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Tetraethylammonium Acetate Tetrahydrate, $(C_2H_5)_4N^+CH_3COO^- \cdot 4H_2O$, a Layer Structure with Cations Sandwiched Between Nets of Puckered Polygons Formed by Hydrogen-Bonded Anions and Water Molecules★

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Abstract. Crystals of $(C_2H_5)_4N^+CH_3COOO^- \cdot 4H_2O$ crystallize in space group $P\bar{1}$, with $a = 12.327(2)$, $b = 17.196(6)$, $c = 8.753(3)$ Å, $\alpha = 94.28(2)$, $\beta = 91.09(2)$, $\gamma = 120.30(2)°$, and $Z = 4$. The structure was solved by direct methods and refined to $R_F = 0.060$ for 4803 Mo$K\alpha$ data. In the crystal structure, ordered $(C_2H_5)_4N^+$ cations are sandwiched between puckered layers of hydrogen-bonded water molecules and acetate anions. Each water-anion layer is constructed from an edge-sharing assembly of six independent, irregular, and non-planar polygons (two nonagons, two hexagons and two pentagons). All protons in the scheme of hydrogen bonding are uniquely located.

Key words: Crystal structure, layer structure, hydrate, hydrogen bonding, tetraethylammonium acetate.

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1. Introduction

X-ray crystallographic studies have revealed that tetraalkylammonium salt hydrates of the general formula $R_4N^+X^- \cdot nH_2O$ exist in a wide variety of stoichiometries and structures [1–3]. About a quarter century ago, $(i\text{-}C_5H_{11})_4NF \cdot 38H_2O$ [4] and $(n\text{-}C_4H_9)_4NF \cdot 32.8H_2O$ [5] were found to be clathrate hydrates, with the bulky cations occupying cavities in a hydrogen-bonded water-anion lattice constructed from a packing of pentagonal dodecahedra. In the tetramethylammonium salt hydrate series, $(CH_3)_4NOH \cdot 5H_2O$ is also a clathrate hydrate based on a water-anion host lattice generated from a close packing of truncated octahedra (each with three cleaved edges) [6], whereas $(CH_3)_4NF \cdot 4H_2O$ [7] and $[(CH_3)_4N]_2SO_4 \cdot 4H_2O$ [8] involve less organized two- and one-dimensional water structures, respectively. After almost a decade of inactivity, crystallographic studies on quaternary ammonium salt hydrates containing alkyl groups of intermediate sizes began to make their appearance. The existence of the hitherto unknown centrosymmetric planar cyclic $(H_2O \cdot Cl^-)_2$ system was found in the crystal structure of $(C_2H_5)_4NCl \cdot H_2O$ [9], and very recently we described $4(C_2H_5)_4NF \cdot 11H_2O$ as a clathrate hydrate containing linear chains of edge-sharing $(H_2O)_4F^-$ tetrahedra and bridging water molecules [10]. In an effort to

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★ Dedicated to Professor G. A. Jeffrey on the occasion of his retirement.

extend our studies through the employment of molecular anions, we have determined the crystal structure of the title compound as described in the present work. The crystal data [11] and a preliminary communication [12] have appeared previously.

2. Experimental

Tetraethylammonium acetate tetrahydrate was obtained from Eastman Kodak, and crystals suitable for diffraction work were obtained by slow evaporation of a saturated solution in a desiccator charged with drierite. A selected crystal (*ca.* 0.4 × 0.4 × 0.3 mm) was covered with petroleum jelly and sealed in a 0.5 mm Lindemann glass capillary. Crystal data and intensity measurements on a Nicolet R3m diffractometer followed the procedures described [13], and relevant parameters are summarized in Table I.

