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Synthesis and characterization of a tertiary amine:boric acid (1:1) co-crystal and a neutral zwitterionic diamine pentaboron adduct.

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Abstract

The syntheses of the 4,4'-trimethylenebis(*N*-methylpiperidine):boric acid (1:1) co-crystal, 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**), and a zwitterionic tetrahydroxidohexaoxidopentaboron adduct, [B₅O₆(OH)₄(κ*N*-NH₂CH₂CH₂NHEt₂)·H₂O (**2**), (NH₂CH₂CH₂NEt₂ = deen) from appropriate combinatorial libraries primed with B(OH)₃, are reported together with their spectroscopic (NMR, IR) and single-crystal XRD characterization data. Solid-state H-bond interactions are the likely strong drivers for their formation, and these are described in detail. H-bond networks present in co-crystal **1** include C₂²(16), R₂²(8), and R₆⁶(36) whilst zwitterionic pentaboron derivative **2** has three R₂²(8) intermolecular H-bond interactions and the Et₂NH- group is involved in a S(7) intramolecular H-bond. Thermal (TGA/DSC) data are also reported for **1** which thermally decomposes to B₂O₃, in a multistage process: dehydration (60-70 °C) and oxidation and further dehydration (90-700 °C).

Keywords: boric acid; co-crystallization; H-bonding; oxidoboron; self-assembly; templated synthesis; XRD; zwitterion.

1. Introduction

Hydroxidooxidoborates [1] are an important class of compounds that have found extensive industrial use [2-4] and also potentially have fine-chemical applications [5-6]. They are structurally diverse and are usually comprised of three- and/or four-coordinate boron centres bound to oxygen atoms that either bridge to other boron centres or terminate as hydroxido groups [7-11]. In some circumstances the oxygen atoms may terminate as O^- [7-9], but more commonly the negative charge of the hydroxidooxidoborate is formally associated with the four-coordinate boron atoms, although QTAIM calculations indicate [12] that these centres carry a positive charge and the overall negative charge is associated with the electronegative oxygen atoms. We have developed a synthetic strategy of using non-metal (organic) or transition-metal complex cations to template and affect the self-assembly of hydroxidooxidoborate anions through crystallization of products from aqueous solutions originally primed with $B(OH)_3$ [10,11]. The various hydroxidooxidoborate species arise through well-known $B(OH)_3/OH^-$ /hydroxidooxidoborate anion equilibria [13,14] and products are templated by the cations present in solution [15,16]. H-bonding, cation steric effects, and cation charge, amongst other things, all play important roles in this templating process [17,18] and the scientific challenge is to get a greater understanding of how and why such interactions/reactions occur so that new materials can be intentionally targeted. The tetrahydroxidohexaoxidopentaborate(1-) anion appears to have exceptional stability [10,19] and can be templated by many cations but the above strategy has also led to the formation of unique and previously unobserved insular anions: *e.g.* $[B_7O_9(OH)_6]^{3-}$ [20] and $[B_8O_{10}(OH)_6]^{2-}$ [21] and to other novel structural hydroxidooxidoborate motifs [22,23]. Occasionally, unexpected products are observed and this manuscript reports on the synthesis and characterization of two such products: the co-crystallized 4,4'-trimethylenebis(*N*-methylpiperidine):boric acid (1:1) compound, 4,4'-(1-MeNC₃H₉)₂(CH₂)₃B(OH)₃ (**1**) and the zwitterionic tetrahydroxidohexaoxidopentaboron adduct $B_5O_6(OH)_4(\kappa N-NH_2CH_2CH_2NHEt_2) \cdot H_2O$ (**2**) ($NH_2CH_2CH_2NEt_2 = \text{deen}$). This manuscript describes in detail their solid-state H-bond interactions that we believe play an important role in their formation.

