

# Crystal Structure of Tetraethylammonium Fluoride-Water (4/11), $4(\text{C}_2\text{H}_5)_4\text{N}^+\text{F}^- \cdot 11\text{H}_2\text{O}$ , a Clathrate Hydrate Containing Linear Chains of Edge-Sharing $(\text{H}_2\text{O})_4\text{F}^-$ Tetrahedra and Bridging Water Molecules\*

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**Abstract.** Crystals of  $4(\text{C}_2\text{H}_5)_4\text{N}^+\text{F}^- \cdot 11\text{H}_2\text{O}$  are orthorhombic, space group  $Pna2_1$ , with  $a = 16.130(3)$ ,  $b = 16.949(7)$ ,  $c = 17.493(7)$  Å, and  $Z = 4$ . The structure was shown to be a clathrate hydrate containing infinite chains of edge-sharing  $(\text{H}_2\text{O})_4\text{F}^-$  tetrahedra extending parallel to the  $a$  axis. The chains are laterally linked by bridging water molecules to form a three-dimensional hydrogen-bonded anion/water framework. The ordered  $(\text{C}_2\text{H}_5)_4\text{N}^+$  cations occupy the voids in two open channel systems running in the  $b$  and  $c$  directions. Final  $R_F = 0.091$  for 2278 observed  $\text{MoK}\alpha$  data measured at  $22^\circ\text{C}$ .

**Key words:** Crystal structure, clathrate hydrate, hydrogen bonding, tetraethylammonium fluoride.

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## 1. Introduction

In 1940, Fowler *et al.* described a series of tetra-*n*-butyl and tetra-*i*-amyl ammonium salt hydrates with unusually high hydration numbers [1]. Nearly two decades later, Jeffrey and co-workers initiated an X-ray crystallographic study of these compounds, for example (*i*- $\text{C}_5\text{H}_{11}$ ) $_4\text{NF} \cdot 38\text{H}_2\text{O}$  [2] and (*n*- $\text{C}_4\text{H}_9$ ) $_4\text{NF} \cdot 32.8\text{H}_2\text{O}$  [3], and showed them to be clathrate inclusion compounds based on anionic hydrogen-bonded cageworks constructed from pentagonal dodecahedral  $(\text{H}_2\text{O})_{20}$  structural units with N and F atoms replacing some of the water sites [4].

In the tetramethylammonium salt hydrate series,  $(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$  [5] is a polyhedral clathrate hydrate, whereas  $(\text{CH}_3)_4\text{NF} \cdot 4\text{H}_2\text{O}$  [6] and  $[(\text{CH}_3)_4\text{N}]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  [7] involve less organized two- and one-dimensional water structures, respectively. The monohydrates  $(\text{CH}_3)_4\text{NF} \cdot \text{H}_2\text{O}$  and  $(\text{CH}_3)_4\text{NOH} \cdot \text{H}_2\text{O}$  were demonstrated to contain discrete  $\text{H}_4\text{O}_2\text{X}_2^-$  ( $\text{X} = \text{F}$  or  $\text{OH}$ ) water-anion clusters [8], but the proposed model of a tetrahedral arrangement of electronegative atoms with bridging protons on the four faces [8, 9] is at variance with the existence of centrosymmetric planar cyclic  $(\text{H}_2\text{O} \cdot \text{Cl}^-)_2$  and  $(\text{H}_2\text{O} \cdot \text{Br}^-)_2$  systems in the crystal structures of  $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot \text{H}_2\text{O}$  [10] and  $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]\text{Br} \cdot \text{H}_2\text{O}$  [11], respectively. Other known lower hydrates of tetramethylammonium salts include  $(\text{CH}_3)_4\text{NOH} \cdot 3\text{H}_2\text{O}$ ,  $(\text{CH}_3)_4\text{NOH} \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $(\text{CH}_3)_4\text{NF} \cdot 3\text{H}_2\text{O}$ , for which the infrared absorption bands associated with water-anion complexes have been measured [8].

\* Dedicated to Professor H. M. Powell.