Table I. Data collection and processing parameters

Molecular formula	$(C_2H_5)_4N^+CH_3COO^- \cdot 4H_2O$ $(C_{10}H_{31}NO_6)$
Molecular weight	261.36
Cell constants	a = 12.327(2) Å α = 94.28(2)°
	b = 17.196(6) β = 91.09(2)°
	c = 8.753(3) γ = 120.30(2)°
	V = 1594.0(8) Å^3 Z = 4
Density (flotation in *n*-hexane/CCl_4)	1.086 g cm^{-3}
Density (calculated)	1.089 g cm^{-3}
Space group	$P\bar{1}$
Radiation	graphite-monochromatized Mo$K\alpha$, λ = 0.71069 Å
Absorption coefficient	0.82 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	$h, \pm k, \pm l$; $2\theta_{max} = 54°$
Unique data measured	6999
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$, n	4803
Number of variable, p	337
$R_F = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.060
Weighting scheme	$w = [\sigma^2(F_o) + 0.0008 \lvert F_o \rvert^2]^{-1}$
$R_{wF} = \{\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2\}^{1/2}$	0.069
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(n - p)]^{1/2}$	1.92
Residual extrema in final difference map	0.19 to −0.17 eÅ^{-3}

The structure was solved by direct phase determination guided by negative quartets [14]. All non-hydrogen atoms in the asymmetric unit (which comprises two cations, two anions, and eight water molecules) were assigned anisotropic thermal parameters. The methylene and methyl H atoms were generated geometrically (C—H fixed at 0.96 Å); the former were allowed to ride on their respective parent C atoms, and the methyl groups were treated as rigid groups. All 16 water protons were located from a subsequent difference Fourier map and held stationary in least-squares cycles. Isotropic temperature factors (slightly larger than those of the corresponding parent C and O atoms) were assigned to the H atoms.

Computations were performed on a Data General Nova 3/12 minicomputer using the SHELXTL program package [15]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [16]. Blocked-cascade least-squares refinement [17] 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

The final positional and thermal parameters are displayed in Table II in accordance with the atom labelling given in Figure 1. The location of all 16 water protons in stereochemically plausible positions indicates an ordered layer structure, which may be conveniently described by reference to the hydrogen bonding scheme shown in Table III.

A stereo drawing of the crystal structure of the $(C_2H_5)_4N^+CH_3COO^- \cdot 4H_2O$ hydrate viewed along the c axis is illustrated in Figure 2. The acetate and water O atoms are linked by hydrogen bonds to form puckered layers parallel to (010), with the $(C_2H_5)_4N^+$ ions located in between every pair of adjacent layers. The whole structure is well ordered, and the thermal

Table II. Fractional coordinates ($\times$ 10^4) and thermal parameters[a] ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}/U_{iso}
(*a*) *Tetraethylammonium ions*				
N(1)	2433(1)	4986(1)	2864(2)	49(1)
C(1)	1028(2)	4344(1)	2668(2)	60(1)
C(2)	2848(2)	5703(1)	1749(2)	63(1)
C(3)	3035(2)	4415(1)	2581(3)	58(1)
C(4)	2824(2)	5488(2)	4453(2)	71(1)
C(5)	230(2)	4779(2)	2792(3)	89(2)
C(6)	2559(3)	5349(2)	75(3)	91(2)
C(7)	4451(2)	4930(2)	2610(4)	89(1)
C(8)	2457(3)	4897(2)	5765(3)	91(2)
N(2)	2425(1)	−42(1)	2553(2)	46(1)
C(9)	1076(2)	−812(1)	2318(3)	66(1)
C(10)	2788(2)	541(1)	1224(2)	62(1)
C(11)	3235(2)	−470(1)	2697(3)	66(1)
C(12)	2613(2)	586(1)	3967(2)	57(1)
C(13)	103(2)	−535(2)	2191(4)	101(2)
C(14)	2676(3)	54(2)	−326(3)	105(2)
C(15)	4632(2)	186(2)	2888(4)	88(1)
C(16)	2283(3)	139(2)	5446(3)	88(2)
(*b*) *Acetate ions*				
O(1)	8921(2)	2608(1)	5501(2)	89(1)
O(2)	7246(2)	2623(1)	4681(2)	85(1)
C(17)	8121(2)	2478(1)	4472(2)	52(1)
C(18)	8222(2)	2119(2)	2899(2)	66(1)
H(18A)	8899	2003	2752	100
H(18B)	7434	1579	2589	100
H(18C)	8326	2592	2291	100
O(3)	3900(1)	2619(1)	6472(2)	74(1)
O(4)	2447(1)	2892(1)	7338(2)	82(1)
C(19)	3307(2)	2721(1)	7525(2)	54(1)
C(20)	3661(2)	2651(2)	9140(2)	75(1)
H(20A)	4009	3250	9649	100
H(20B)	4276	2466	9191	100
H(20C)	2928	2239	9636	100
(*c*) *Water molecules*				
O(5)	3898(1)	2872(1)	3418(2)	71(1)
H(5′)	3783	2863	4451	100
H(5″)	3080	2575	2951	100
O(6)	1322(2)	1869(1)	1967(2)	86(1)
H(6′)	1035	2014	2902	100
H(6″)	1168	2178	1389	100
O(7)	812(2)	2284(2)	4795(2)	100(1)
H(7′)	159	2469	5171	100
H(7″)	1434	2510	5663	100
O(8)	958(1)	2819(1)	9685(2)	72(1)
H(8′)	1330	2847	8843	100
H(8″)	353	2910	9262	100
O(9)	8992(2)	3055(1)	8641(2)	80(1)
H(9′)	8938	2977	7620	100
H(9″)	8100	2746	8930	100
O(10)	6479(2)	2016(1)	9591(2)	97(1)
H(10′)	6038	2039	8658	100
H(10″)	6149	2203	10371	100
O(11)	5826(2)	2648(1)	2243(2)	86(1)
H(11′)	5228	2799	2653	100
H(11″)	6384	2768	3157	100
O(12)	5389(1)	1869(1)	6745(2)	73(1)
H(12′)	6020	2212	6045	100
H(12″)	4998	2189	6583	100