2. Experimental

2.1. General

Reagents were commercially available. ^1H , ^{13}C and ^{11}B NMR spectra were obtained in D_2O solutions on a Bruker Avance 400 spectrometer and data are reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B) or TMS (^{13}C and ^1H). TGA/DSC analysis (in air) was performed on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles between 20-800 °C with a temperature ramp-rate of 10 °C min^{-1} . FTIR spectra were obtained on a Perkin-Elmer 100 FTIR spectrometer as KBr pellets. Single-crystal X-ray crystallographic analyses were performed at the EPSRC National Crystallography service at the University of Southampton. CHN analysis was obtained from OEA laboratories Ltd in Callington, Cornwall.

2.2. Synthesis of 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (1)

4,4'-(1-MeNC₅H₉)₂(CH₂)₃ (4.8 g, 20.0 mmol) and B(OH)₃ (2.5 g, 40.0 mmol) were dissolved in 1:1 MeOH:H₂O (100 mL) with gentle warming. The solution was allowed to stand for 1 h before removal of the solvent under reduced pressure gave a dark cream solid which was oven dried at 50 °C for 24 h (7.3 g). The crude product was dissolved in and crystallized from H₂O to afford colourless needle-like crystals (1.5g, 25%) suitable for X-ray diffraction studies. M.p: 72-74 (dec) °C. ^1H (δ /ppm): 1.26-1.35 (m, 10H), 1.47 (br 2H), 1.87 (d, 4H), 2.6 (m, br 10H), 3.22 (d, 4H), 4.79 (HOD, OH rapidly exchanging in D_2O). ^{13}C (δ /ppm): 22.66 (CH₂), 29.98 (4CH₂), 32.75 (2CH), 35.20 (2CH₂), 43.54 (2CH₃), 54.68 (4CH₂); ^{11}B (δ /ppm): +4.7. IR (KBr, ν_{max} /cm⁻¹): 3345(br m), 3271(br,m), 2925(s), 2853(s), 2804(s), 2384(w), 1880(w), 1629(w), 1457(s), 1429(s), 1412(s), 1379(m), 1281(s), 1217(br, m), 1143(s), 1113(w), 1099(w), 1072(m), 1042(w), 988(m), 976(m) 960(m), 869(m), 832(m), 798(br,m), 766 (s), 706 (w), 680(s), 530(m), 506(m), 444(m). Elemental analysis, *calc.* for C₁₅H₃₃N₂BO₃: C, 60.0%, H, 11.1%, N, 9.3%; *found*: C, 59.6%, H, 11.0%, N, 9.3%. TGA: Loss of 1H₂O (60-70 °C): 6.1% (6.0% calc), residual B₂O₃ (>600 °C) 11.7% (11.6% calc.). sc-XRD: C₁₅H₃₃BN₂O₃, $M_r = 300.24$, Triclinic, $P-1$, $a = 6.29840(10)$ Å, $b = 10.7174(2)$ Å, $c = 13.9659(3)$ Å, $\alpha = 92.059(2)^\circ$, $\beta = 102.412(2)^\circ$, $\gamma = 100.376(2)^\circ$, $V = 902.90(3)$ Å³, $T = 100(2)$ K, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.075$ mm⁻¹ 15600 reflections measured, 4119 unique ($R_{\text{int}} =$

0.0212) which were used in all calculations. The final wR_2 was 0.0975 (all data) and R_1 was 0.0370 ($I > 2\sigma(I)$).

