

NEt₄OH·4H₂O containing infinite hydroxide–water ribbons

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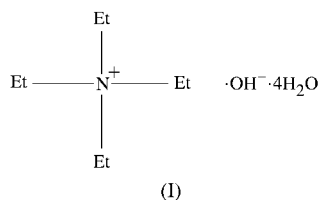
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In tetraethylammonium hydroxide tetrahydrate, C₈H₂₀N⁺·OH⁻·4H₂O, the array of mirror symmetric NEt₄⁺ cations gives rise to a system of parallel channels which are filled with hydrogen-bonded anionic ribbons. The central part of each ribbon is constituted by a [OH⁻(HOH)_{4/2}] spiro-chain, with each hydroxide ion accepting four strong linear hydrogen bonds [*d*(O··O) between 2.692 (1) and 2.727 (1) Å] but donating none. Additional (two-coordinate) H₂O molecules bridge between the (four-coordinate) H₂O molecules of the spiro-chain [*d*(O··O) between 2.831 (1) and 2.835 (1) Å].

Comment

Higher hydrates of tetraalkylammonium hydroxides are well known to crystallize as ionic clathrate hydrates (Jeffrey, 1996). Detailed structural information about lower hydrates is however scarce. The crystal structures of both phases of dimorphic NMe₄OH·2H₂O have been determined (Mootz & Seidel, 1990). In the course of studies on tetraalkylammonium silicate hydrates, we have also prepared crystalline NEt₄OH·4H₂O, (I). The hydrogen-bonding system of this tetrahydrate, which is obtained by removal of water from aqueous solutions of NEt₄OH at room temperature, has previously been investigated by IR spectroscopy (Harmon *et al.*, 1994). We report here a single-crystal X-ray structure analysis of (I).



The NEt₄⁺ cations of approximate $\bar{4}2m$ (*D*_{2d}) molecular symmetry (Fig. 1) lie with their N atoms on crystallographic mirror planes parallel to (010) and give rise to channels extending along [100] that have approximately hexagonal cross-sections (Fig. 2). Each channel is occupied by a hydroxide–water ribbon (Fig. 1), the hydrogen-bonding geometry of which is listed in Table 1. The OH⁻ ion does not act as a proton donor, but its O1 atom accepts four strong linear

hydrogen bonds from four O2 water molecules. The water O2 atoms form a planar rectangle, with the bonded hydroxide O1 atom slightly away from the plane [0.820 (1) Å]. Every water molecule donates hydrogen bonds to two OH⁻ ions. Thus, [OH⁻(HOH)_{4/2}] spiro-chains are formed with the hydroxide protons protruding alternately to both sides. Additional (two-coordinate) O3 water molecules bridge neighbouring (four-coordinate) O2 water molecules by donating weaker linear hydrogen bonds. The two crystallographically distinct four-membered oxygen rings of the ribbons, *i.e.* O1–O2–O1–O2 and O1–O2–O3–O2, are nearly planar. Regarding the ribbon–cation interactions, the peripheral and two-coordinate water O3 atom builds the shortest contact distance, namely O3···H21B–C21, which may be considered as a very weak hydrogen bond [with *d*(C–H) normalized to 1.08 Å, we find: *d*(O··H) = 2.35 Å, <(O··H–C) = 139° and *d*(O··C) = 3.251 (1) Å]. The remaining O··H–C and O··C distances, including those of the OH⁻ ion, are considerably longer.

The presence of OH⁻ ions not acting as hydrogen-bond donors and two-coordinate H₂O molecules has already been inferred from IR data (Harmon *et al.*, 1994). The coordination geometry observed for the OH⁻ ion in NEt₄OH·4H₂O is quite common in crystalline hydroxide hydrates (for a recent review, see Lutz, 1995). Similar [OH⁻(HOH)₄] surroundings exist, for example, in *M*(OH)·2H₂O (*M* = K, Rb; Rütter & Mootz, 1991; Jacobs & Schardey, 1988), CsNa₂[O(H,D)]₃·6(H,D)₂O (Mootz *et al.*, 1994) and Ba[O(H,D)]*X*·2(H,D)₂O (*X* = Cl, Br; Lutz *et al.*, 1989; Kellersohn *et al.*, 1991), as well as α- and β-NMe₄OH·2H₂O (Mootz & Seidel, 1990).

NEt₄OH·4H₂O is structurally closely related to both forms of dimorphic NMe₄OH·2H₂O. The latter phases differ essen-