[a] Equivalent isotropic temperature factor U_{eq} for non-hydrogen atoms calculated as one-third of the trace of the orthogonalized U_{ij} matrix; form of isotropic temperature factor for hydrogen atoms: $\exp(-8\pi^2 U_{iso} \sin^2 \theta/\lambda^2)$.

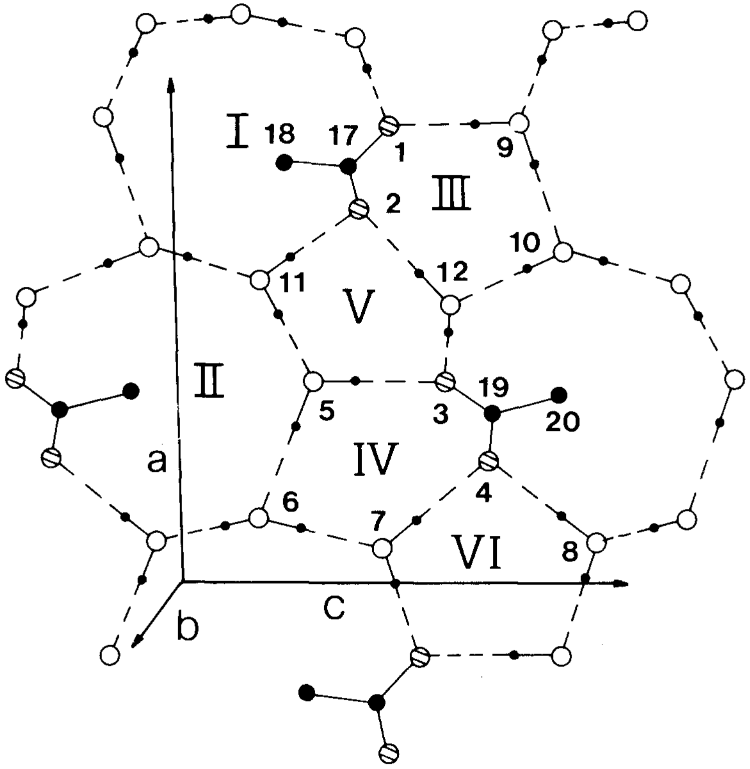

Fig. 1. Water molecules and acetate ions linked by hydrogen bonds into a puckered layer parallel to (010). The water oxygen, acetate oxygen, and carbon atoms are represented by open, half-shaded, and blackened circles, respectively. In this simplified drawing, the ordered water protons, as represented by black dots, are placed on the O···O lines, and the methyl hydrogen atoms have been omitted. The atom and polygon labels correspond to those given in Tables II and III.