2.3. Synthesis of $B_5O_6(OH)_4(\kappa N-NH_2CH_2CH_2NHEt_2) \cdot H_2O$ (**2**)

ZnSO₄·H₂O (1.4 g, 8 mmol) was dissolved in H₂O (10 mL) and deen (2.0 g, 17 mmol) was added dropwise with stirring over 10 mins. An aqueous solution (10 mL) of Ba(OH)₂·8H₂O (2.5 g, 8 mmol) was then added to the solution and left to stir for a further 5 mins. BaSO₄ was removed by filtration and B(OH)₃ (5.2 g, 85 mmol) was added to the filtrate and stirred for 30 minutes. The solution was filtered into several vials and left for 3 weeks to allow for slow evaporation of *ca.* 50% of the solvent. A few drops of EtOH were added to each vial to encourage crystallization of the product. After a few days colourless crystals of **2** had formed and these were collected by filtration, combined, and placed in an oven for 30 mins to dry (1.6 g, 27%). These crystals were suitable for single-crystal XRD studies. M.p.: >300 °C. NMR (D₂O): ¹H (δ/ppm): 1.2 (t, 6H), 3.0 (q, 4H), 3.03 (br m, 4H), 4.79 (9H, HOD, NH, OH rapidly exchanging in D₂O); ¹³C (δ/ppm): 8.8 (CH₃), 47.1 (CH₂CH₃), 51.6 (CH₂NEt₂), 35.6 (CH₂NH₂); ¹¹B (δ/ppm): +16.2. IR (KBr, ν_{max}/cm^{-1}): 3556(s), 3481(br), 3370(), 3275(br), 3103(m), 1619(m), 1498(w), 1472(w), 1449(m), 1406(s), 1371(s), 1318(s), 1215(m), 1083(s), 1042(s), 1009(m), 937(m), 899(s), 708(w). Elemental analysis, *Calc.* for C₆H₂₂N₂B₅O₁₁: C, 20.4%, H, 6.6%, N, 7.9%; *Found*: C, 20.0%, H, 6.7%, N, 7.5%. sc-XRD: C₆H₂₃B₅N₂O₁₁, $M_r = 353.31$, triclinic, P-1 (No. 2), $a = 8.9225(3) \text{ \AA}$, $b = 9.3115(3) \text{ \AA}$, $c = 9.9764(4) \text{ \AA}$, $\alpha = 85.001(3)^\circ$, $\beta = 75.559(3)^\circ$, $\gamma = 78.425(3)^\circ$, $V = 785.74(5) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $Z' = 1$, $\mu(\text{CuK}\alpha) = 1.133 \text{ mm}^{-1}$, 10752 reflections measured, 2842 unique ($R_{int} = 0.0230$) which were used in all calculations. The final wR_2 was 0.0834 (all data) and R_1 was 0.0304 ($I > 2\sigma(I)$).

2.4. X-ray crystallography

A suitable crystal of **1** was mounted on Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with HF Varimax optics (100µm focus). A suitable crystal of **2** was mounted on a MITIGEN holder in perfluoroether oil on a Rigaku 007HF equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000 detector. The crystals were kept at $T = 100(2) \text{ K}$ during data collection. Data collection for **1** was

obtained using *CrystalClear-SM Expert 3.1 b27* [24]. Data collection for **2** and cell determination, data reduction, cell refinement and absorption correction for **1** and **2** were obtained using *CrysAlisPro* [25]. Using Olex2 [26] the structures were solved with the ShelXT [27] structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2018/3 of ShelXL [28] using Least Squares minimisation.

