Tetraethylammonium Chloride Tetrahydrate, a 'Double Channel' Host Lattice Constructed from $(H_2O)_4Cl^-$ Tetrahedra Linked Between Vertices*

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Abstract. Crystals of $(C_2H_5)_4NCl \cdot 4H_2O$ are orthorhombic, space group *Ccca*, with $a = 19.104(3)$, $b = 23.084(4)$, $c = 13.330(3)$ Å, and $Z = 16$. The structure features an anionic host lattice constructed from the linkage of $(H_2O)_4Cl^-$ tetrahedra by hydrogen bonds between vertices, generating two open linear channel systems which accommodate the ordered cations. Final $R_F = 0.080$ for 1516 observed Mo$K\alpha$ data measured at 22°C.

1. Introduction

Crystallization of tetraethylammonium chloride, $(C_2H_5)_4NCl$, in water under various conditions results in two well-defined crystalline phases. The monohydrate is significant in that it contains the first reported centrosymmetric cyclic hydrogen-bonded $(H_2O \cdot Cl^-)_2$ species [1, 2]. In the case of the tetrahydrate, although an optical study was made nearly eight decades ago [3], its unit-cell dimensions and space group remained unknown until 1978 [4]. We have now determined its crystal structure by X-ray analysis, and the present report constitutes a sequel to our recent crystallographic characterization of the tetraethylammonium salt hydrates $4(C_2H_5)_4NF \cdot 11H_2O$ [5] and $[(C_2H_5)_4N]CH_3COO \cdot 4H_2O$ [6].

2. Experimental

Tetraethylammonium chloride (labelled as a pentahydrate with $14.0 \pm 0.4\%$ Cl by weight) was obtained from Fluka AG, and colorless crystals of the tetrahydrate (correct stoichiometry established by density and unit-cell measurements) were obtained by slow evaporation of a saturated solution in a desiccator charged with drierite. A selected single crystal (*ca.* $0.40 \times 0.40 \times 0.45$ mm) was taken out of the mother liquor, quickly covered with petroleum jelly, and sealed in a 0.5 mm Lindemann glass capillary. Measurement of the crystal data and

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* Dedicated to Professor G. A. Jeffrey

Table I. Data collection and processing parameters

Molecular formula	$(C_2H_5)_4NCl \cdot 4H_2O\,(C_8H_{28}NClO_4)$
Molecular weight	237.76
Cell constants	$a = 19.104(3),\ b = 23.084(4),\ c = 13.330(3)$ Å, $V = 5878(2)$ Å^3,
	$Z = 16$
Density (flotation in n-hexane/CCl$_4$)	1.084 g cm^{-3}
Density (calculated)	1.075 g cm^{-3}
Space group	$Ccca$ (No. 68)
Radiation	graphite-monochromatized Mo$K\alpha$, $\lambda = 0.71069$ Å
Absorption coefficient	2.53 cm^{-1}
Scan type and speed	ω-2θ; 2.02–8.37 deg min^{-1}
Scan range	$1°$ below $K\alpha_1$ to $1°$ above $K\alpha_2$
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	h, k, l; $2\theta_{max} = 54°$
Unique data measured	3226
Observed data[a] with $|F_o| > 3\sigma(|F_o|)$, n	1516
Number of variables, p	140
$R_F = \Sigma \|F_o| - |F_c\| / \Sigma |F_o|$	0.080
Weighting scheme	$w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$
$R_G = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$	0.088
$S = [\Sigma w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$	1.851
Residual extrema in final difference map	$+ 0.53$ to $- 0.26\ e$Å^{-3}

[a] Excluding reflections (004), (080), (400), (220) and (221), which were given zero weight in least-squares refinement.

reflection intensities on a Nicolet R3m diffractometer followed the procedures previously described [7], and relevant parameters are summarized in Table I.

Reflections with h even and $(h + k) \neq 0$ (mod 4) were either weak or absent. The Patterson synthesis indicated the existence of a supersymmetry problem. We therefore decided to expand the data to a half-sphere of reflections and to solve the structure in space group $P1$. This strategy helped to avoid possible space-group ambiguity arising from the pseudo systematic absences. A regular pattern of 16 'carbon' atoms, consistent with the Patterson map, were input to the program DIRDIF [8,9]. The automatic origin- and enantiomorph-fixing procedure led to the acceptance of another eight strong peaks. A consecutive DIRDIF run with 24 'carbon' atoms as input yielded the entire structure. The locations of the symmetry elements were then deduced, and an independent part of the structure shifted to its proper position in space group $Ccca$.