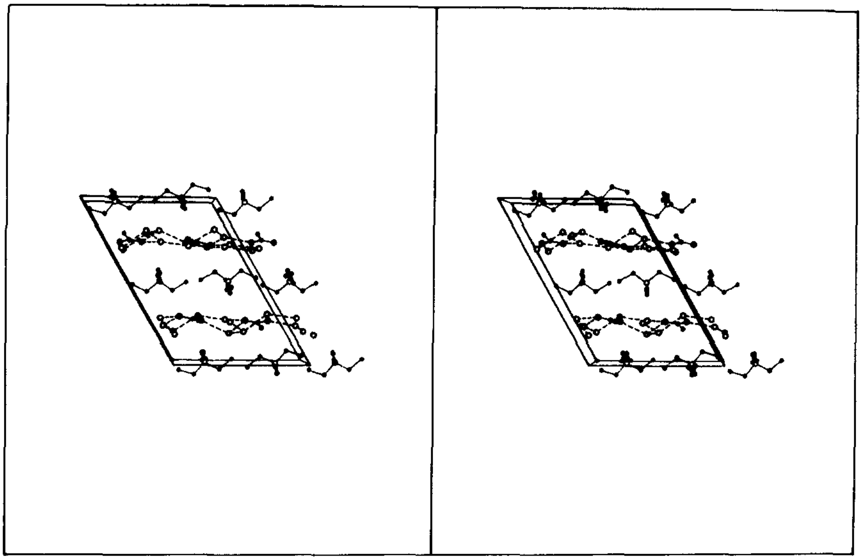

Fig. 2. Stereo drawing of the crystal structure of $(C_2H_5)_4N^+ CH_3COO^- \cdot 4H_2O$. The origin of the unit cell lies at the lower left corner, with *a* pointing from left to right, *b* upwards at a slant, and *c* towards the reader. Hydrogen atoms have been omitted for clarity, and atom types are distinguished by size and shading. Broken lines represent hydrogen bonds.

Table III. Scheme of hydrogen bonding, bond distances (Å), bond angles (deg), and torsion angles (deg) in the water-anion layer structure.[a]

(a) Scheme of hydrogen bonding

Water oxygen atoms	Donor bonds to	Acceptor bonds from
O(5)	O(3), O(6)	O(11)
O(6)	O(7), O(8)$^{\text{i}}$	O(5)
O(7)	O(1)$^{\text{ii}}$, O(4)	O(6)
O(8)	O(4), O(9)$^{\text{ii}}$	O(6)$^{\text{iii}}$
O(9)	O(1), O(10)	O(8)$^{\text{iv}}$
O(10)	O(1)$^{\text{iii}}$, O(12)	O(9)
O(11)	O(2), O(5)	O(10)$^{\text{i}}$
O(12)	O(2), O(3)	O(10)

(b) Hydrogen bond lengths

O(1)···O(7)$^{\text{iv}}$	2.728	O(1)···O(9)	2.786
O(2)···O(11)	2.751	O(2)···O(12)	2.775
O(3)···O(5)	2.741	O(3)···O(12)	2.740
O(4)···O(7)	2.732	O(4)···O(8)	2.749
O(5)···O(6)	2.944	O(5)···O(11)	2.795
O(6)···O(7)	2.698	O(6)···O(8)$^{\text{i}}$	2.837
O(8)···O(9)$^{\text{ii}}$	2.799	O(9)···O(10)	2.866
O(10)···O(11)$^{\text{iii}}$	2.792	O(10)···O(12)	2.741

(c) Hydrogen bond angles

C(17)—O(1)···O(7)$^{\text{iv}}$	119.2	C(17)—O(1)···O(9)	129.2
C(17)—O(2)···O(11)	121.0	C(17)—O(2)···O(12)	127.5
C(19)—O(3)···O(5)	131.5	C(19)—O(3)···O(12)	124.5
C(19)—O(4)···O(7)	124.3	C(19)—O(4)···O(8)	121.1
O(7)$^{\text{iv}}$···O(1)···O(9)	111.4	O(11)···O(2)···O(12)	99.4
O(5)···O(3)···O(12)	103.7	O(7)···O(4)···O(8)	103.1
O(3)···O(5)···O(6)	110.9	O(3)···O(5)···O(11)	106.2
O(6)···O(5)···O(11)	121.5	O(7)···O(6)···O(8)$^{\text{i}}$	113.2
O(5)···O(6)···O(8)$^{\text{i}}$	112.1	O(5)···O(6)···O(7)	80.9
O(1)$^{\text{ii}}$···O(7)···O(4)	106.7	O(1)$^{\text{ii}}$···O(7)···O(6)	126.6
O(4)···O(7)···O(6)	124.9	O(4)···O(8)···O(9)$^{\text{ii}}$	110.8
O(4)···O(8)···O(6)	107.3	O(6)···O(8)···O(9)$^{\text{ii}}$	136.2
O(1)···O(9)···O(10)	107.5	O(1)···O(9)···O(8)$^{\text{iv}}$	100.3
O(8)$^{\text{iv}}$···O(9)···O(10)	122.5	O(11)$^{\text{iii}}$···O(10)···O(12)	122.1
O(9)···O(10)···O(11)$^{\text{iii}}$	118.7	O(9)···O(10)···O(12)	93.6
O(2)···O(11)···O(5)	108.0	O(2)···O(11)···O(10)$^{\text{i}}$	107.5
O(5)···O(11)···O(10)$^{\text{i}}$	142.0	O(2)···O(12)···O(3)	107.2
O(2)···O(12)···O(10)	109.5	O(3)···O(12)···O(10)	117.9