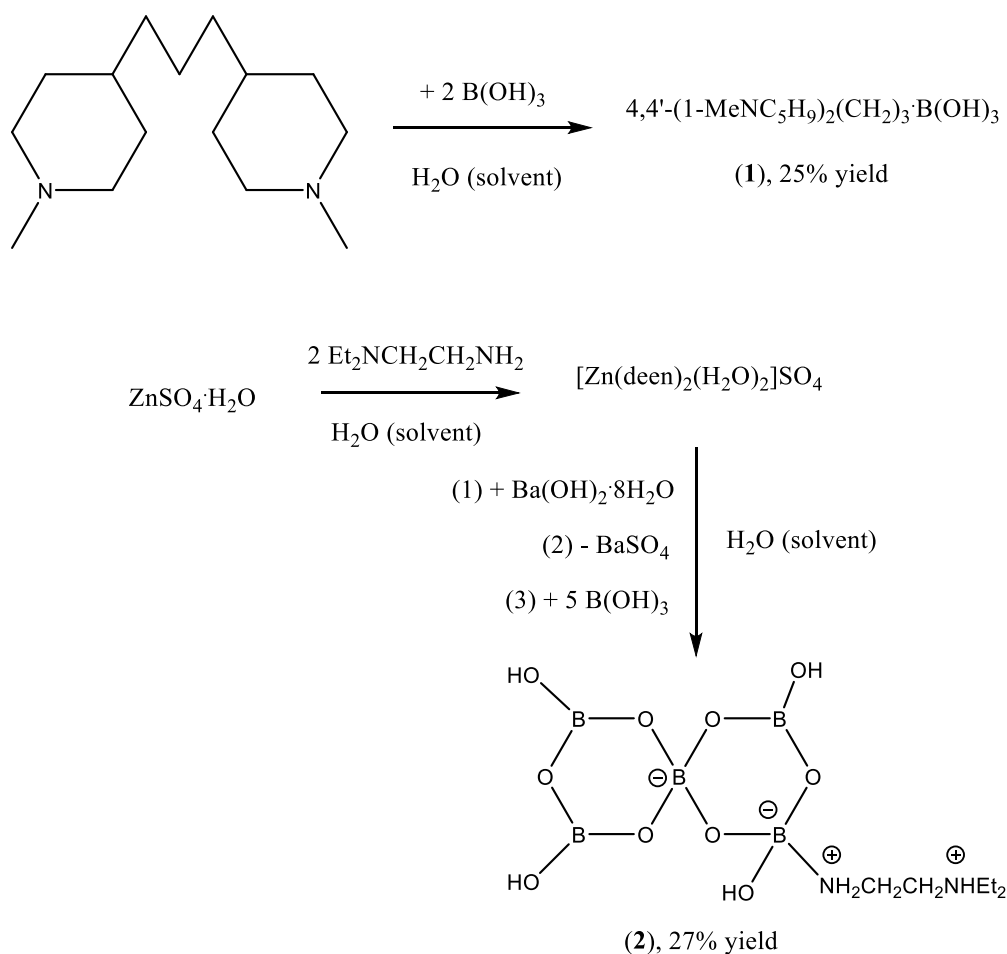
3. Results and Discussion

3.1. Synthesis and characterisation

The synthetic strategy for the preparation of the new compounds involves crystallization at room temperature from aqueous or ethanolic aqueous solutions by self-assembly from appropriate dynamic combinatorial libraries [13-15,16]. Solutions primed with B(OH)₃ and non-metal cations generally afford hydroxidooxidoborate salts [10] and those primed with B(OH)₃ and transition metal complex cations generally afford either hydroxidooxidoborate salts or hydroxidooxidoborate complexes [10,11]. The reagents/solvents for the formation of **1** and **2** are given in Scheme 1.

Tetrahydroxyhexaoxidopentaborate(1-) salts are most commonly prepared from unipositive amine based cations in aqueous solution irrespective of the amine:B(OH)₃ ratio, although yields are generally quantitative with a 1:5 ratio [10]. Amine cations that can be dipositive have been known to afford tetrahydroxidotrioxidotriborate(1-) anions especially at lower amine:B ratios [10,29]. Cognisant of this we attempted the synthesis of a hydroxidooxidoborate salt from 4,4'-trimethylenebis(*N*-methylpiperidine) at a nitrogen:boron ratio of 1:1 and **1** crystallized from the aqueous solution in low yield. The crystals obtained were suitable for a X-ray diffraction study and a single crystal X-ray analysis revealed that **1** was not a hydroxidooxidoborate salt but an unexpected co-crystallized material of the starting compounds in a 1:1 stoichiometry. This observed product may arise through preferential crystallization of a neutral product from the polar aqueous solvent. Co-crystallized materials containing B(OH)₃ are not uncommon and B(OH)₃ often fills 'voids' as H-bonded spacers between anions in hydroxidooxidoborate salts with sterically demanding cations [30-33]. Boric acid also forms co-crystallized materials with lactams [34], aromatic amines [35,36] and Ph₃PO [37]; to our knowledge **1** is the first example of B(OH)₃ co-crystallized with a tertiary amine. One can only speculate as to why this product was obtained in preference to a hydroxidooxidoborate salt, but solubility, and solid-state intermolecular interactions (*e.g.* packing and H-bonding) and reactant stoichiometry are logical drivers. Solid-state interactions

are discussed in detail in section 3.2.