Relatively little is known about quaternary ammonium salt hydrates containing alkyl groups of intermediate sizes. The hexa-, tri- and dihydrates of tetrapropylammonium fluoride have been prepared [12], but no structural data are available apart from the observation that the solid-state infrared spectrum of the hexahydrate is similar to those of  $(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$  and  $(\text{CH}_3)_4\text{NF} \cdot 4\text{H}_2\text{O}$ , and the infrared spectrum of the dihydrate matches those of  $(\text{CH}_3)_4\text{NOH} \cdot \text{H}_2\text{O}$  and  $(\text{CH}_3)_4\text{NF} \cdot \text{H}_2\text{O}$  [12].

In 1977, Harmon and co-workers reported the preparation of penta-, tri-, di-, and monohydrates of tetraethylammonium fluoride and studied the water-anion complex species in these hydrates by deuterium labelling and infrared spectroscopy at  $300^\circ$  and  $10^\circ\text{K}$  [13]. Our crystallization and X-ray stoichiometric study, carried out at about the same time, yielded a hydration number of  $2\frac{1}{2}$  for the crystalline phase (presumably Harmon's trihydrate) which deposited first from a saturated solution of tetraethylammonium fluoride and assigned its space group as *Pbcn* [14]. In view of the notorious difficulty encountered in establishing the exact stoichiometry of this type of hydrate by dehydration methods and chemical analyses [15], we decided to resolve the discrepancy in hydration number via a single-crystal structure determination. As described in the present work, the previously reported 'trihydrate' of tetraethylammonium fluoride [13] should be reformulated as  $4(\text{C}_2\text{H}_5)_4\text{NF} \cdot 11\text{H}_2\text{O}$ , and the correct space group is *Pna2*<sub>1</sub> with a different choice of axes.

## 2. Experimental

Tetraethylammonium fluoride (labelled as a dihydrate) was obtained from Eastman Kodak, and colorless crystals of the  $2\frac{3}{4}$  hydrate were obtained by slow evaporation of a saturated solution in a desiccator charged with drierite. A selected single crystal (*ca.*  $0.4 \times 0.4 \times 0.4$  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 reflection intensities on a Nicolet R3m diffractometer followed the procedures previously described [16], and relevant parameters are summarized in Table I.

The correct stoichiometry and space group was established after several attempts at structure solution by direct methods based on negative quartets [17]. Success was achieved by picking the origin fixing and multiresolution reflections by hand. The 15 independent F and O atoms, which constitute the anionic host lattice, were assigned anisotropic thermal parameters, whereas the N and C atoms of the four cationic guest species in the asymmetric unit were treated isotropically. The methylene and methyl H atoms were generated geometrically (C—H fixed at  $0.96 \text{ \AA}$ ) and allowed to ride on their respective parent C atoms. All but five of the 22 water protons were located from subsequent difference Fourier maps and held stationary in refinement. Isotropic temperature factors (slightly larger than those of the corresponding C atoms) were assigned to all H atoms. Computation details have been noted [16], and the final *R* indices and residual electron-density extrema are listed in Table I.

## 3. Results and Discussion

The final positional parameters for the non-hydrogen atoms are displayed in Table II in accordance with the atom labelling given in Figure 1. The location of most of the water protons in stereochemically reasonable positions strongly indicates an ordered host structure, which may be conveniently described by reference to the hydrogen bonding scheme shown in Table III.

Stereo views of the crystal structure of the  $4(\text{C}_2\text{H}_5)_4\text{NF} \cdot 11\text{H}_2\text{O}$  hydrate along the *c* and