(d) Torsion angles

Nonagon I			
O(1)—C(17)—O(2)···O(11)	167.4	C(17)—O(2)···O(11)···O(10)$^{\text{i}}$	9.6
O(2)···O(11)···O(10)$^{\text{i}}$···O(9)$^{\text{i}}$	− 64.7	O(11)···O(10)$^{\text{i}}$···O(9)$^{\text{i}}$···O(8)$^{\text{v}}$	88.5
O(10)$^{\text{i}}$···O(9)$^{\text{i}}$···O(8)$^{\text{v}}$···O(6)$^{\text{iv}}$	− 9.9	O(9)$^{\text{i}}$···O(8)$^{\text{v}}$···O(6)$^{\text{iv}}$···O(7)$^{\text{iv}}$	− 54.7
O(8)$^{\text{v}}$···O(6)$^{\text{iv}}$···O(7)$^{\text{iv}}$···O(1)	37.8	O(6)$^{\text{iv}}$···O(7)$^{\text{iv}}$···O(1)—C(17)	7.3
O(7)$^{\text{iv}}$···O(1)—C(17)—O(2)	− 178.6		
Nonagon II			
O(3)—C(19)—O(4)···O(8)	169.7	C(19)—O(4)···O(8)···O(6)$^{\text{iii}}$	− 15.3
O(4)···O(8)···O(6)$^{\text{iii}}$···O(5)$^{\text{iii}}$	66.3	O(8)···O(6)$^{\text{iii}}$···O(5)$^{\text{iii}}$···O(11)$^{\text{iii}}$	− 89.8
O(6)$^{\text{iii}}$···O(5)$^{\text{iii}}$···O(11)$^{\text{iii}}$···O(10)	18.6	O(5)$^{\text{iii}}$···O(11)$^{\text{iii}}$···O(10)···O(12)	21.7
O(11)$^{\text{iii}}$···O(10)···O(12)···O(3)	9.8	O(10)···O(12)···O(3)—C(19)	− 27.7
O(12)···O(3)—C(19)—O(4)	− 165.2		

Table III (continued)

Hexagon III			
O(1)—C(17)—O(2)···O(12)	−58.1	C(17)—O(2)···O(12)···O(10)	49.3
O(2)···O(12)···O(10)···O(9)	5.2	O(12)···O(10)···O(9)···O(1)	−26.5
O(10)···O(9)···O(1)—C(17)	40.6	O(9)···O(1)—C(17)—O(2)	7.8
Hexagon IV			
O(3)—C(19)—O(4)···O(7)	32.7	C(19)—O(4)···O(7)···O(6)	−26.9
O(4)···O(7)···O(6)···O(5)	−14.7	O(7)···O(6)···O(5)···O(3)	33.0
O(6)···O(5)···O(3)—C(19)	−53.2	O(5)···O(3)—C(19)—O(4)	7.5
Pentagon V			
O(2)···O(12)···O(3)···O(5)	34.0	O(12)···O(3)···O(5)···O(11)	−13.3
O(3)···O(5)···O(11)···O(2)	−11.6	O(5)···O(11)···O(2)···O(12)	30.8
O(11)···O(2)···O(12)···O(3)	−40.0		
Pentagon VI			
O(4)···O(8)···O(9)^{ii}···O(1)^{ii}	20.5	O(8)···O(9)^{ii}···O(1)^{ii}···O(7)	−4.4
O(9)^{ii}···O(1)^{ii}···O(7)···O(4)	−12.8	O(1)^{ii}···O(7)···O(4)···O(8)	24.4
O(7)···O(4)···O(8)···O(9)^{ii}	−28.8		

Symmetry transformations: ^{i} $x, y, -1 + z$; ^{ii} $-1 + x, y, z$;
^{iii} $x, y, 1 + z$; ^{iv} $1 + x, y, z$;
^{v} $1 + x, y, -1 + z$.