All non-hydrogen atoms in the asymmetric unit (which comprises three chloride ions in special positions, plus one cation and four water molecules in general positions) were varied anisotropically. The hydrogen atoms of the methylene groups were generated geometrically (C—H fixed at 0.96 Å); the former were allowed to ride on their respective parent C atoms, and the latter were treated as rigid groups [10]. All but two of the eight water protons were located from a difference Fourier map, and these were subsequently held stationary in least-squares cycles. Isotropic temperature factors (slightly larger than those of the corresponding parent C and O atoms) were assigned to all H atoms.

Computations were performed on a Data General Nova 3/12 minicomputer using the SHELXTL program package [11]. Analytic expressions of neutral-atom scattering were employed, and anomalous dispersion corrections were incorporated [12]. Blocked-cascade least-squares refinement [13] converged to the R indices listed in Table I, which also shows the residual electron-density extrema in the final difference map.

3. Results and Discussion

3.1. THE WATER-ANION HOST LATTICE

The final positional and thermal parameters for the non-hydrogen atoms are displayed in Table II in accordance with the atom labelling scheme shown in Figure 1. The positions of the two remaining water protons, which were missing in the final difference map, could be deduced from bonding and stereochemical considerations. The resulting proton-ordered host lattice (Figure 1) may be conveniently described by reference to the hydrogen bonding scheme given in Table III.
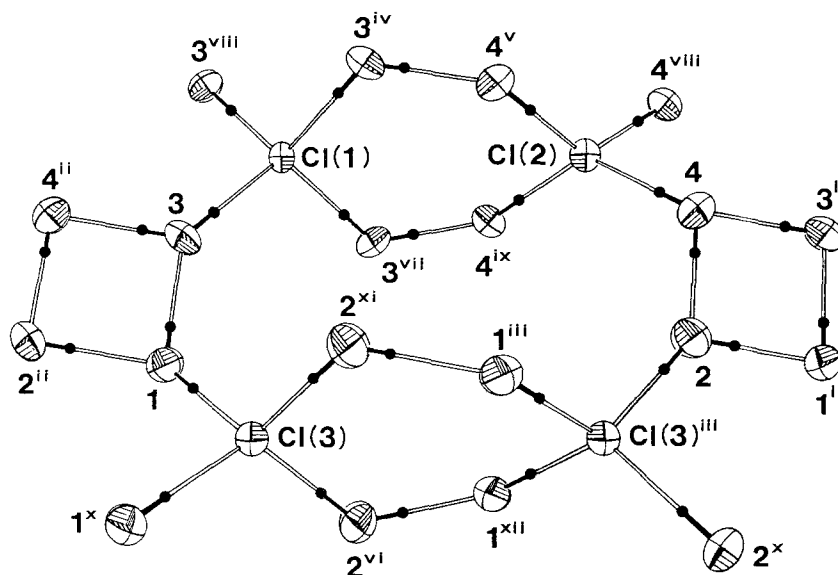
Fig. 1. Perspective view, approximately along the a axis, showing the linkage of $(H_2O)_4Cl^-$ tetrahedra to generate twisted $Cl(H_2O)_4Cl$ rings and nearly planar $(H_2O)_4$ quadrilaterals. The c axis is horizontal. Thermal ellipsoids have been drawn at the 35% probability level, and the atom labels correspond to those given in Tables II and III. The idealized positions of the ordered water protons are represented by small black circles.