Scheme 1. Reaction conditions for the formation of **1** and **2**.

We have shown that cationic complexes containing Zn^{II} and amine/ammine ligands such as $[\text{Zn}(\text{dac})_2(\text{H}_2\text{O})_2]^{2+}$ (dac = 1,2-diaminocyclohexane), $[\text{Zn}(\text{dien})_2]^{2+}$ (dien = $\text{NH}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$), $[\text{Zn}(\text{NH}_3)_6]^{2+}$, and $[\text{Zn}(\text{en})_3]^{2+}$ (en = 1,2-diaminoethane) can template the formation of hydroxidooxidoborate salts *e.g.* $[\text{Zn}(\text{dac})_2(\text{H}_2\text{O})_2][\text{B}_7\text{O}_9(\text{OH})_5] \cdot \text{H}_2\text{O}$ [38], or the formation of complexes containing hydroxidooxidoborate ligands *e.g.* $[\text{NH}_4]_2[\text{Zn}\{\text{B}_6\text{O}_7(\text{OH})_6\}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ [39], $[\text{Zn}(\text{dien})\{\text{B}_6\text{O}_7(\text{OH})_6\}] \cdot 0.5\text{H}_2\text{O}$ [39] and $[\text{Zn}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}] \cdot 2\text{H}_2\text{O}$ [40]. We employed the same reaction methodology as used in the cited examples with deen as the amine ligand for the synthesis/crystallization of **2** and despite being confident that the labile complex salt, $[\text{Zn}(\text{deen})_2(\text{H}_2\text{O})_2](\text{OH})_2$ had been prepared *in situ* compound **2** surprisingly did not contain Zn. This was confirmed by a single-crystal X-ray diffraction study since the crystals obtained for **2** were suitable for such a study. This study

revealed that **2** was $B_5O_6(OH)_4(\kappa N-NH_2CH_2CH_2NHEt_2)\cdot H_2O$, a further example of an otherwise rare zwitterionic tetrahydroxidohexaoxidopentaborate(1-) adduct. Other known examples are limited to $B_5O_6(OH)_4\{NH_2(CH_2)_nNH_3\}$ ($n = 5, 6$) and $[H_3N(CH_2)_8NH_3][B_5O_6(OH)_4\{NH_2(CH_2)_8NH_2\}-B_5O_6(OH)_4] \cdot 2B(OH)_3 \cdot 2H_2O$ [33,41]. It is likely that since **2** was obtained in low yield there were Zn-borate species present in the reaction solution but these failed to crystallize under the prevailing conditions. The observed product may therefore arise through preferential crystallization of a neutral product from the polar medium. Again, solid-state intermolecular interactions (*e.g.* packing and H-bonding) are logical drivers for the formation of crystalline **2** and solid-state interactions are discussed in detail in section 3.3.

Solution NMR (1H , ^{11}B , and ^{13}C) spectra of samples of **1** and **2** were obtained in D_2O . However, these were largely uninformative and did not reflect the anticipated spectra for **1** and **2**. Rather, the spectra obtained reflected the various combinatorial components of **1** and **2** arising through the rapidly attained equilibria reactions associated with hydroxidooxidoborates in aqueous solution [14]. Thus, ^{13}C spectra arising from **1** and **2** have 6 and 4 signals at the expected chemical shifts for 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ and deen, respectively. The ^{11}B spectrum of **1** is not that expected for $B(OH)_3$ (+18 ppm) but is shifted considerably upfield to + 4.7 ppm due to $B(OH)_3/[B(OH)_4]^-$ equilibria arising through aqueous protonation of the 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ with release of $[OH]^-$ [13,14]. The ^{11}B spectrum of **2** has an one equilibrium signal at + 16.2 ppm, close to that generally observed, and predicted [14,19], for dilute hydroxidooxidopentaborate(1-) salts again resulting from the $B(OH)_3/[B(OH)_4]^-$ equilibria in a less basic solution. Although **2** is formally an adduct of a hydroxidooxidopentaborate(1-), with an additional 4-coordinate boron centre, dissociation of the ligand in solution would result in the salt $[Et_2NHCH_2CH_2NH_2][B_5O_6(OH)_4]$ which would then undergo the expected hydroxidooxidoborate equilibria reactions.