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[a] Estimated standard deviations of individual hydrogen bond lengths, bond angles, and torsion angles are 0.004 Å, 0.2°, and 0.5° respectively.

vibrational parameters of the atoms in the cations are not significantly different from those of the atoms which constitute the layer (Table II). As shown in Figure 1, each water-anion layer is constructed from a combination of O—H···O hydrogen bonds and C—O covalent bonds (bond order = 1.5), generating a set of six independent, irregular, and non-planar polygons which may be likened to the pieces in a jigsaw puzzle. The methyl group of each independent acetate ion points approximately towards the center of a nonagon. All O atoms are three-coordinate, with full utilization of the ordered water protons in consolidating the hydrogen-bonded layer structure. The bonding configurations about the O(1), O(3), O(7) and O(11) atoms are virtually planar. It is further noted that the nonagons I and II share edges to form a infinite zigzag chain extending in the direction of the *a* axis; the hexagons III and IV and pentagons V and VI together constitute a similar chain, and alternation of these two series of parallel chains in the *c* direction gives rise to a two-dimensional array (Figure 1). Puckering of this water-anion layer is described quantitatively by the torsion angles listed in Table III and illustrated in Figure 3, which also shows the non-linearity of the O—H···O hydrogen bonds.

The hydrogen bonding distances and angles vary over an unusually wide range (Table III). Interestingly, the water oxygen O(6) atom, which exhibits the most pyramidal bonding configuration (sum of the three valence angles about it is 306.2°, as compared to corresponding values of over 330° for the other water oxygen atoms), is associated with the shortest (2.698 Å) and longest (2.944 Å) O···O hydrogen bond lengths as well as the smallest O···O···O bond angle (80.9°). The measured dimensions of the crystallographically distinct $(C_2H_5)_4N^+$ and CH_3COO^- ions (Table IV) are quite regular except for some of the C—N—C angles, which are presumably more susceptible to distortion in a tight fitting of the cations between the water-anion layers.

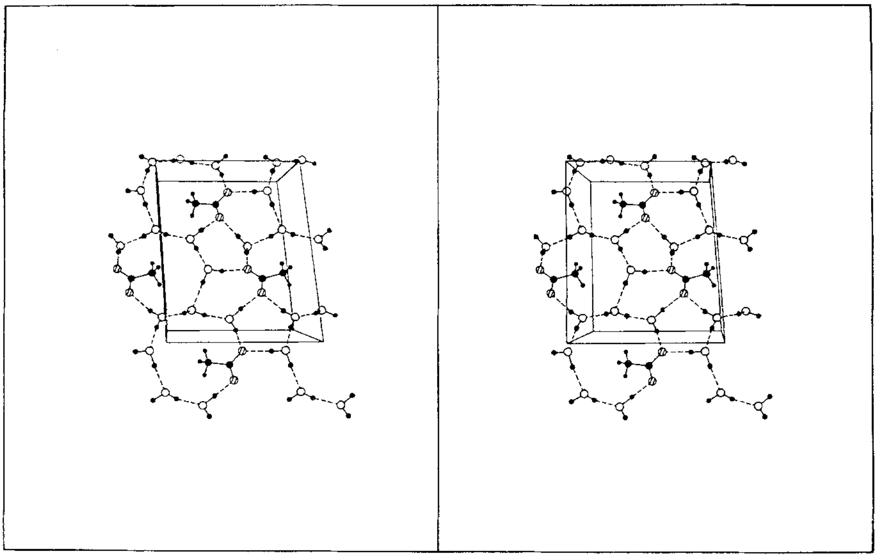

Fig. 3. Stereo drawing showing the extent of puckering in a water-anion layer and the non-linearity of the O—H···O hydrogen bonds.

