

Benzyltrimethylammonium hydroxide trihydrate containing hydroxide–water layers

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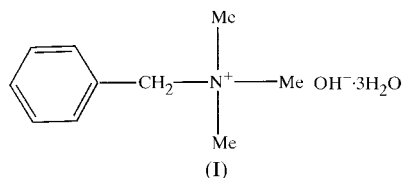
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In the title compound, $C_{10}H_{16}N^+ \cdot OH^- \cdot 3H_2O$, two-dimensional bilayer-like arrays of organic cations and corrugated anionic hydroxide–water layers are stacked alternately along the c axis. All hydroxide and water H atoms are in ordered positions, giving rise to a network of hydrogen bonds [$O \cdots O$ 2.639 (2)–2.927 (2) Å for water donors and $O \cdots O$ 3.323 (2) Å for hydroxide donors] with four- and six-membered rings.

Comment

Higher hydrates of tetraalkylammonium hydroxides crystallize as ionic clathrate hydrates (Jeffrey, 1996), and the crystal structures of the ten existing hydrates of tetramethylammonium hydroxide with at least four water molecules per base molecule have been determined by single-crystal X-ray diffraction methods, which did not reveal conclusively the H-atom positions in cases of disorder (McMullan *et al.*, 1966; Mootz & Seidel, 1990; Mootz & Stäben, 1992; Hesse & Jansen, 1991). The hydrogen-bonding systems of those three-dimensional anionic host structures have therefore been interpreted by evaluating the oxygen–oxygen distances and assuming that every H atom is involved in hydrogen-bonding interactions. However, our recent X-ray structural study on tetraethylammonium nonahydrate, a novel ionic clathrate hydrate, gave



some indications that the latter assumption need not be valid (Wiebcke & Felsche, 2001). Also, detailed structural information about lower non-clathrate hydrates of alkylammonium hydroxides is scarce. The crystal structures of the dihydrates of tetramethylammonium (Mootz & Seidel, 1990) and *N,N*-dimethylpyrrolidinium hydroxide (Stäben *et al.*, 1998), as well as of the tetra- and pentahydrates of tetraethylammonium hydroxide (Wiebcke & Felsche, 2000*a,b*) are available. We report here a single-crystal X-ray structure analysis of

benzyltrimethylammonium hydroxide trihydrate, (I), which possesses a novel layered structure.

The molecular details and atomic numbering are displayed in Fig. 1. As can be seen in Fig. 2(*a*), the $NBnMe_3^+$ cations of nearly ideal m (C_s) molecular symmetry are assembled into two-dimensional bilayer-like arrays parallel to (001) which are interleaved by corrugated anionic hydroxide–water layers. Each anionic layer (Fig. 2*b*) is based on a planar (3,5)-connected net with a ratio of three- to five-connected nodes of 3:1 [the short Schläfli symbol (O'Keeffe & Brese, 1992) is $(4^2.6), (4.6^2)_2, (4^3.6^2)$]. This net contains four- and six-membered rings in the ratio 2:1.

The five-connected nodes are occupied by the hydroxide ions (atom O1), which possess a distorted square-pyramidal coordination by water molecules (Fig. 1). The ions are acceptors and donors in hydrogen bonds with the equatorial and apical water molecules, respectively. Each water molecule (atoms O2, O3 and O4) donates two and accepts one hydrogen bond. The well known differences in donor and acceptor strength of the OH^- and H_2O species is clearly reflected in the hydrogen-bonding geometries, which are listed in Table 1. In particular, the $OH^- \cdots OH_2$ interactions [$O1 \cdots O3^i$ 3.323 (2) Å; symmetry code: (i) $x, y + 1, z$] are by far the longest (weakest) hydrogen bonds. As can be seen in Figs. 2(*a*) and 2(*b*), flat ribbons containing exclusively shorter hydrogen bonds donated by the water molecules [$O \cdots O$ 2.639 (2)–