Table I. Data collection and processing parameters

Molecular formula	$4(\text{C}_2\text{H}_5)_4\text{N}^+\text{F}^- \cdot 11\text{H}_2\text{O}$ ( $\text{C}_{32}\text{H}_{102}\text{N}_4\text{O}_{11}\text{F}_4$ )
Molecular weight	795.18
Cell constants	$a = 16.130(3)$ , $b = 16.949(7)$ , $c = 17.493(7)$ Å, $V = 4782(2)$ Å <sup>3</sup> , $Z = 4$
Density (flotation in <i>n</i> -hexane/ $\text{CCl}_4$ )	$1.08 \text{ g cm}^{-3}$
Density (calculated)	$1.104 \text{ g cm}^{-3}$
Space group	$Pna2_1$
Radiation	graphite-monochromatized $\text{MoK}\alpha$ , $\lambda = 0.71069$ Å
Absorption coefficient	$0.85 \text{ cm}^{-1}$
Scan type and speed	$\omega$ - $2\theta$ ; $2.02$ – $8.37 \text{ deg min}^{-1}$
Scan range	$1^\circ$ below $K\alpha_1$ to $1^\circ$ above $K\alpha_2$
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	$h, k, l$ ; $2\theta_{\text{max}} = 50^\circ$
Unique data measured	4391
Observed data with $ F_o  > 3\sigma( F_o )$ , $n$	2278
Number of variables, $p$	327
$R_F = \Sigma F_o  -  F_c  / \Sigma F_o $	0.091
Weighting scheme	$w = [\sigma^2(F_o) + 0.0008 F_o ^2]^{-1}$
$R_{wF} = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2]^{1/2}$	0.090
$S = [\Sigma w( F_o  -  F_c )^2 / (n - p)]^{1/2}$	1.91
Residual extrema in final difference map	0.31 to $-0.34 e\text{Å}^{-3}$

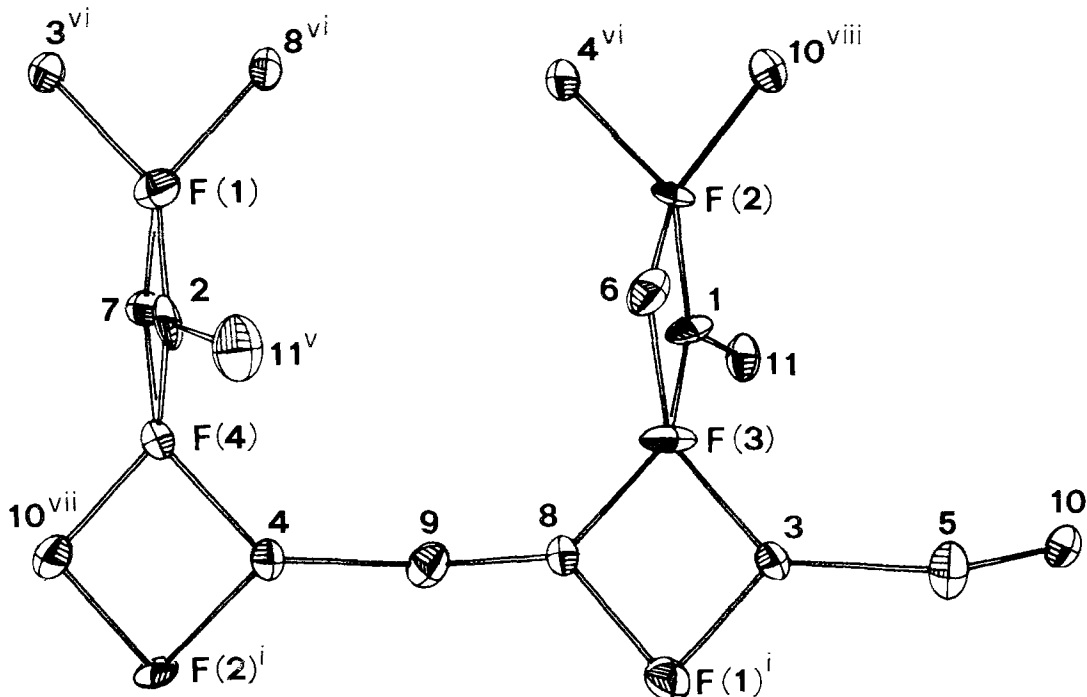


Fig. 1. Perspective view, approximately along the  $c$  axis, of the edge-sharing  $(\text{H}_2\text{O})_4\text{F}^-$  tetrahedra and bridging water molecules. The thermal ellipsoids have been drawn at the 40% probability level and the atoms labelled according to the scheme given in Table III. Hydrogen atoms have been omitted for clarity.