Table II. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors[a] ($\text{Å}^2 \times 10^3$) for non-hydrogen atoms

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Cl(1)	0	2500	2500	62(1)	C(1)	552(2)	3738(2)	5537(3)	74(2)
Cl(2)	0	2500	7500	76(1)	C(2)	433(4)	4265(3)	6203(5)	119(3)
Cl(3)	2500	5000	2378(1)	69(1)	C(3)	1228(2)	4278(2)	4243(3)	64(2)
O(1)	1399(2)	4425(2)	864(3)	91(1)	C(4)	651(3)	4284(3)	3474(4)	94(2)
O(2)	1603(2)	4200(2)	8830(3)	115(2)	C(5)	1259(2)	3203(2)	4345(3)	63(2)
O(3)	951(2)	3287(2)	1050(3)	102(2)	C(6)	1875(3)	3150(3)	3649(5)	107(3)
O(4)	1114(2)	3081(2)	9037(3)	100(2)	C(7)	1859(3)	3822(2)	5603(3)	73(2)
N(1)	1226(2)	3760(2)	4938(2)	45(1)	C(8)	1947(3)	3343(3)	6388(4)	114(3)

[a] Origin at $\bar{1}$. U_{eq} is calculated as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ matrix.

Table III.   Scheme of hydrogen bonding, bond distances (Å), and bond angles (deg) in the anionic host lattice[a]

(a) Scheme of hydrogen bonding

Water oxygen atom	Donor bonds to	Acceptor bonds from
O(1)	O(3), Cl(3)	O(2)[ii]
O(2)	O(1)[i], Cl(3)[iii]	O(4)
O(3)	O(4)[ii], Cl(1)	O(1)
O(4)	O(2), Cl(2)	O(3)[i]
Chloride ion		
Cl(1)	O(3), O(3)[iv], O(3)[vii], O(3)[viii]	
Cl(2)	O(4), O(4)[v], O(4)[viii], O(4)[ix]	
Cl(3)	O(1), O(1)[x], O(2)[vi], O(2)[xi]	

(b) Hydrogen bond lengths

O(1)···O(2)[ii]	2.789	O(2)···O(4)	2.761
O(1)···O(3)	2.773	O(3)···O(4)[ii]	2.744
Cl(1)···O(3)	3.216	Cl(2)···O(4)	3.244
Cl(3)···O(1)	3.203	Cl(3)···O(2)[vi]	3.177

(c) Hydrogen bond angles

O(3)···O(1)···O(2)[ii]	87.3	O(1)···O(2)[ii]···O(4)[ii]	91.7
O(2)[ii]···O(4)[ii]···O(3)	88.5	O(4)[ii]···O(3)···O(1)	92.4
O(3)···O(1)···Cl(3)	122.6	O(2)[ii]···O(1)···Cl(3)	126.7
O(4)···O(2)···Cl(3)[iii]	141.9	O(1)[i]···O(2)···Cl(3)[iii]	124.0
O(1)···O(3)···Cl(1)	139.8	O(4)[ii]···O(3)···Cl(1)	123.6
O(2)···O(4)···Cl(2)	123.1	O(3)[i]···O(4)···Cl(2)	128.0
O(3)···Cl(1)···O(3)[iv]	111.2	O(3)···Cl(1)···O(3)[viii]	106.1
O(4)···Cl(2)···O(4)[v]	98.0	O(4)···Cl(2)···O(4)[viii]	101.7
O(4)···Cl(2)···O(4)[ix]	131.2	O(1)···Cl(3)···O(1)[x]	101.9
O(1)···Cl(3)···O(2)[vi]	105.7	O(1)···Cl(3)···O(2)[xi]	119.8

Symmetry transformations:

[i]	$x, y, 1+z$	[ii]	$x, y, -1+z$	[iii]	$\frac{1}{2}-x, y, \frac{1}{2}+z$
[iv]	$x, \frac{1}{2}-y, \frac{1}{2}-z$	[v]	$x, \frac{1}{2}-y, 1\frac{1}{2}-z$	[vi]	$x, 1-y, -\frac{1}{2}+z$
[vii]	$-x, y, \frac{1}{2}-z$	[viii]	$-x, \frac{1}{2}-y, z$	[ix]	$-x, y, \frac{1}{2}-z$
[x]	$\frac{1}{2}-x, 1-y, z$	[xi]	$\frac{1}{2}-x, y, -\frac{1}{2}+z$	[xii]	$x, 1-y, \frac{1}{2}+z$

[a] Estimated standard deviations: about 0.005 Å for Cl···O, 0.007 Å for O···O, 0.4° for O···Cl···O, 0.5° for Cl···O···O, and 0.7° for O···O···O.