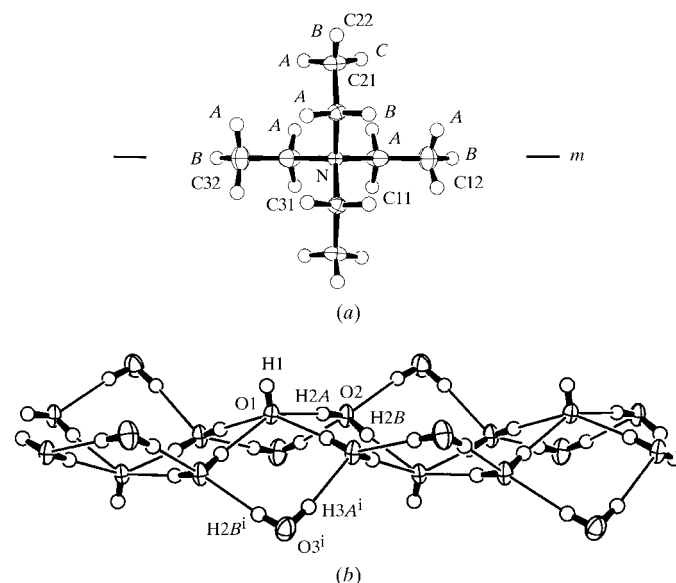


Figure 1
(a) One cation and (b) part of a hydroxide–water ribbon with atomic labelling (H atoms of the cation have the same numbers as the C atoms to which they are bonded and are distinguished by an additional letter). Displacement ellipsoids correspond to the 50% probability level. H atoms are represented by spheres of arbitrary radii (ORTEP-3; Farrugia, 1997). [Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$]

tially only in the existence (β -form) and absence (α -form) of cation disorder, but have a similar array of the cations. This array gives rise to parallel channels that, due to the smaller size of the NMe_4^+ species, have smaller cross-sections and are therefore filled only with $[\text{OH}^-(\text{HOH})_{4/2}]$ spiro-chains, which constitute the central part of the ribbons in $\text{NEt}_4\text{OH}\cdot 4\text{H}_2\text{O}$. Cooperativity of hydrogen bonding explains the shorter $\text{HOH}\cdots\text{OH}^-$ distances in the tetraethylammonium compound compared with the tetramethylammonium compounds [α -form: $d(\text{O}\cdots\text{O})$ between 2.751 and 2.762 Å].

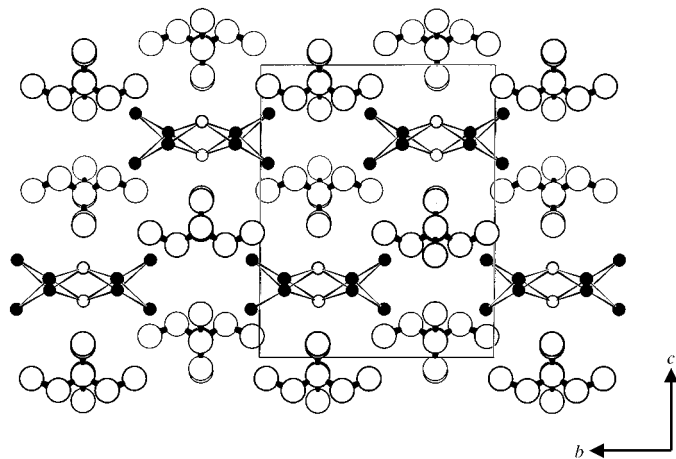


Figure 2
The structure of (I) as seen along the a direction. Only non-H atoms are shown. Large open spheres are atoms of cations, small open spheres are hydroxide O atoms and black spheres are water O atoms (DIAMOND; Brandenburg & Berndt, 1999).

Experimental

Removal of water *in vacuo* from an aqueous NEt_4OH solution (Fluka, ca 40%) at room temperature yielded air-sensitive crystals of $\text{NEt}_4\text{OH}\cdot 4\text{H}_2\text{O}$. A suitable crystal was embedded in a droplet of a perfluorinated polyether oil for protection and freeze-fixed on the tip of a glass fibre at the low temperature of the X-ray measurements.

Crystal data

$\text{C}_8\text{H}_{20}\text{N}^+\cdot\text{OH}^-\cdot 4\text{H}_2\text{O}$
 $M_r = 219.32$
 Orthorhombic, $Pnma$
 $a = 7.766(2)$ Å
 $b = 11.670(2)$ Å
 $c = 14.385(2)$ Å
 $V = 1303.7(4)$ Å³
 $Z = 4$
 $D_x = 1.117$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.40$ – 18.12°
 $\mu = 0.090$ mm⁻¹
 $T = 153$ K
 Plate, white
 $0.42 \times 0.22 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.893$, $T_{\max} = 1.000$
 2968 measured reflections
 2963 independent reflections
 1627 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$
 $\theta_{\text{max}} = 34.90^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 18$
 $l = 0 \rightarrow 23$
 3 standard reflections every 100 reflections
 intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.141$
 $S = 0.930$
 2963 reflections
 134 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0834P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2A}\cdots\text{O1}$	0.87 (2)	1.82 (2)	2.6919 (12)	175 (1)
$\text{O2}-\text{H2B}\cdots\text{O1}^i$	0.85 (2)	1.88 (2)	2.7267 (12)	174 (1)
$\text{O3}-\text{H3A}\cdots\text{O2}^{ii}$	0.87 (2)	1.96 (2)	2.8314 (13)	174 (2)
$\text{O3}-\text{H3B}\cdots\text{O2}^{iii}$	0.82 (2)	2.02 (2)	2.8355 (13)	171 (2)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (iii) $1 - x, -y, 1 - z$.

All H atoms were located on a difference Fourier map and refined independently [$\text{C}-\text{H}$ 0.95 (2)–1.05 (4) Å and $\text{O1}-\text{H1}$ 0.76 (3) Å]. The large anisotropic displacement parameters of atom C32 and the features near this atom on the final difference Fourier map may indicate some kind of disorder of the corresponding methyl group which could not however be modelled with the X-ray data.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET-4* in *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1137). Services for accessing these data are described at the back of the journal.

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