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$NEt_4OH\cdot 5H_2O$ containing hydroxide–water layers

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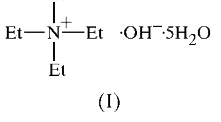
In the title compound, tetraethylammonium hydroxide pentahydrate, $C_8H_{20}N^+\cdot OH^-\cdot 5H_2O$, layers of approximately hexagonally close-packed NEt_4^+ cations and anionic layers of hydroxide and water molecules are stacked alternately along the *b* axis. All hydroxide and water H atoms are in ordered positions, giving rise to a network of hydrogen bonds [O···O 2.633 (1)–2.947 (2) Å] with four- and six-membered rings. The hydroxide ion accepts four hydrogen bonds from four water molecules but does not act as a proton donor.

Comment

Higher hydrates of tetraalkylammonium hydroxides crystallize as ionic clathrate hydrates (Jeffrey, 1996). This has been demonstrated in particular for the binary system tetramethylammonium hydroxide–water by detailed phase analytical and structural investigations (Mootz & Seidel, 1990; Mootz & Stäben, 1992; Hesse & Jansen, 1991). As many as ten stable and metastable solid hydrate phases containing at least four water molecules per base molecule have been found to exist in this system. Reports of various hydrates of tetraethylammonium hydroxide are also available (Harmon *et al.*, 1994), but only the crystal structure of the tetrahydrate has so far been determined (Wiebcke & Felsche, 2000). In the course of our investigations of alkylammonium silicate hetero-network clathrates, we are also performing structural studies on polyhydrates of alkylammonium hydroxides. We report here the X-ray structure of the low-melting title compound, tetraethylammonium hydroxide pentahydrate, (I).



$$\mathrm{Et}-\overset{\mathrm{Et}}{\underset{\mathrm{Et}}{\overset{+}{\mathrm{N}}}}-\mathrm{Et}\;\cdot OH^-\cdot 5H_2O$$

(I)

One NEt_4^+ cation of approximate $\bar{4}2m$ (D_{2d}) molecular symmetry and one six-membered ring of hydrogen-bonded hydroxide and water molecules, which together comprise the asymmetric unit of (I), are shown in Fig. 1. As can be seen in Fig. 2, slightly corrugated cationic layers, *A*, and anionic hydroxide–water layers, *a*, extend parallel to (010) and stack alternately along [010] in the sequence *AaAa*. Each anionic layer is based on a planar (3,4)-connected net (Wells, 1984) with a ratio of three- to four-connected nodes of 2:1 [the short Schläfli symbol (O'Keeffe & Brese, 1992) is $(4.6^2)_2,(4^2.6^2)$]. This net contains equal numbers of four- and six-membered rings.

The four-connected nodes are occupied by the hydroxide ion (atom O3) and one water molecule (O1). The OH^- ion does not act as a proton donor but its O3 atom accepts four hydrogen bonds from four water molecules in an approximately square-planar configuration. Each water molecule donates two, and accepts one (O2, O4, O5 and O6) or two (O1) hydrogen bonds. All H atoms are in ordered positions. The hydrogen-bonding geometry is listed in Table 1. Three crystallographically distinct four- and six-membered oxygen rings exist, which differ in the number of hydroxide ions involved (two, one or none). The rings containing two or no OH^- ions are arranged around inversion centres of the space group; some six-membered rings are slightly puckered. The proton positions clearly reflect the well known co-operativity in extended hydrogen-bonding systems, in that those rings which are built exclusively from water molecules are homodromic (Jeffrey & Saenger, 1994). Co-operativity is interrupted by the OH^- ions, which act only as proton acceptors.

The NEt_4^+ cations in (I) interleave the hydroxide–water layers in two-dimensional approximately hexagonal close-packed arrays, with each N atom being located above and below the centres of two symmetry-related (by translation along [010]) six-membered oxygen rings [Figs. 1 and 2(*b*)]. The water O1, O2, O5 and O6 atoms and the hydroxide O3 atom are each involved in one C—H···O interaction which may be considered as a very weak hydrogen bond. The geometric parameters are given in Table 1. It should be noted that the C—H···O contact at the OH^- ion is in a *trans* position relative to the hydroxide proton, and that this is the longest and most bent C—H···O interaction considered.