Of the three independent chloride ions in the asymmetric unit (Figure 1), two are situated on sites of 222 symmetry while the third [Cl(3) in Wyckoff position 8(h)] lies on a crystallographic diad. Each chloride ion is tetrahedrally coordinated by water molecules with O—H···Cl bonds in the range 3.177(5)–3.244(5) Å (Table III). Distortion of the resulting $(H_2O)_4Cl^-$ aggregates from idealized tetrahedral geometry increases in the order Cl(1) < Cl(3) < Cl(2). As the z coordinate of Cl(3) is very close to 1/4, all $(H_2O)_4Cl^-$ units are stacked, with effectively the same c/2 spacing, in columns in the direction of the c axis. Within each column, adjacent $(H_2O)_4Cl^-$ tetrahedra have different orientations, and their vertices are linked pairwise by O—H···O hydrogen bonds to form an infinite chain of twisted six-membered $Cl(H_2O)_4Cl$ rings joined in a junction-sharing fashion. As illustrated in Figures 1 and 2, neighbouring columns are further interconnected by lateral O—H···O hydrogen bonds to generate a three-dimensional network featuring the occurrence of virtually planar, almost square $(H_2O)_4$ quadrilaterals. The water protons are fully utilized in an ordered

scheme of hydrogen bonding, such that the O atoms conform to a donor/acceptor sequence around each $(H_2O)_4$ quadrilateral (Figure 1). All four independent water molecules are three-coordinated, and their bonding configurations vary from almost planar to pyramidal [values for the sum of the three valence angles about an oxygen atom are 336.6, 357.6, 355.8 and 339.6° for O(1), O(2), O(3) and O(4), respectively (Table III)].

The three-dimensional assembly of $(H_2O)_4Cl^-$ tetrahedra, interlinked by O—H···O hydrogen bonds between vertices, gives rise to two crisscross, planar channel systems normal to the c axis (Figure 2). Specifically, one system consists of parallel and equally spaced channels lying at the intersections of the (001) and ($2\bar{2}0$) families of planes. The second system, made up of channels directed along the intersections of the (002) plane with the (220) set of planes, may be generated from the first by either of the two c glide operations of the $Ccca$ space group.
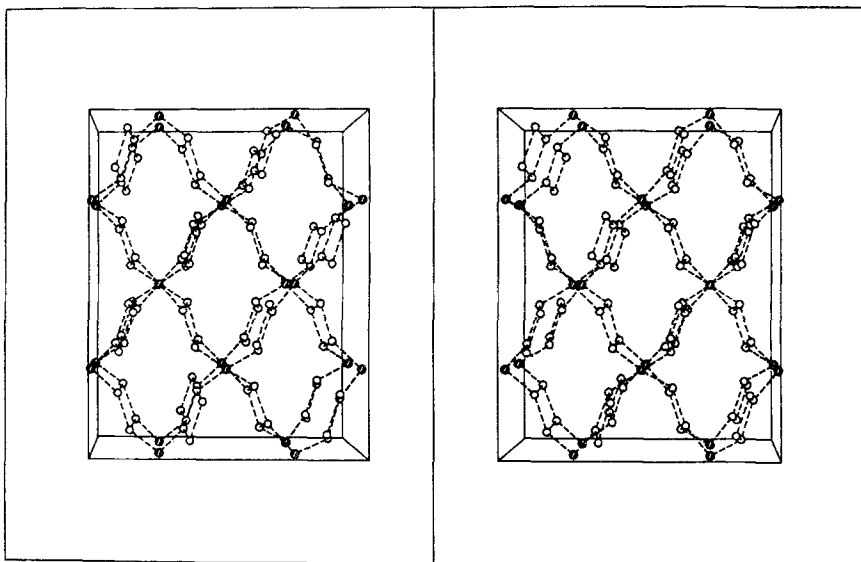

Fig. 2. Stereo drawing showing the two channel systems in the *empty* water-anion host lattice of $(C_2H_5)_4NCl \cdot 4H_2O$. The origin of the unit cell lies at the lower left corner, with a pointing from left to right, b upwards, and c towards the reader. Open and shaded circles stand for O and Cl atoms, respectively, and both O—H···O and O—H···Cl hydrogen bonds are represented by broken lines.