The IR spectrum of **1** showed a broad peak at 3271 cm^{-1} and strong broad bands at 1429 , 1143 and 869 cm^{-1} that can be assigned to $\nu(O-H)$, $\nu_{as}(B-O)$, $\nu_{as}(B-O)$ and $\nu_s(B-O)$ of $B(OH)_3$, respectively [42], and the other signals can be attributed to the organic moiety. Likewise, the IR of spectrum of **2** has signals that can be attributed to the $Et_2NHCH_2CH_2NH_2$ fragment and other strong signals at 1371 , 1042 , 937 and 899 cm^{-1} which may be assigned to the tetrahydroxidohexaoxidopentaborate(1-) unit as $\nu_{as}(B_{trig}-O)$, $\nu_{as}(B_{tet}-O)$, $\nu_s(B_{trig}-O)$ and $\nu_s(B_{tet}-O)$ stretches [42]. A band at 937 cm^{-1} is observed in the zwitterionic compound **2** and this is likely to be related to the diagnostic band observed at *ca.* 925 cm^{-1} for

tetrahydroxidohexaoxidopentaborate(1-) salts [10,19,29-32].

Compound **1** was a crystalline low melting solid that decomposed at its melting point. This thermal decomposition was investigated by TGA/DSC. Compound **1** is thermally decomposed to a glassy B₂O₃ residue (calc. 11.6%, found 11.7%) in a multistep process: the first lower temperature step occurred at 60-70 °C. This first step is endothermic and appears to be consistent with loss of one H₂O by dehydration and cross-linking of B(OH)₃ to HBO₂ [4,43]. Subsequent steps, with both exothermic and endothermic DSC peaks, are likely to be associated with the oxidation of the amine and further loss of 1/2H₂O. Such behaviour has been observed before in many non-metal cation hydroxidooxidoborates [10,19,28-33] although the initial dehydration/crosslinking step generally occurs at a higher temperature (*ca.* >200 °C) than that observed for **1**. However, B(OH)₃ is known to start to dehydrate at 60-90 °C [4, 43] and the lower temperature dehydration of **1** is not inconsistent with this.

3.2. X-ray structure of 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**)

The solid-state structure of **1** is free from disorder and comprises one molecule of B(OH)₃ and one molecule of 4,4'-trimethylenebis(*N*-methylpiperidine) in the asymmetric unit. A diagram of **1** showing non-hydrogen atomic numbering is given in Figure 1.

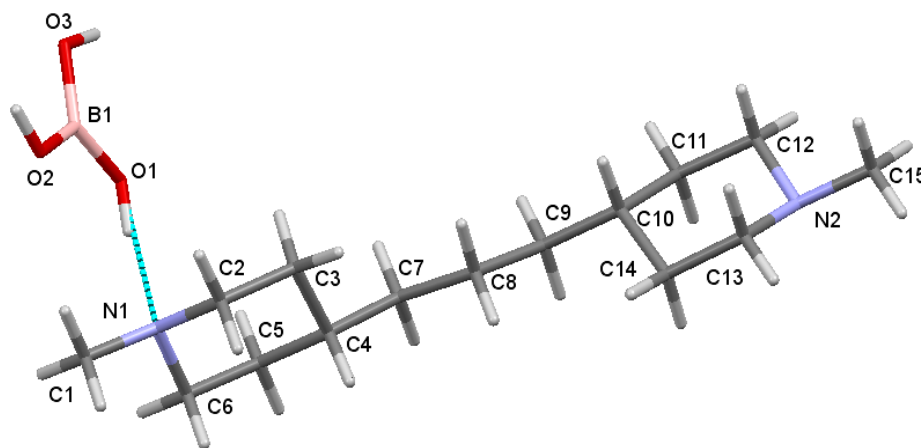


Figure 1. Drawing of the structure of **1** showing non-hydrogen atomic numbering.