Table II. Fractional coordinates ( $\times 10^4$ ) and thermal parameters<sup>a</sup> ( $\text{\AA}^2 \times 10^3$ ) for non-hydrogen atoms

Atom	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
N(1)	2172(7)	2450(6)	0	37(3)
C(1)	1407(5)	2699(5)	449(5)	41(2)
C(2)	1945(5)	1801(5)	-564(5)	38(2)
C(3)	2860(6)	2218(6)	596(6)	63(3)
C(4)	2464(9)	3134(8)	-426(8)	43(4)
C(5)	1149(8)	2170(8)	1116(7)	93(4)
C(6)	2544(10)	1571(9)	-1118(8)	54(4)
C(7)	3107(8)	2780(8)	1205(8)	93(4)
C(8)	1884(6)	3420(5)	-1044(5)	44(2)
N(2)	2171(7)	7486(6)	-379(4)	42(3)
C(9)	1466(7)	7752(6)	-879(7)	69(3)
C(10)	2466(10)	8136(9)	183(8)	54(5)
C(11)	2881(5)	7198(5)	-859(5)	45(2)
C(12)	1903(6)	6820(6)	111(5)	57(3)
C(13)	1066(6)	7136(6)	-1383(6)	53(3)
C(14)	1841(7)	8365(7)	833(6)	75(3)
C(15)	3208(7)	7788(6)	-1441(6)	62(3)
C(16)	2592(7)	6596(7)	771(6)	73(3)
N(3)	87(4)	5254(4)	2137(4)	38(2)
C(17)	8(10)	4702(8)	1500(10)	63(5)
C(18)	550(7)	5927(7)	1715(7)	84(4)
C(19)	563(6)	4987(7)	2844(7)	73(3)
C(20)	-741(7)	5532(7)	2426(7)	47(4)
C(21)	-453(8)	3985(7)	1704(7)	90(4)
C(22)	695(10)	6552(8)	2385(9)	117(5)
C(23)	1486(7)	4749(6)	2640(6)	66(3)
C(24)	-1321(7)	5754(7)	1926(6)	79(3)
N(4)	109(5)	248(4)	-2451(4)	52(2)
C(25)	-739(10)	409(9)	-2830(10)	85(6)
C(26)	9(9)	-340(8)	-1792(9)	45(4)
C(27)	540(5)	925(5)	-2123(5)	30(2)
C(28)	599(5)	-102(6)	-3133(5)	52(3)
C(29)	-1257(6)	999(6)	-2172(6)	63(3)
C(30)	-314(7)	-1116(7)	-2038(7)	83(4)
C(31)	731(7)	1588(6)	-2618(7)	67(3)
C(32)	1388(8)	-440(8)	-2907(7)	97(4)
F(1)	844(5)	84(5)	187(6)	82(4)
F(2)	822(4)	5082(5)	-488(6)	68(4)
F(3)	3400(3)	4982(4)	-233(4)	88(3)
F(4)	3363(3)	20(3)	-114(4)	67(2)
O(1)	2228(4)	5340(4)	-1307(4)	66(3)
O(2)	2201(4)	317(3)	940(3)	57(2)
O(3)	4650(7)	5972(6)	57(7)	68(4)
O(4)	4625(7)	1025(6)	-390(7)	70(5)
O(5)	4692(9)	7567(6)	623(8)	88(6)
O(6)	1910(4)	4708(4)	602(4)	72(3)
O(7)	1995(4)	-259(4)	-930(4)	52(2)
O(8)	4585(7)	3914(5)	-50(6)	62(4)
O(9)	4768(8)	2576(7)	-926(8)	85(5)
O(10)	4555(8)	8988(6)	-203(8)	85(5)
O(11)	2525(11)	6139(3)	-2677(8)	79(2)

<sup>a</sup> Form of isotropic temperature factor for C and N atoms:  $\exp(-8\pi^2 U_{\text{iso}} \sin^2 \theta / \lambda^2)$ .  $U_{\text{eq}}$  (for F and O atoms) is equivalent isotropic temperature factor calculated as one-third of the trace of the  $U_{ij}$  matrix.