Table IV. Bond distances (Å) and angles (deg) in the four independent tetraethylammonium and acetate ions

N(1)—C(1)	1.510(2)	N(1)—C(2)	1.516(3)	C(1)—N(1)—C(2)	110.8(2)	C(1)—N(1)—C(3)	106.4(1)
N(1)—C(3)	1.512(3)	N(1)—C(4)	1.513(2)	C(2)—N(1)—C(3)	111.3(2)	C(1)—N(1)—C(4)	111.3(2)
C(1)—C(5)	1.507(5)	C(2)—C(6)	1.507(3)	C(2)—N(1)—C(4)	106.2(1)	C(3)—N(1)—C(4)	111.0(2)
C(3)—C(7)	1.506(3)	C(4)—C(8)	1.512(3)	N(1)—C(1)—C(5)	115.7(2)	N(1)—C(2)—C(6)	115.2(2)
N(2)—C(9)	1.512(2)	N(2)—C(10)	1.516(2)	N(1)—C(3)—C(7)	115.4(2)	N(1)—C(4)—C(8)	115.4(2)
N(2)—C(11)	1.517(4)	N(2)—C(12)	1.514(2)	C(9)—N(2)—C(10)	111.1(2)	C(9)—N(2)—C(11)	106.6(2)
C(9)—C(13)	1.502(4)	C(10)—C(14)	1.505(3)	C(10)—N(2)—C(11)	111.1(2)	C(9)—N(2)—C(12)	111.2(2)
C(11)—C(15)	1.506(3)	C(12)—C(16)	1.511(3)	C(10)—N(2)—C(12)	105.6(1)	C(11)—N(2)—C(12)	111.3(2)
O(1)—C(17)	1.244(3)	O(2)—C(17)	1.237(3)	N(2)—C(9)—C(13)	115.4(2)	N(2)—C(10)—C(14)	115.2(2)
C(17)—C(18)	1.500(3)	O(3)—C(19)	1.242(3)	N(2)—C(11)—C(15)	115.2(2)	N(2)—C(12)—C(16)	114.8(2)
O(4)—C(19)	1.246(3)	C(19)—C(20)	1.503(3)	O(1)—C(17)—O(2)	123.5(2)	O(1)—C(17)—C(18)	118.0(2)
				O(2)—C(17)—C(18)	118.5(2)	O(3)—C(19)—O(4)	124.5(2)
				O(3)—C(19)—C(20)	118.2(2)	O(4)—C(19)—C(20)	117.3(2)

It is of interest to compare the acetate ion with the hydroxide, fluoride, chloride, and sulfate ions as an ingredient for the construction of the water-anion lattice in a tetraalkylammonium salt hydrate. The preference of a monatomic anion for tetrahedral coordination is well manifested in the open framework structures of $(CH_3)_4NOH \cdot 5H_2O$ [6], $(CH_3)_4NF \cdot 4H_2O$ [7], $4(C_2H_5)_4NF \cdot 11H_2O$ [10], and $(C_2H_5)_4NCl \cdot 4H_2O$ [18]. In $[(CH_3)_4N]_2SO_4 \cdot 4H_2O$ [8], the highly symmetric molecular anion is disordered such that it has no well-defined hydrogen bonding interaction with neighbouring chains of egde-sharing puckered $(H_2O)_6$ hexagons. In contrast to this, the essentially planar acetate anion plays a dominating role in generating a net-like assembly of polygons in the present hydrate. The size, shape, and hydrogen bonding (acceptor) capability of the counter anion are thus important factors which dictate the crystal structure of a given tetraalkylammonium salt hydrate.

The water-anion layer structure of $(C_2H_5)_4N^+CH_3COO^- \cdot 4H_2O$ bears a close resemblance to the two-dimensional arrays of puckered edge-sharing pentagons formed by water and hydroxyl groups in the tetrahydrates of 2,5-dimethyl-2,5-hexanediol [19] and 2,7-dimethyl-2,7-octanediol [20]. Our attempt to prepare analogous crystalline hydrates of tetramethylammonium acetate has so far been unsuccessful. Presumably sufficient separation of two adjacent water-acetate layers of the present type necessitates the use of tetraalkylammonium ions no smaller than $(C_2H_5)_4N^+$, and it would therefore be of interest to carry out further studies on higher analogues involving $(n\text{-}C_3H_7)_4N^+$ and bulkier cations.

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