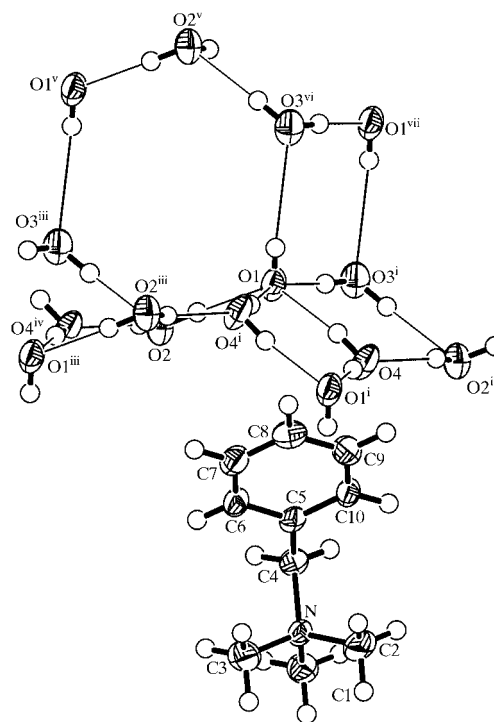


Figure 1

The molecular view (*DIAMOND*; Brandenburg & Berndt, 1999) of (I) showing the local environment of the hydroxide ion, including the distinct four- and six-membered oxygen rings and one organic cation. Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x, -y + 1, -z + 1$; (iv) $x - 1, y, z$; (v) $-x, -y + 2, -z + 1$; (vi) $x, y + 1, z$; (vii) $-x + 1, -y + 2, -z + 1$.]

2.927 (2) Å] and running along the [100] direction can be identified. These ribbons are linked by long $\text{OH}^- \cdots \text{OH}_2$ bonds into corrugated anionic layers. The crystallographically distinct four- and six-membered oxygen rings are also shown in Fig. 1.

Within the organic bilayers, all aryl rings are oriented approximately perpendicular to the [010] direction, and pairs of cations (across inversion centres at $\frac{1}{2}, 0, 0$) have inter-ring distances (3.40 Å) and ring-centroid offsets (1.38 Å) that are indicative of attractive face-to-face (*ff*) aryl-aryl interactions (Hunter, 1994). Further close *ff* contacts are hindered by the NMe_3 moieties which protrude on one side of an aryl ring. Of the numerous $\text{C}-\text{H} \cdots \text{O}$ interactions which may be very weak hydrogen bonds (Steiner & Desiraju, 1998), only the shortest are listed in Table 1. It should be noted that the $\text{C}-\text{H} \cdots \text{O}$ contact at the OH^- ion in the *trans* position to the hydroxide H atom is rather long [$\text{H}8 \cdots \text{O}1$ 2.96 (3), $\text{C}8 \cdots \text{O}1$ 3.817 (3) Å

and $\text{C}8-\text{H}8 \cdots \text{O}1$ 158 (2)°]. This is possibly because the O atom is well coordinated by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

The coordination and bonding observed for the OH^- ion in $\text{NBnMe}_3\text{OH} \cdot 3\text{H}_2\text{O}$, *i.e.* donor in one and acceptor in four $\text{O}-\text{H} \cdots \text{O}$ bonds, is as yet uncommon in crystalline alkylammonium and metal hydroxide hydrates. Similar geometries exist only in $\text{CsOH} \cdot 2\text{H}_2\text{O}$ and $\text{CsOH} \cdot 3\text{H}_2\text{O}$, if weak interactions with the caesium cations are not taken into account (Mootz & Rütter, 1992).

Experimental

Removal of water *in vacuo* from an aqueous solution of NBnMe_3OH (Fluka, *ca* 40%) at room temperature yielded air-sensitive crystals of $\text{NBnMe}_3\text{OH} \cdot 3\text{H}_2\text{O}$. A suitable crystal was embedded in a droplet of 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

$\text{C}_{10}\text{H}_{16}\text{N}^+ \cdot \text{OH}^- \cdot 3\text{H}_2\text{O}$
 $M_r = 221.29$
 Triclinic, $P\bar{1}$
 $a = 6.337$ (1) Å
 $b = 8.028$ (1) Å
 $c = 12.169$ (2) Å
 $\alpha = 80.53$ (1)°
 $\beta = 84.12$ (1)°
 $\gamma = 85.40$ (1)°
 $V = 606.2$ (2) Å³

$Z = 2$
 $D_x = 1.212$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.68$ – 24.24 °
 $\mu = 0.092$ mm⁻¹
 $T = 183$ K
 Needle, white
 $0.55 \times 0.25 \times 0.23$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 2854 measured reflections
 2610 independent reflections
 1922 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$

$\theta_{\text{max}} = 26.91$ °
 $h = 0 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -15 \rightarrow 15$
 3 standard reflections every 200 reflections
 intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.161$
 $S = 1.013$
 2610 reflections
 228 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1127P)^2 + 0.0601P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