Table III. Scheme of hydrogen bonding, bond distances (Å), and bond angles (deg) in the anionic host lattice<sup>a</sup>

## (a) Scheme of hydrogen bonding

Water oxygen atom	Donor bonds to	Acceptor bonds from
O(1)	F(2), F(3)	O(11)
O(2)	F(1), F(4)	O(11) <sup>v</sup>
O(3)	F(1) <sup>i</sup> , F(3)	O(5)
O(4)	F(2) <sup>j</sup> , F(4)	O(9)
O(5)	O(3), O(10)	
O(6)	F(2), F(3)	
O(7)	F(1), F(4)	
O(8)	F(1) <sup>i</sup> , F(3)	O(9)
O(9)	O(4), O(8)	
O(10)	F(2) <sup>iii</sup> , F(4) <sup>ii</sup>	O(5)
O(11)	O(1), O(2) <sup>iv</sup>	

## (b) Hydrogen bond lengths

F(1)···O(2)	2.586	F(1)···O(3) <sup>vi</sup>	2.639
F(1)···O(7)	2.758	F(1)···O(8) <sup>vi</sup>	2.680
F(2)···O(1)	2.718	F(2)···O(4) <sup>vi</sup>	2.697
F(2)···O(6)	2.669	F(2)···O(10) <sup>viii</sup>	2.628
F(3)···O(1)	2.734	F(3)···O(3)	2.671
F(3)···O(6)	2.851	F(3)···O(8)	2.652
F(4)···O(2)	2.676	F(4)···O(7)	2.670
F(4)···O(4)	2.698	F(4)···O(10) <sup>vii</sup>	2.605
O(5)···O(3)	2.881	O(5)···O(10)	2.816
O(9)···O(4)	2.801	O(9)···O(8)	2.752
O(11)···O(1)	2.794	O(11)···O(2) <sup>iv</sup>	2.826

## (c) Hydrogen bond angles

O(2)···F(1)···O(3) <sup>vi</sup>	140.0	O(2)···F(1)···O(7)	79.8
O(2)···F(1)···O(8) <sup>vi</sup>	128.6	O(3) <sup>vi</sup> ···F(1)···O(7)	106.7
O(3) <sup>vi</sup> ···F(1)···O(8) <sup>vi</sup>	82.2	O(7)···F(1)···O(8) <sup>vi</sup>	122.3
O(1)···F(2)···O(4) <sup>vi</sup>	137.9	O(1)···F(2)···O(6)	82.3
O(1)···F(2)···O(10) <sup>viii</sup>	130.7	O(4) <sup>vi</sup> ···F(2)···O(6)	105.1
O(4) <sup>vi</sup> ···F(2)···O(10) <sup>viii</sup>	81.3	O(6)···F(2)···O(10) <sup>viii</sup>	121.6
O(1)···F(3)···O(3)	120.9	O(1)···F(3)···O(6)	78.8
O(1)···F(3)···O(8)	137.1	O(3)···F(3)···O(6)	129.9
O(3)···F(3)···O(8)	82.1	O(6)···F(3)···O(8)	115.7
O(2)···F(4)···O(4)	122.2	O(2)···F(4)···O(7)	79.8
O(2)···F(4)···O(10) <sup>vii</sup>	133.2	O(4)···F(4)···O(7)	129.8
O(4)···F(4)···O(10) <sup>vii</sup>	81.7	O(7)···F(4)···O(10) <sup>vii</sup>	117.3
F(2)···O(1)···F(3)	100.3	F(2)···O(1)···O(11)	132.3
F(3)···O(1)···O(11)	125.4	F(1)···O(2)···F(4)	102.3
F(1)···O(2)···O(11) <sup>v</sup>	130.1	F(4)···O(2)···O(11) <sup>v</sup>	125.0
F(1) <sup>i</sup> ···O(3)···F(3)	98.1	F(1) <sup>i</sup> ···O(3)···O(5)	126.2
F(3)···O(3)···O(5)	132.2	F(2) <sup>j</sup> ···O(4)···F(4)	96.5
F(2) <sup>j</sup> ···O(4)···O(9)	125.0	F(4)···O(4)···O(9)	135.6
O(3)···O(5)···O(10)	128.6	F(2)···O(6)···F(3)	98.6
F(1)···O(7)···F(4)	98.0	F(1) <sup>j</sup> ···O(8)···F(3)	97.6
F(1) <sup>i</sup> ···O(8)···O(9)	121.8	F(3)···O(8)···O(9)	125.0
O(4)···O(9)···O(8)	125.3	F(2) <sup>iii</sup> ···O(10)···F(4) <sup>ii</sup>	100.5
F(2) <sup>iii</sup> ···O(10)···O(5)	123.3	F(4) <sup>ii</sup> ···O(10)···O(5)	126.9
O(1)···O(11)···O(2) <sup>iv</sup>	121.5		