The coordination geometry observed for the OH^- ion is quite common in crystalline alkylammonium and metal

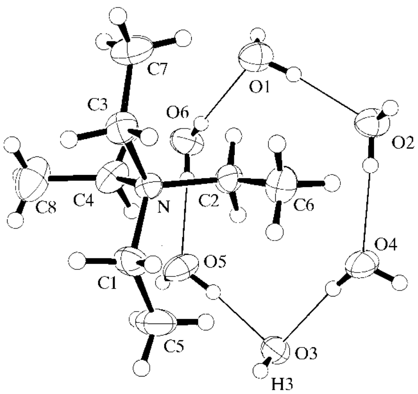
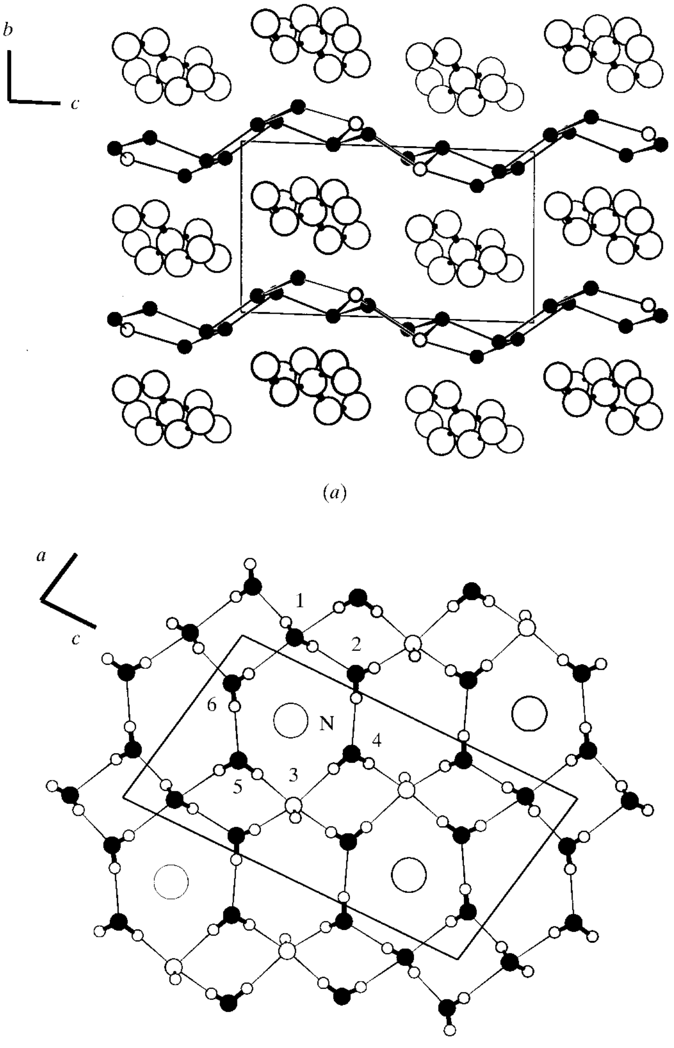


Figure 1
The molecular view (*ORTEP*-3; Farrugia, 1997) of (I) showing one cation and an adjacent six-membered hydroxide–water ring. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



(a)

(b)

Figure 2
(*a*) The layered structure as seen along the *a* axis; only non-H atoms are shown. (*b*) One hydroxide–water layer as seen along the *b* axis, with N atoms of adjacent NEt_4^+ cations, and hydroxide and water O atoms in the asymmetric unit indicated by their respective numbers. Large open spheres are N and C atoms of the cations, medium-sized black spheres are water O atoms, medium-sized open spheres are hydroxide O atoms and small open spheres are H atoms.