3.2. THE TETRAETHYLAMMONIUM ION

The coordinates of the N atom approximate closely to $(\frac{1}{8}, \frac{3}{8}, \frac{1}{2})$, so that the $(C_2H_5)_4N^+$ ions neatly fill the two channel systems of the water-anion host framework in regular arrays (Figures 3 and 4). The tetrahedral cation is well ordered, has normal dimensions, and nearly attains idealized 222 molecular symmetry (Table IV). Each tetraethylamonium ion is surrounded by six chloride ions and six $(H_2O)_4$ quadrilaterals; two of the latter are oriented in an approximately facial fashion whereas the other four are in the side-on mode. Conversely, the nearest neighbours of each chloride ion are four cations and the corner atoms of four $(H_2O)_4$ quadrilaterals, which alternately occupy the eight vertices of a cube (Figure 4). As a consequence of the highly regular arrangement of the $(C_2H_5)_4N^+$ and $(H_2O)_4Cl^-$ moieties
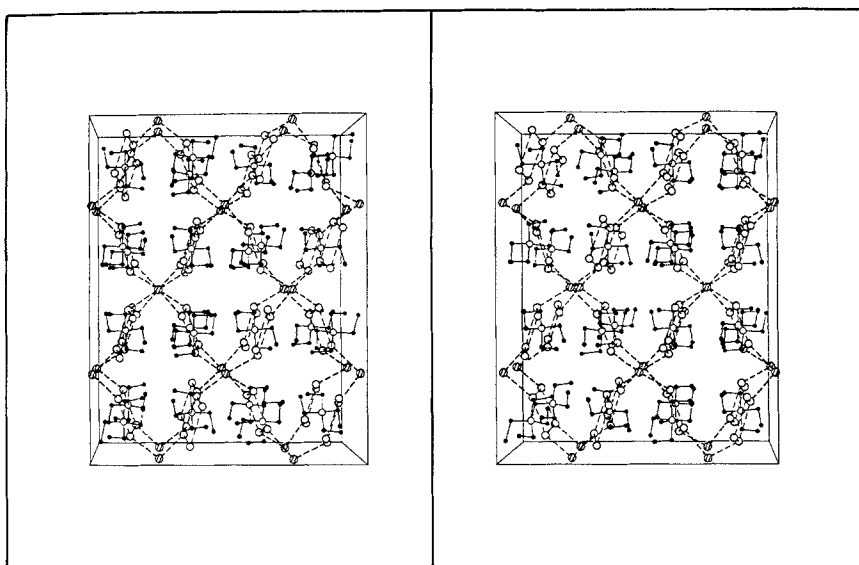
Fig. 3. Stereo drawing of the crystal structure of $(C_2H_5)_4NCl \cdot 4H_2O$ viewed parallel to c; the empty channels illustrated in Figure 2 are now filled by the quaternary ammonium ions. Hydrogen atoms have been omitted for clarity, and atom types are distinguished by size and shading. Broken lines represent hydrogen bonds.
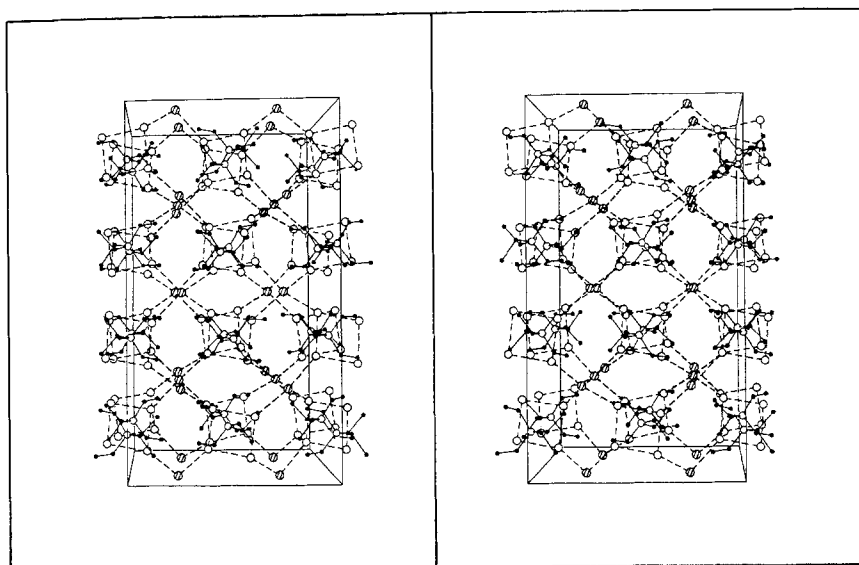

Fig. 4. Stereo drawing of the crystal structure viewed parallel to a. The unit-cell origin lies at the upper left corner, with a pointing towards the reader, b downwards, and c from left to right.