Symmetry transformations: <sup>i</sup>  $\frac{1}{2} + x, \frac{1}{2} - y, z$ ; <sup>ii</sup>  $x, 1 + y, z$ ; <sup>iii</sup>  $\frac{1}{2} + x, 1\frac{1}{2} - y, z$ ; <sup>iv</sup>  $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$ ; <sup>v</sup>  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$ ; <sup>vi</sup>  $-\frac{1}{2} + x, \frac{1}{2} - y, z$ ; <sup>vii</sup>  $x, -1 + y, z$ ; <sup>viii</sup>  $-\frac{1}{2} + x, 1\frac{1}{2} - y, z$ .

<sup>a</sup> Estimated standard deviations: about 0.007 Å for F···O, 0.010 Å for O···O, 0.4° for O···F···O, 0.6° for F···O···O and 0.09° for O···O···O.

$b$  axial directions are presented in Figures 2 and 3, respectively. As illustrated in Figure 1, the four independent fluoride ions are each tetrahedrally coordinated, and the resulting  $(\text{H}_2\text{O})_4\text{F}^-$  tetrahedra share pairs of opposite edges to form  $[(\text{H}_2\text{O})_2\text{F}^-]_\infty$  infinite chains

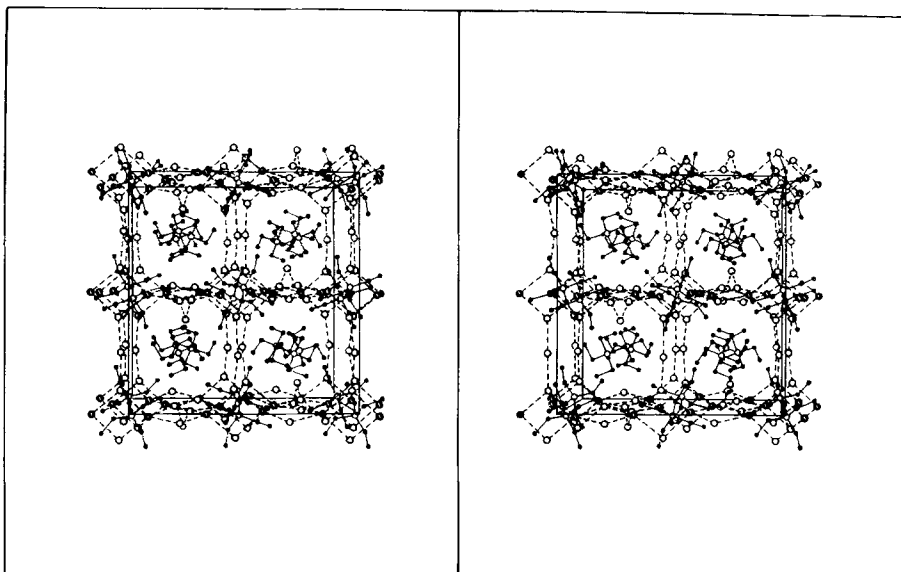


Fig. 2. Stereo drawing of the crystal structure of  $4(\text{C}_2\text{H}_5)_4\text{NF} \cdot 11\text{H}_2\text{O}$  viewed parallel to  $c$ . The origin of the unit cell lies at the lower left corner, with  $a$  pointing from left to right,  $b$  upwards, and  $c$  towards the reader. Hydrogen atoms have been omitted for clarity, and atom types are distinguished by size and shading. Broken lines represent hydrogen bonds.

