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Tetramethylammonium pentaborate 0.25-hydrate

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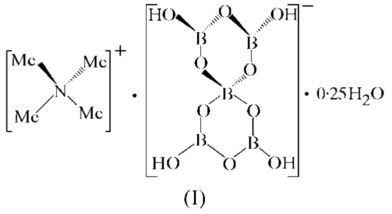
The title compound, tetramethylammonium 4,4′,6,6′-tetrahydroxy-2,2′-spirobi(cyclotriboroxane) 0.25-hydrate, $C_4H_{12}N^+\cdot B_5H_4O_{10}^-\cdot 0.25H_2O$, was synthesized under mild solvothermal conditions. The $B_5O_6(OH)_4^-$ clusters are connected by strong hydrogen-bonding interactions into a three-dimensional structure containing rectangular channels along the *a* axis, in which the $C_4H_{12}N^+$ ions and water molecules are located.

Comment

Borates have provided a rich area of research for over 50 years because of their diverse crystalline structures and potential applications in mineralogy and non-linear optical materials. So far, a number of borates exhibiting one-dimensional chains, two-dimensional layers and three-dimensional open structures have been reported (Salentine, 1987; Touboul *et al.*, 1999; Menchetti *et al.*, 1982; Nowogrocki *et al.*, 2003; Huppertz & Heymann, 2003), most of which were grown by a high-temperature flux method. Recently, hydrothermal and related techniques have been widely used for the preparation of inorganic materials, including phosphates and germanates (Yang *et al.*, 1999; Zhou *et al.*, 2001; Plevert *et al.*, 2001). Interesting borates, such as $Pb_6B_{11}O_{18}(OH)_9$ (Yu *et al.*, 2002) and $Zn_6B_{12}O_{24}$ (Choudhury *et al.*, 2002), have also been obtained from hydrothermal systems. The hydrothermal technique is of perpetual interest in the construction of novel structures, because different kinds of templates, especially organic molecules, with a wide variety of shapes and sizes can be incorporated into the systems to shape diverse inorganic frameworks. Nevertheless, such research efforts have rarely been made in the borate field (Schubert *et al.*, 2000; Weakley, 1985).



(I)

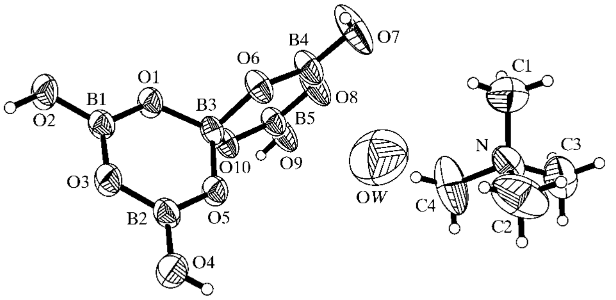


Figure 1
The ionic and molecular components of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Water H atoms have been omitted for clarity.

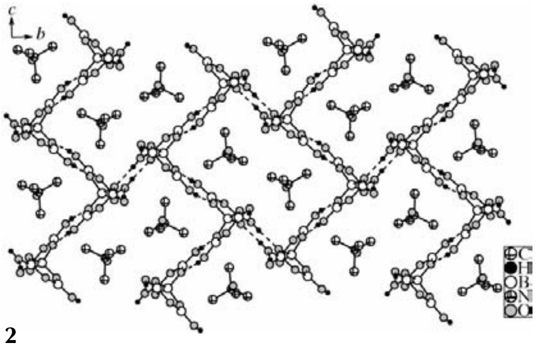


Figure 2
The crystal packing of (I), viewed along the *a* axis. H atoms attached to C atoms have been omitted for clarity.

We report here the X-ray structure analysis of the title compound, (I) (Fig. 1). Compound (I) is composed of $C_4H_{12}N^+$ cations, $B_5O_6(OH)_4^-$ anions and solvent water molecules. The $B_5O_6(OH)_4^-$ anion consists of two B_3O_3 rings, each containing one tetrahedrally and two trigonally coordinated B atoms; pairs of B_3O_3 rings are connected by sharing their tetrahedrally coordinated B atoms. The $B_5O_6(OH)_4^-$ clusters are further connected by strong hydrogen-bonding interactions into a three-dimensional structure (Table 1). Interestingly, this three-dimensional structure possesses a rectangular channel along the *a* axis (Fig. 2) formed by six $B_5O_6(OH)_4^-$ units connected *via* hydrogen bonds. Two $C_4H_{12}N^+$ cations and one water molecule are located in each rectangular channel. The trigonally coordinated B atoms exhibit B—O bond lengths in the range 1.336 (4)–1.379 (4) Å, while the tetrahedrally coordinated B atoms have B—O distances of 1.449 (4)–1.474 (4) Å. The O—B—O angles lie in the ranges 115.8 (3)–122.9 (3) and 108.0 (3)–110.9 (2)°, respectively.