The B-O bond-lengths in **1** range from 1.3612 (14)-1.3723(13) Å (*av.* 1.3671(14) Å) and are not significantly different from those observed in other co-crystallised B(OH)₃ structures [30-37], or B(OH)₃ [44] itself. Likewise, OBO bond angles range from 119.79(10)-120.27(9)° (*av.* 120.00(10)°) and their sum at 360.00(10)° confirms the expected trigonal planar boron centre. The two *N*-methyl piperidines of the organic component of the co-crystal

are crystallographically non-equivalent and both adopt chair conformations, with methyl groups equatorial, and have typical C-C and C-N bond-lengths. The C-N-C angles at N1 and N2 range from 110.19(8)-110.77(8) $^{\circ}$ (*av.* 110.51(8) $^{\circ}$) and 109.71(8)-110.76(7) $^{\circ}$ (*av.* 110.39(8) $^{\circ}$), respectively. The sum of the angles at N1 (331.52(8) $^{\circ}$) and N2 (331.18(8) $^{\circ}$) confirms that these centres are trigonal pyramidal, as are expected for tertiary amines.

We believe H-bonding plays an important role in building the lattice of **1** with each B(OH)₃ forming two donor bonds (O1-H1 \cdots N1 and O2-H2 \cdots N2') as a bridge between two 4,4','-trimethylenebis(*N*-methylpiperidine) molecules. This results in the formation of infinite alternating diamine/B(OH)₃ C₂²(16) chains [45]. Furthermore, the third hydroxy group on B1 is associated with a dimeric reciprocal R₂²(8) interaction with a neighbouring B(OH)₃ (O3-H3 \cdots O1'-B1'-O3'-H1' \cdots O1-B1-). Since there is only one crystallographically unique B(OH)₃ in **1** this neighbouring B(OH)₃ also bridges two 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ molecules and forms a C₂²(16) chain. Overall, this results in cross-linking of the two chains with the formation of larger R₆⁶(36) rings (Figure 2). As the two nitrogen atoms of the 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ units are crystallographically non-equivalent (N1 and N2), as are the two piperidine rings, and the resulting larger R₆⁶(36) rings are centrosymmetric with their chains running in opposite directions.

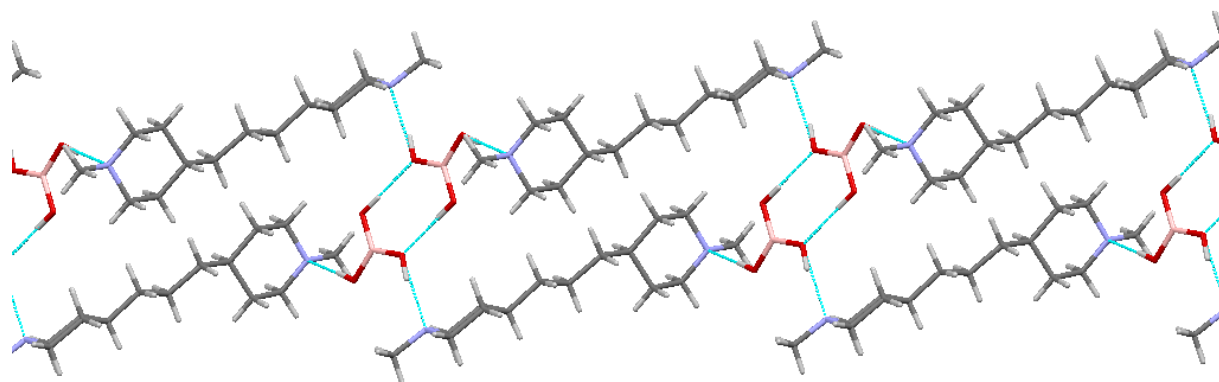


Figure 2. H-bonding interactions **1** illustrating C₂²(16) chains crosslinked by R₂²(8) borate interactions and resulting in the formation of larger centrosymmetric R₆⁶(36) interchain rings.

