Brønsted Conjugate Acid–Base Species $B(OH)_3/[BO(OH)_2]^-$ Coexist in the Crystalline Solid $(NEt_4)_2[BO(OH)_2]_2 \cdot B(OH)_3 \cdot 5H_2O$

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X-Ray structure analysis reveals that in the title compound, which crystallizes in the ternary system $(NEt_4)_2O–B_2O_3–H_2O$ from strongly basic solutions, extensive intermolecular hydrogen bonding links the species $B(OH)_3$, $[BO(OH)_2]^-$ and H_2O into two-dimensional anionic layers that are interleaved by NEt_4^+ cations.

It is well established that in aqueous solutions upon neutralization orthoboric acid, $B(OH)_3$, behaves not as a Brønsted acid with the formation of the conjugate base anion $[BO(OH)_2]^-$, but rather as a Lewis acid with the formation of the tetrahedral anion $[B(OH)_4]^-$.[1] Since oligomerization of borate monomers takes place at higher concentrations and medium pH values, the ionic compounds that crystallize from aqueous solutions commonly contain one of a variety of oligomeric (or polymeric) hydroxo(oxo)borate anions or the monomeric $[B(OH)_4]^-$ entity.[2] While the $[BO(OH)_2]^-$ anion is unknown in solution, it has thus far been found to exist in one crystalline compound, namely $Cu_2[BO(OH)_2](OH)_3$.[3] Crystal structure analysis based on powder X-ray diffraction data did not permit a determination of the hydrogen-atom positions. On the other hand, Brønsted-acid behaviour of $B(OH)_3$ has very recently been observed in the gas phase by mass spectrometric studies.[4] This communication deals with preparation and structure determination (including hydrogen atoms) of the title compound—a crystalline solid in which, remarkably, both $B(OH)_3$ molecules and their conjugate base species $[BO(OH)_2]^-$ coexist.

Aqueous tetraethylammonium hydroxide solution, boric acid and deionized water were combined to give a liquid mixture of composition $(NEt_4)_2O:B_2O_3:H_2O = 1:1:90$ which was refluxed for 30 min. The solution was evaporated in a desiccator at room temp., and eventually when the volume had decreased to approximately one fifth of the initial value and the liquid had become highly viscous (pH > 13) colourless, strongly hygroscopic crystals of composition $2(NEt_4)_2O \cdot 3B_2O_3 \cdot 17H_2O$ deposited.†

Single-crystal X-ray structure analysis‡ has unambiguously revealed that in the solid besides NEt_4^+ cations there occur $B(OH)_3$ molecules, their conjugate base anions $[BO(OH)_2]^-$ and H_2O molecules resulting in the structural formula $(NEt_4)_2[BO(OH)_2]_2 \cdot B(OH)_3 \cdot 5H_2O$.

The planar borate species $[BO(OH)_2]^-$ and $B(OH)_3$ are linked *via* hydrogen bonds O–H···O into planar infinite anionic ribbons [Fig. 1(*a*)]. The average B–O bond lengths of the three crystallographically distinct borate species are nearly equal [$d(B–O)_{av}$ = 1.358, 1.361 and 1.364 Å] and are close to the corresponding value found in crystalline orthoboric acid [$d(B–O)_{av}$ = 1.367 Å].[5] However, there exists considerable scatter in the individual B–O bond lengths, which clearly reflects the connection of the oxygen atoms with the hydrogen atoms by covalent O–H and/or hydrogen O···H bonds [$d(B–O^-)$ between 1.316 and 1.326 Å, d(B–OH) between 1.346 and 1.395 Å; d(O···O) in hydrogen bonds between 2.545 and 2.790 Å, ∢(O–H···O) in hydrogen bonds between 168 and 174°]. Most interesting is the hydrogen-bonding pattern with larger rings of six (homodromic)[6] O–H···O bonds and smaller rings of pairwise O–H···O bonds, which makes the anionic ribbons very similar to infinite neutral ribbons of hydrogen-bonded $B(OH)_3$ molecules that can be cut out of the well-known layered structure of crystalline orthoboric acid (see illustration in ref. 7).

The H_2O molecules are hydrogen-bonded into infinite ribbons of six-membered rings which share a common molecule at every connection [Fig. 1(*b*)]. The twist of the nearly flat $(H_2O)_6$ rings at the common H_2O molecules is 56.2° [hydrogen bond parameters: d(O···O) between 2.749 and 2.913 Å, ∢(O–H···O) between 148 and 176°]. Both water ribbons and borate ribbons, in turn, are arranged into only slightly puckered composite layers extended parallel to the crystallographic x,y plane (Fig. 2). All hydrogen bonds that link adjacent water and borate ribbons are donated exclusively