Experimental

In a typical synthesis of (I), H_3BO_3 (0.232 g) was dissolved in a mixed solvent containing pyridine (4.2 ml), distilled water (0.1 ml) and tetramethylammonium hydroxide ($C_4H_{12}N^+\cdot OH^-$, 1.1 ml, 25%). The mixture, with a typical H_3BO_3/py/H_2O/$C_4H_{13}NO$ molar ratio of 3.7:52.0:51.4:3.0, was stirred mechanically at room temperature to a final pH of ∼8 and then placed in an autoclave at 443 K for 7 d. Colorless block-shaped crystals, identified as (I), were obtained in

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18.21% yield (based on B). The X-ray powder diffraction pattern of the bulk product is in good agreement with the calculated pattern based on the single-crystal solution, indicating the phase purity of the sample. Thermogravimetric analysis (TGA) showed that there were four steps of weight loss. The initial weight loss, of ~1.5% (calculated 1.52%) from 400 to 490 K, corresponds to the removal of the water molecule. The second loss, ~9% (calculated 9.1%) from 470 to 570 K, was assigned to the removal of three hydroxy groups. The third loss, from 570 to 1027 K, was assigned to the partial release of $C_4H_{12}N^+ \cdot OH^-$, resulting from the decomposition of the framework. When heated further, the volatile boron oxide phases are partly separated from the phase. The IR spectrum (4000–400 cm^{-1}, KBr pellets) of (I) contains the characteristic bands of the BO_3 and BO_4 groups, corresponding to two strong bands at ~1317 and 1087 cm^{-1}, respectively. The wide peak between 1350 and 1500 cm^{-1} was assigned to the bending bands of CH_2 and the stretching bands of CN groups. The stretching vibration bands of the water OH groups are observed at ~3266 cm^{-1} (Liu *et al.*, 2003) and the stretching vibration of the OH groups attached to the B atoms is at ~3370 cm^{-1} (Yu *et al.*, 2002).

Crystal data

$C_4H_{12}N^+ \cdot B_5H_4O_{10}^- \cdot 0.25H_2O$
$M_r = 296.23$
Monoclinic, $P2_1/c$
$a = 9.2623$ (4) Å
$b = 16.8814$ (7) Å
$c = 9.2119$ (5) Å
$\beta = 96.281$ (3)°
$V = 1431.73$ (12) Å^3
$Z = 4$
$D_x = 1.374$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 57 reflections
$\theta = 2.4$–25.1°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.48 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.942$, $T_{\max} = 0.963$
4012 measured reflections
2538 independent reflections
1654 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 25.1°$
$h = -11 \rightarrow 11$
$k = -20 \rightarrow 16$
$l = -10 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.177$
$S = 1.12$
2470 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 1.0501P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.011 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O9$^{\rm i}$	0.87 (4)	1.88 (4)	2.745 (3)	174 (4)
O4—H4···O6$^{\rm ii}$	0.79 (5)	1.94 (5)	2.733 (4)	173 (5)
O7—H7···O5$^{\rm iii}$	0.79 (6)	1.89 (6)	2.671 (4)	171 (6)
O9—H9···O10$^{\rm iv}$	0.79 (5)	1.90 (5)	2.688 (3)	176 (5)

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

H atoms bonded to O atoms were located from difference density maps and their parameters were refined freely. All H atoms attached to C atoms were positioned geometrically (C—H = 0.97 Å) and were allowed to ride on their parent C atoms. The solvent water molecules are located in the channels, 4.08 (2) Å from the N atoms. In Fig. 2, the water molecule and N atom almost overlap each other because of the closeness of their *b* and *c* coordinates. The small solvent molecules are probably absorbed from the solution by the structure after synthesis, a phenomenon that can be explained by the fact that the borate structure is very polar as a result of the large number of hydroxy groups in the voids of the structure, as shown in Fig. 2. Such absorption of small molecules is a familiar occurrence in microporous materials. For example, $Na_4Ge_{16}O_{28}(OH)_{12}$ (van den Berg *et al.*, 2004) absorbs small gas molecules owing to voids in its structure. The value of 0.25 was determined according to the $U_{\rm eq}$ values and the refinement. The presence of hydration water molecules was established experimentally by TGA and IR spectroscopy.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999) and *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1187). Services for accessing these data are described at the back of the journal.

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