Table IV. Bond lengths (Å) and angles (deg) in the tetraethylammonium ion

N(1)—C(1)	1.516(6)	N(1)—C(3)	1.513(6)
N(1)—C(5)	1.510(6)	N(1)—C(7)	1.507(6)
C(1)—C(2)	1.523(8)	C(3)—C(4)	1.506(7)
C(5)—C(6)	1.503(7)	C(7)—C(8)	1.532(8)
C(1)—N(1)—C(3)	110.6(3)	C(1)—N(1)—C(5)	106.4(3)
C(3)—N(1)—C(5)	110.6(3)	C(1)—N(1)—C(7)	112.1(3)
C(3)—N(1)—C(7)	106.4(3)	C(5)—N(1)—C(7)	110.8(3)
N(1)—C(1)—C(2)	114.0(4)	N(1)—C(3)—C(4)	114.9(4)
N(1)—C(5)—C(6)	115.2(4)	N(1)—C(7)—C(8)	114.9(4)

in the unit cell, the structure looks somewhat alike when viewed from the a and b axial directions (Figure 3).

3.3. COMPARISON WITH RELATED TETRAALKYLAMMONIUM HALIDE HYDRATES

The present $(C_2H_5)_4NCl \cdot 4H_2O$ hydrate displays most of the structural characteristics of its $(CH_3)_4NF \cdot 4H_2O$ analogue which crystallizes in space group $I4_1/a$ [14], yet differs from it in several important aspects. Both salt hydrates consist of tetrahedral R_4N^+ ions accommodated in two channel systems within an open framework of hydrogen-bonded water molecules and halide ions, with neither proton disorder in the O—H···O bonds nor orientational disorder of the alkyl groups. However, the configuration of the $(H_2O)_4F^-$ unit in $(CH_3)_4NF \cdot 4H_2O$ is closer to square planar than to tetrahedral, so that linkage of these flattened tetrahedra by hydrogen bonds in 4_1 spirals generates zigzag chains of junction-sharing chair-like $F(H_2O)_4F$ rings extending in both the a and b axial directions. Within the resulting open water-anion framework, the $(CH_3)_4N^+$ cations lie at the junctions of buckled channels which likewise extend in the a and b directions (see Figure 2 of ref. [14]). These structural features of $(CH_3)_4NF \cdot 4H_2O$ are to be contrasted with (i) the more nearly tetrahedral geometry of the $(H_2O)_4Cl^-$ aggregates, (ii) the *linear* arrangement of *twisted* $Cl(H_2O)_4Cl$ rings extending in *only* the c direction, (iii) the generation of nearly square $(H_2O)_4$ moieties through linkage of neighbouring columnar stacks of $(H_2O)_4Cl^-$ tetrahedra, (iv) the accommodation of the $(C_2H_5)_4N^+$ ions in *straight* channels, and (v) the non-equivalent though somewhat similar views of the structure from the a and b directions in the present $(C_2H_5)_4NCl \cdot 4H_2O$ hydrate. Taking into account the fact that both tetraalkylammonium halide tetrahydrates are inclusion compounds of the channel type and comprise salt-like assemblies of tetrahedral cations and $(H_2O)_4X^-$ aggregates, their lack of structural isomorphism may be attributed to a subtle interplay between molecular ionic sizes and O—H···X bond lengths.

As compared to both $(CH_3)_4NF \cdot 4H_2O$ [14] and the present hydrate, $4(C_2H_5)_4NF \cdot 11H_2O$ [5] differs mainly in that it contains infinite chains of *edge-sharing* $(H_2O)_4F^-$ tetrahedra which are laterally linked by bridging water molecules to form a host framework with structural characteristics approaching those of the clathrate hydrates [15–17]. The crystal structure of this 11/4 hydrate is also well ordered, and the cations likewise occupy the voids in two open channel systems.

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