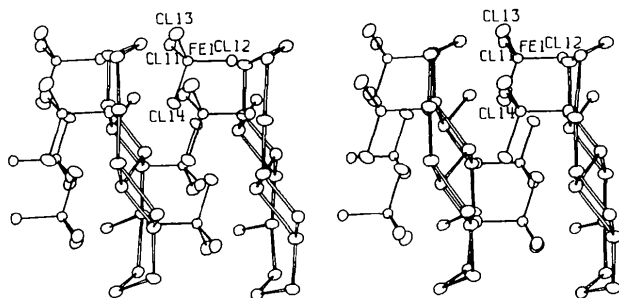

Fig. 2. A stereoscopic drawing of the structure. Fe—Cl bonds are single lines and O—H···O bonds are open. Thermal ellipsoids are drawn to include 50% probability. The *ab* plane is vertical and parallel to the viewing direction.
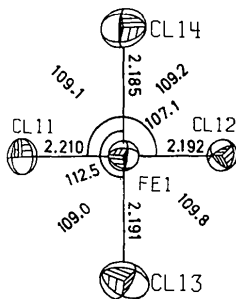

Fig. 3. The geometry of the tetrahedral FeCl$_4^-$ complex. Standard deviations of distances and angles are less than 0·001 Å and 0·025°, respectively.
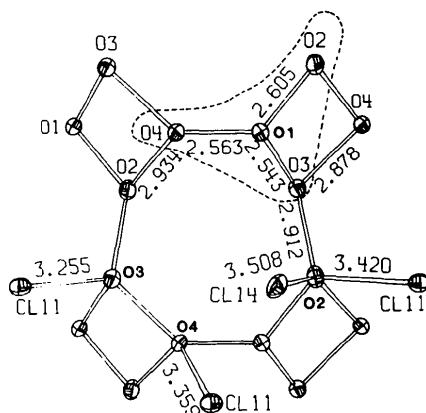

Fig. 4. The hydrogen-bond system viewed along **c**. The H$_9$O$_4^+$ complex is indicated. The darker atom labels indicate positions where the complete surroundings of each atom are shown. Standard deviations are less than 0·002 Å.

O(1) shifted significantly when O(1A) was included in the model. The two largest shifts were 12σ in the z coordinate and 14σ in β_{33}. The final $\Delta\rho$ map contained no peaks larger than $0 \cdot 07$ e Å^{-3} in the vicinity of O(1) and O(1A). This type of disorder, where the coordination pyramid around H_3O^+ is turned inside out, has been described earlier (Lundgren, 1979; Gustafsson, 1985).

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Structure of Tetrapotassium Copper *cyclo*-Triphosphate Tetrahydrate

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Abstract. $CuK_4(P_3O_9)_2.4H_2O$, $M_r = 765 \cdot 84$, monoclinic, $P2_1/a$, $a = 8 \cdot 510\,(5)$, $b = 14 \cdot 303\,(8)$; $c = 8 \cdot 487\,(5)$ Å, $\beta = 96 \cdot 51\,(2)°$, $V = 1026\,(2)$ Å^3, $Z = 2$, $D_x = 2 \cdot 478$ Mg m^{-3}, $\lambda(\text{Ag } K\bar{\alpha}) = 0 \cdot 5608$ Å, $\mu = 1 \cdot 272$ mm^{-1}, $F(000) = 758$, $T = 293$ K, final $R = 0 \cdot 028$ for 2336 independent reflexions. The crystal structure is built up by double layers of KO_n polyhedra alternating with layers of CuO_6 octahedra, both perpendicular to the c axis. The phosphoric anion P_3O_9 is a trimeric ring.

Introduction. Copper–alkali (or monovalent cation) cyclophosphates are not very common. In order of increasing condensation one can only mention: $Na_4Cu(P_3O_9)_2.4H_2O$ (Durif & Averbuch-Pouchot, 1984), $Li_2Cu_2P_6O_{18}$ (Laügt & Durif, 1974), $Cu_3M_2^IP_8O_{24}$ ($M^I = NH_4$, Cs, Tl, Rb) (Laügt & Guitel, 1975). The present study describes the chemical preparation and crystal structure of a new copper–potassium *cyclo*-triphosphate.

Experimental. $CuK_4(P_3O_9)_2.4H_2O$ was prepared by the metathesis reaction of Boullé (1941) using silver trimetaphosphate monohydrate as starting material. An aqueous solution of $CuCl_2.2H_2O$ and KCl in stoichiometric proportions is added with the corresponding amount of $Ag_3P_3O_9.H_2O$. The reaction scheme is:

$$CuCl_2 + 4KCl + 2Ag_3P_3O_9 \rightarrow CuK_4(P_3O_9)_2 + 6\,AgCl.$$
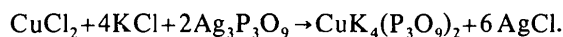
After filtration, to eliminate the insoluble silver chloride,

the resulting solution is kept at room temperature until the formation of $CuK_4(P_3O_9)_2.4H_2O$ crystals; they appear as thick monoclinic platelets; density not measured. Cubic fragment $0 \cdot 22 \times 0 \cdot 22 \times 0 \cdot 22$ mm. Philips PW 1100 diffractometer; graphite monochromator; systematic absences: $0k0$ ($k = 2n$), $h0l$ ($h = 2n$); 21 reflexions ($9 \cdot 5 < \theta < 11 \cdot 5°$) for refining the unit-cell dimensions, ω scan; 3078 reflexions measured ($3 < \theta < 30°$), 2916 unique, $R_{\text{int}} = 0 \cdot 000$, $\pm h,k,l$, $h_{\text{max}} = 15$, $k_{\text{max}} = 25$, $l_{\text{max}} = 10$; scan width $1 \cdot 20°$; scan speed $= 0 \cdot 02°$ s^{-1}; total background measuring time 20 s. Two orientation and intensity control reflexions ($\bar{1}1\bar{2}$ and $1\bar{1}2$) every 2 h, no variation. Lorentz–polarization corrections, no absorption correction. Direct methods (*MULTAN*77, Main, Lessinger, Woolfson, Germain & Declercq, 1977) used to solve the structure. Anisotropic full-matrix least-squares refinement (on F); unit weights; hydrogen atoms located on difference Fourier maps and refined isotropically; final refinements with 2336 reflexions corresponding to $I > 5\sigma(I)$; final $R = 0 \cdot 028$ ($wR = 0 \cdot 032$). For the complete set of unique reflexions $R = 0 \cdot 032$. Extinction coefficient refined: $0 \cdot 69 \times 10^{-7}$ (Stout & Jensen, 1968), $S = 1 \cdot 182$, max. $\Delta/\sigma = 0 \cdot 02$ (extinction coefficient). Maximum peak height in final difference Fourier map $0 \cdot 63$ e Å^{-3}. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer: PDP 11–70.