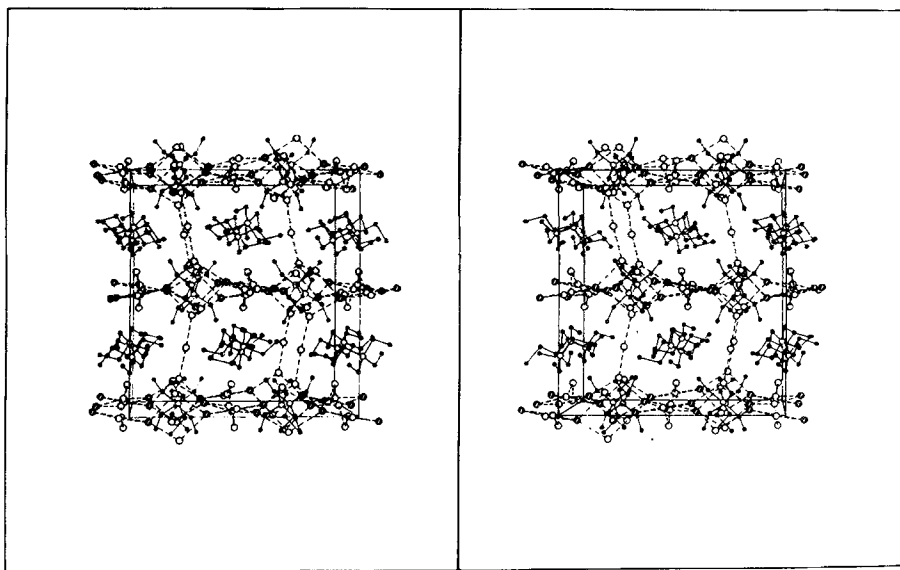


Fig. 3. Stereo drawing of the crystal structure viewed parallel to  $b$ . The unit-cell origin lies at the upper left corner, with  $a$  pointing from left to right,  $b$  towards the reader, and  $c$  upwards.

running through the structure in the direction of the  $a$  axis. These chains are cross linked through O(5), O(9) and O(11) to give a three-dimensional water-anion framework. Of the 11 crystallographically distinct water molecules, six are three-coordinate and the rest, including the three that serve bridging functions, are two-coordinate; consequently all water protons are fully utilized in consolidating the hydrogen-bonded host lattice.

When viewed down the  $c$  (Figure 2) and  $b$  axes (Figure 3), the structure is seen to possess two open channels extending parallel to the respective axial directions, each accommodating half of the ordered  $(C_2H_5)_4N^+$  cations. It is worth noting that whereas adjacent  $[(H_2O)_2F^-]_\infty$  chains are fully bridged by water molecules O(5) and O(9) to form hydrogen-bonded layers parallel to (001) (Figure 2), only half as many bridging  $O\cdots H-O$  hydrogen bonds [involving O(11)] exist in layers parallel to (010) (Figure 3). The close approach of two alkyl groups of neighboring cations (Figure 3) is seen to preclude the incorporation of an additional bridging water molecule which, if present, would correspond to a simpler stoichiometry for the present hydrate and render the two channel systems more nearly alike. The columnar stacks of  $(C_2H_5)_4N^+$  cations in each channel are partitioned by protrusions caused by the bridging water molecules, such that each cation may be regarded as occupying a cavity sandwiched by a pair of diamond-shaped  $(H_2O \cdot F^-)_2$  moieties (Figure 2 and 3).