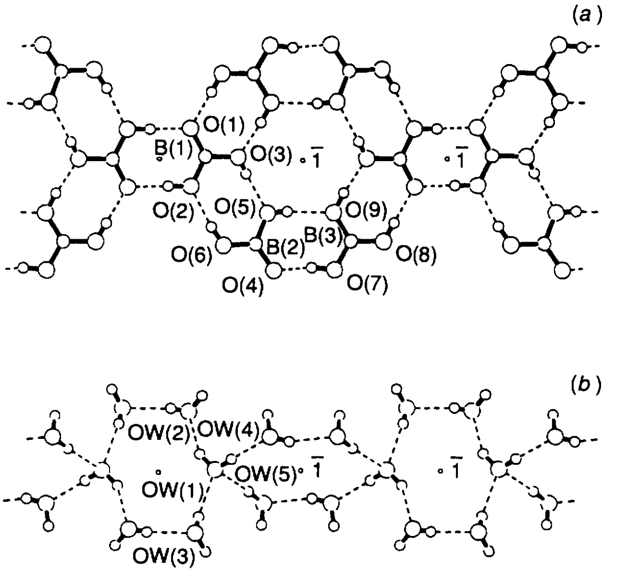

Fig. 1 Infinite ribbon built from hydrogen-bonded $[BO(OH)_2]^-$ anions and $B(OH)_3$ molecules (*a*) and infinite ribbon built from hydrogen-bonded H_2O molecules (*b*). Thick lines represent covalent bonds, dashed lines represent hydrogen bonds; inversion centres ($\bar{1}$) are marked by ○.

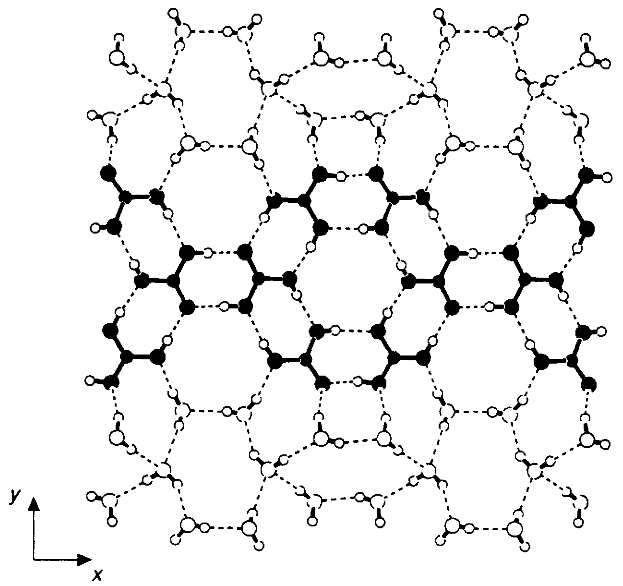

Fig. 2 Two-dimensional borate-water layer. The boron and oxygen atoms in borate ribbons are shown as black balls; see also the legend of Fig. 1.

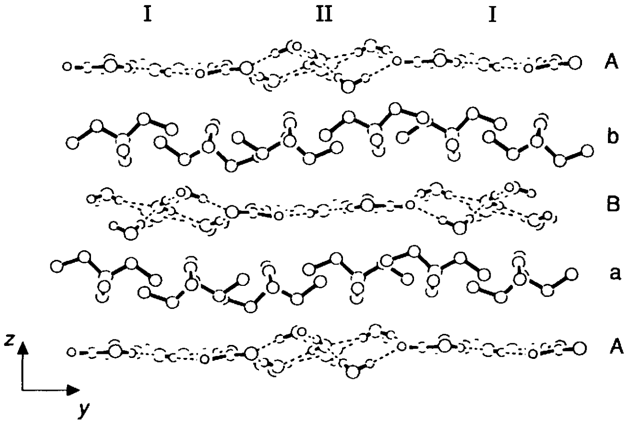

Fig. 3 Stacking (AB) of anionic borate-water layers and stacking (ab) of cationic NEt_4^+ layers along the crystallographic *z* direction. The view is parallel to the extension of the infinite borate and water ribbons (*x* direction); the location of borate and water ribbons within the uppermost layer is indicated by I and II, respectively.

by H_2O molecules [d(O···O) between 2.632 and 2.833 Å, ∢(O-H···O) between 164 and 171°]. Interestingly, within the composite layers borate species and H_2O molecules occur not intimately mixed but rather are partly separated form each other, reflecting on the molecular level the facts that orthoboric acid is only moderately soluble in water and that solid hydrates of $B(OH)_3$ have thus far not been reported.

The anionic borate–water layers are stacked along the crystallographic *z* direction in $A\underline{B}$ sequence and are separated by layers of NEt_4^+ cations with $\bar{4}2m(D_{2d})$ conformation[8] (Fig. 3). The two shortest, i.e. strongest, C–H···O hydrogen bonds[9] [d(C···O) = 2.37 and 2.42 Å, ∢(C–H···O) = 156 and 151°] are accepted by the deprotonated oxygen atoms of the two $[BO(OH)_2]^-$ anions; additionally, three-connected H_2O molecules of the borate-water layers accept more and stronger C–H···O bonds than four-connected H_2O molecule, in agreement with recent observations.[10]

It should be noted that the distribution of protons in the title compound violates Rule 3 proposed by Christ and Clark,[11] according to which hydrogen atoms are attached to protonable oxygen atoms in hydrated borates in the order of decreasing Lewis-base strength as deduced from valence-bond arguments and a survey of crystal structures: $O^{2-} > B(sp^3)\text{-}O^- > B(sp^2)\text{-}O^- > OH^-$. This, erroneously, suggests the hydrous species $B(OH)_3$, OH^- (instead of $[BO(OH)_2]^-$) and H_2O for the title compound. Since Lewis-base strength of anions can vary considerably depending on the state of bonding,[12] Rule 3 should be applied very carefully.