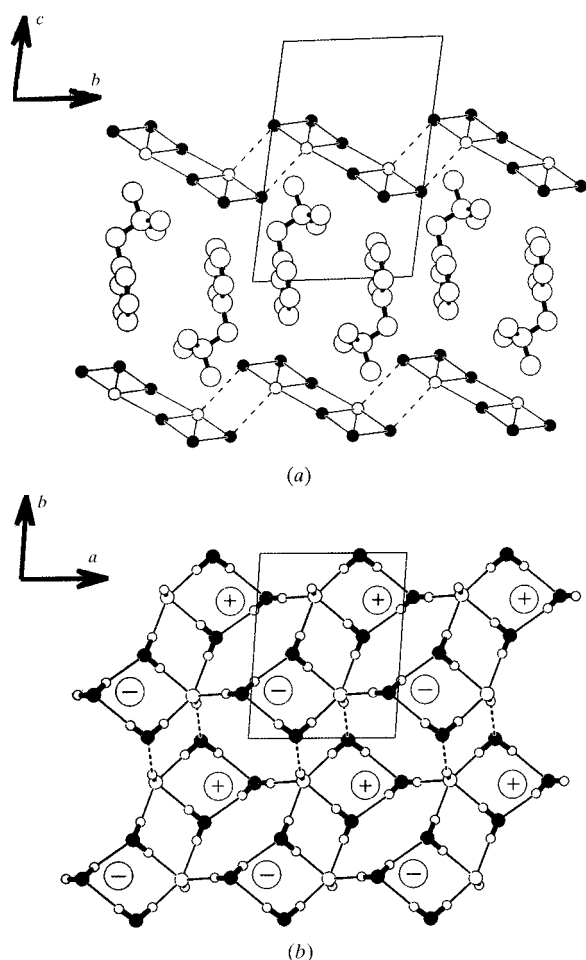


Figure 2
 (a) The layered structure as seen along the *a* axis; only non-H atoms are shown. (b) One hydroxide-water layer as seen along the *c* axis, with N atoms of adjacent NBnMe_3^+ cations; + and - symbols distinguish between N atoms lying directly above and below the given layer. Large open spheres are N and C atoms of cations, medium-sized black spheres are water O atoms, medium-sized open spheres are hydroxide O atoms and small open spheres are H atoms. Dashed lines indicate the long $\text{OH}^- \cdots \text{OH}_2$ hydrogen bonds (DIAMOND; Brandenburg & Berndt, 1999).

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O}1-\text{H}1 \cdots \text{O}3^{\text{i}}$	0.80 (3)	2.55 (3)	3.323 (2)	165 (3)
$\text{O}2-\text{H}21 \cdots \text{O}1$	0.90 (4)	1.74 (4)	2.639 (2)	174 (4)
$\text{O}2-\text{H}22 \cdots \text{O}4^{\text{ii}}$	0.83 (4)	2.02 (4)	2.818 (2)	161 (3)
$\text{O}3-\text{H}31 \cdots \text{O}1^{\text{iii}}$	0.90 (3)	1.81 (3)	2.704 (2)	173 (3)
$\text{O}3-\text{H}32 \cdots \text{O}2^{\text{iv}}$	0.91 (3)	2.03 (4)	2.927 (2)	171 (3)
$\text{O}4-\text{H}42 \cdots \text{O}1$	0.87 (4)	1.86 (4)	2.719 (2)	169 (3)
$\text{O}4-\text{H}41 \cdots \text{O}1^{\text{iii}}$	0.88 (4)	1.93 (4)	2.806 (2)	176 (3)
$\text{C}1-\text{H}1A \cdots \text{O}3^{\text{v}}$	1.01 (3)	2.49 (3)	3.465 (3)	165 (2)
$\text{C}2-\text{H}2B \cdots \text{O}4^{\text{vi}}$	0.99 (2)	2.41 (2)	3.340 (3)	158 (2)
$\text{C}4-\text{H}4A \cdots \text{O}2^{\text{vii}}$	0.96 (3)	2.52 (2)	3.285 (2)	136 (2)
$\text{C}4-\text{H}4B \cdots \text{O}3^{\text{viii}}$	0.96 (2)	2.45 (2)	3.377 (3)	163 (2)
$\text{C}9-\text{H}9 \cdots \text{O}2^{\text{ix}}$	0.96 (2)	2.47 (2)	3.395 (3)	163 (2)

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

All H atoms were located on a difference Fourier map and refined independently [C–H = 0.91 (2)–1.01 (3) Å].

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995) and *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *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: DE1162). Services for accessing these data are described at the back of the journal.

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