It is of interest to compare the structure of the present clathrate hydrate with that of  $(CH_3)_4NF \cdot 4H_2O$ , which has a different hydrogen-bonded water-anion framework [ $F\cdots H-O = 2.630(2)$ ,  $O\cdots H-O = 2.732(2)$  Å] composed of four-coordinate fluoride ions and three-coordinate, almost trigonal planar water molecules [6]. In the tetrahydrate, considerably flattened  $(H_2O)_4F^-$  tetrahedra lying along  $\bar{4}$  axes are each connected to four others via pairs of  $O\cdots H-O$  hydrogen bonds to form a buckled network of chair-shaped  $F(H_2O)_4F$  hexagons related by fourfold screw spirals (see Figure 2 of ref. [6]). The  $(CH_3)_4N^+$  cations, each sandwiched by a pair of  $(H_2O)_4F^-$  tetrahedra lying alternately along the same  $\bar{4}$  axis, are located at the intersections of buckled channels extending in the  $a$  and  $c$  axial directions.

The tetramethyl- and tetraethylammonium fluoride hydrates differ mainly in the linkage mode of the  $(H_2O)_4F^-$  structural units, and in the occurrence of bridging water molecules only in the latter structure. Both feature water-anion host lattices containing two-dimensional channel systems for the accommodation of guest  $R_4N^+$  cations, and there is no evidence of proton disorder in the hydrogen bonds and orientational disorder of the alkyl groups. An interesting pattern emerges when the structural characteristics of these two hydrates are compared with those of related salt hydrates. The sequence  $[(CH_3)_4N]_2SO_4 \cdot 4H_2O$  [7],  $(CH_3)_4NF \cdot 4H_2O$  [6],  $4(C_2H_5)_4NF \cdot 11H_2O$  (this work),  $(CH_3)_4NOH \cdot 5H_2O$  [5] and  $HMF_6 \cdot HF \cdot 5H_2O$  (M = P, As, and Sb) [18, 19] illustrates an increasing trend of water-anion hydrogen bonding to yield a more organized host framework. The isostructural  $HMF_6 \cdot HF \cdot 5H_2O$  acid hydrates, for many years incorrectly described as  $HMF_6 \cdot 6H_2O$  [20], have been shown to be polyhedral clathrates in which disordered  $MF_6^-$  ions are encaged in a fully hydrogen-bonded cationic host lattice built of close-packed truncated octahedra [21, 22] whose common vertices correspond to randomly distributed  $H_2O$ ,  $H_3O^+$ , and HF molecules [19]. The  $(CH_3)_4NOH \cdot 5H_2O$  basic hydrate has a very similar structure, except that the host lattice is anionic and three edges of each truncated octahedra are cleaved to provide more room for the relatively bulky  $(CH_3)_4N^+$  cation, which behaves as a slightly hindered axial rotor [5]. In  $[(CH_3)_4N]_2SO_4 \cdot 4H_2O$ , at the other end of the sequence, the water molecules are hydrogen bonded into puckered hexagons which form infinite chains by sharing pairs of opposite edges. The chains are cross linked by interaction with disordered  $SO_4^{2-}$  anions, generating channels which accommodate the ordered  $(CH_3)_4N^+$  cations [7]. Between this one-dimensional channel structure and the polyhedral clathrates lie the two

tetraalkylammonium fluoride hydrates. In  $(\text{CH}_3)_4\text{NF} \cdot 4\text{H}_2\text{O}$ , discrete  $(\text{CH}_3)_4\text{N}^+$  and  $(\text{H}_2\text{O})_4\text{F}^-$  species are clearly discernible, and the stacked columns of alternate ions are laterally linked by hydrogen bonds between vertices of neighboring  $(\text{H}_2\text{O})_4\text{F}^-$  tetrahedra. The salt-like assembly of ions, which dominates the  $[(\text{CH}_3)_4\text{N}]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  and  $(\text{CH}_3)_4\text{NF} \cdot 4\text{H}_2\text{O}$  structures, becomes less prominent in the  $4(\text{C}_2\text{H}_5)_4\text{NF} \cdot 11\text{H}_2\text{O}$  clathrate hydrate. Indeed the present host lattice, constructed from linear chains of edge-sharing  $(\text{H}_2\text{O})_4\text{F}^-$  tetrahedra and lateral bridging water molecules, furnishes a unique example of a two-dimensional channel framework with structural characteristics closely approaching that of a three-dimensional cagework.

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