hydroxide hydrates and also exists in the hydroxide–water ribbons of $NEt_4OH{\cdot}4H_2O$ (references are given in Wiebcke & Felsche, 2000). Quite a large number of chemically very different inorganic and organic compounds containing neutral, cationic or anionic hydrogen-bonded layers composed mainly of water molecules have been structurally characterized. Such layers have been characterized in some recent compilations according to the sizes of the component rings (Jeffrey, 1996; Mootz & Rütter, 1992; Stäben & Mootz, 1993; Mootz & Stäben, 1993). However, it is also interesting to look at the connectivities of the atoms or molecules in the layers. Most of those layers are based on (3,4)-connected nets with ratios of three- to four-connected nodes of 2:1, which are otherwise rare in crystal chemistry (Wells, 1984). Layers with the same topology as those in (I) occur in the form of neutral water layers in the different forms of deuterated and undeuterated trifluoroacetic acid tetrahydrate (Mootz & Schilling, 1992) and, with regard to the Si atoms, in a layered tetramethylammonium silicate hydrate named RUB15 (Oberhagemann *et al.*, 1996).

Experimental

To prepare compound (I), an aqueous solution of NEt_4OH, with a molar ratio of base to water of 1:7.8, was sealed in a thin-walled glass capillary with a diameter of 0.3 mm and placed in the cold gas stream of the X-ray diffractometer. Crystal growth was performed at 258 K by applying a miniature zone-melting technique using focused heat radiation (Brodalla *et al.*, 1985).

Crystal data

$C_8H_{20}N^+{\cdot}OH^-{\cdot}5H_2O$
$M_r = 237.34$
Triclinic, $P\overline{1}$
$a = 7.306\ (2)$ Å
$b = 7.759\ (2)$ Å
$c = 13.141\ (3)$ Å
$\alpha = 89.28\ (2)^\circ$
$\beta = 79.34\ (2)^\circ$
$\gamma = 75.63\ (2)^\circ$
$V = 708.7\ (3)$ Å^3

$Z = 2$
$D_x = 1.112$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.49$–18.08°
$\mu = 0.092$ mm^{-1}
$T = 213$ K
Irregular polyhedron, white
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4409 measured reflections
4105 independent reflections
2584 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$

$\theta_{\rm max} = 29.94^\circ$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$
3 standard reflections
every 100 reflections
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 0.976$
4105 reflections
260 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O6$^{\rm i}$	0.77 (2)	1.99 (2)	2.751 (2)	167 (2)
O1—H12···O2	0.83 (2)	1.89 (2)	2.703 (2)	163 (1)
O2—H21···O3$^{\rm ii}$	0.82 (2)	1.90 (2)	2.709 (1)	170 (2)
O2—H22···O4	0.84 (2)	1.96 (2)	2.800 (2)	174 (2)
O4—H41···O3	0.82 (2)	1.94 (2)	2.766 (1)	174 (2)
O4—H42···O3$^{\rm iii}$	0.83 (2)	1.95 (2)	2.774 (1)	175 (2)
O5—H51···O3	0.86 (2)	1.78 (2)	2.633 (1)	174 (2)
O5—H52···O1$^{\rm iv}$	0.80 (2)	2.15 (2)	2.947 (2)	170 (2)
O6—H61···O5	0.81 (2)	1.92 (2)	2.719 (2)	175 (2)
O6—H62···O1	0.75 (2)	2.10 (2)	2.838 (2)	166 (2)
C1—H1*A*···O3$^{\rm v}$	0.96 (1)	2.72 (1)	3.243 (2)	115 (1)
C2—H2*A*···O1	0.91 (1)	2.56 (1)	3.425 (2)	158 (1)
C3—H3*A*···O2$^{\rm v}$	0.95 (1)	2.67 (1)	3.342 (2)	128 (1)
C3—H3*B*···O6$^{\rm v}$	0.95 (1)	2.72 (1)	3.575 (2)	150 (1)
C4—H4*A*···O5	0.95 (1)	2.52 (1)	3.444 (2)	164 (1)

Symmetry codes: (i) $2 - x, -y, -z$; (ii) $1 + x, y, z$; (iii) $1 - x, -y, 1 - z$; (iv) $x - 1, y, z$; (v) $x, 1 + y, z$.

All H atoms were located on a difference Fourier map and refined independently [C—H 0.89 (2)–0.98 (2) Å].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1475). Services for accessing these data are described at the back of the journal.

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