Whether trigonal-planar $[BO(OH)_2]^-$ anions also occur in the strongly basic mother liquour of crystalline $(NEt_4)_2[BO(OH)_2]_2{\cdot}B(OH)_3{\cdot}5H_2O$ or possibly in any strongly basic borate solution, independent of the nature of cation present, has still to be investigated. We note, however, that both the solid under study and its mother liquor are strongly hygroscopic. This suggests that $[BO(OH)_2]^-$ anions may be formed at very high pH from the common tetrahedral $[B(OH)_4]^-$ anions by dehydration reaction ($[B(OH)_4]^- \rightarrow [BO(OH)_2]^- + H_2O$). Then, the increased H_2O content could lead to a better solvation of anionic entities and, thereby, an equilibrium of Brønsted acid–base species $B(OH)_3/[BO(OH)_2]^-$ (estimated pK_a 12.6)[13] could result.

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Footnotes

† Satisfactory chemical analysis. Phase purity checked by powder X-ray diffraction.

‡ *Crystal data* for $(NEt_4)_2[BO(OH)_2]_2{\cdot}B(OH)_3{\cdot}5H_2O$: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.977(2)$, $b = 16.873(1)$, $c = 14.776(2)$ Å, $\beta = 94.37(1)°$, $U = 2977.4$ Å^3, room temp., $D_c = 1.192$ Mg m^{-3}, μ(Mo-K$\bar{\alpha}$) = 0.10 mm^{-1}, $M_r = 534.18$. Single crystal (0.36 × 0.30 × 0.21 mm^3) enclosed in a thin-walled glass capillary, Enraf-Nonius CAD4 diffractometer, intensities of 5489 reflections measured by a variable ω/2θ-scan technique up to $(\sin\theta)/\lambda = 0.595$ Å^{-1} using Mo-K$\bar{\alpha}$ radiation (λ = 0.71073 Å), absorption effects considered negligible. Solution of phase problem by direct methods. All 5225 unique reflections included in the refinement based on F^2 (SHELXL-93 program system),[14] H atoms of the NEt_4^+ cations geometrically constructed and treated "riding" on the respective C atoms, coordinates of H atoms attached to borate species and water molecules determined by difference-Fourier methods and refined independently, anisotropic displacement parameters for all non-H atoms varied, isotropic displacement parameters for H atoms kept fixed, the final refinement with 316 parameters converged at $wR2 = 0.152$ (based on F^2 for all data)[14], $R1 = 0.050$ [based on F for 2361 reflections with $F_o > 4\sigma(F_o)$], S = 0.945 (based on F^2), $w = 1/[\sigma^2(F_o^2) + (0.0759P)^2]$ with $P = [\text{Max}(F_o^2, O) + 2F_c^2]/3$. Maximum features in final difference Fourier synthesis: −0.18, +0.15 e Å^{-3}. Finally, the H-atom coordinates have been approximately corrected for the well-known systematic error of X-ray methods by adjusting the lengths of covalent bonds to the 'standard' values d(C-H) = 1.08 and d(O-H) = 0.96 Å.

Atomic coordinates, thermal parameters, and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J. B. Farmer, *Adv. Inorg. Chem. Radiochem.*, 1982, **25**, 187; J. M. Coddington and M. J. Taylor, *J. Coord. Chem.*, 1989, **20**, 27.

2 G. Heller, *Top. Curr. Chem.*, 1986, **131**, 39; B. P. Tarasevich and E. V. Kuznetsov, *Russ. Chem. Rev.*, 1987, **56**, 203.

3 H. Behm and Ch. Baerlocher, *Acta Crystallogr., Sect. C*, 1985, **41**, 5.

4 M. Attina, F. Cacace, G. Occhiucci and A. Ricci, *Inorg. Chem.*, 1992, **31**, 3114.

5 M. Gajhede, S. Larsen and S. Rettrup, *Acta Crystallogr., Sect. B*, 1986, **42**, 545.

6 G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991, p. 38.

7 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon, Oxford, 1984, p. 1067.

8 R. W. Alder, C. M. Maunder and A. G. Orpen, *Tetraheron Lett.*, 1990, **31**, 6717.

9 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290; T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1992, **114**, 10146.

10 T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540.

11 C. L. Christ and J. R. Clark, *Phys. Chem. Miner.*, 1977, **2**, 59.

12 I. D. Brown, *Acta Crystallogr., Sect. B*, 1992, **48**, 553.

13 R. P. Bell, J. O. Edwards and R. B. Jones in *The Chemistry of Boron and its Compounds*, ed. E. L. Muetteries, Wiley, New York, 1967, p. 215.

14 G. M. Sheldrick, SHELXL-93, University of Göttingen, 1993.