3.3. X-ray structure of B₅O₆(OH)₄(κN-NH₂CH₂CH₂NHEt₂)·H₂O (**2**)

The solid-state structure of **2** is comprised of neutral zwitterionic hydroxidooxidopentaborate(2-) derivative, $B_5O_6(OH)_4(\kappa N-NH_2CH_2CH_2NHEt_2)$, co-crystallized with one water of crystallization. The structure is disorder free. The hydroxidooxidoborate containing moiety in **2** is structurally derived from a substituted pentahydroxidohexaoxidopentaborate(2-) anion with a FBB of $5:2T+3A$ [7,9] with one of the two hydroxido groups on the tetrahedral ring boron in $[B_5O_6(OH)_5]^{2-}$ replaced by a monoprotonated diammine ligand. Thus, $[H_2NCH_2CH_2NHEt_2]^+$, is coordinated to B2 via the lone pair on the unprotonated N1 atom (see Figure 3 for non-hydrogen atomic numbering). Hydroxidooxidopentaborate (2-) derivatives with this FBB occur in several minerals *e.g.* ezcurrite, $Na_{2n}\{[B_5O_7(OH)_3]_n\} \cdot 2nH_2O$ [46] and a few synthetic nonmetal hydroxidooxidopentaborates *e.g.* $[H_3N(CH_2)_3NH_3]_n\{[B_5O_8(OH)]_n\}$ [47]; these species are both comprised of more highly condensed hydroxidooxidoborate networks rather than insular moieties. Insular hydroxidooxidopentaborate(2-) derivatives with this FBB are uncommon and are currently limited to the three zwitterionic derivatives noted earlier [33,41].

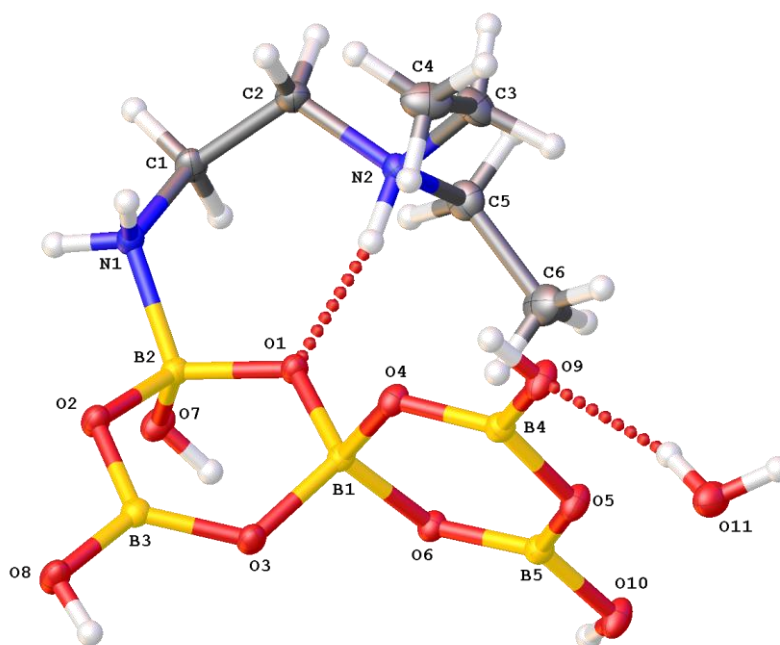


Figure 3. A drawing of **2** showing non-hydrogen atomic numbering, the S(7) intramolecular H-bond and the intermolecular O11-H11 \cdots O9 H-bond.

The B-O bond-lengths associated with the trigonal and tetrahedron boron atoms in **2** range from 1.3544(16)-1.3892(16) Å and 1.4418(16)-1.4872(15) Å, respectively and are typical of hydroxidooxidoborate structures [19,22,29-33]. The O-B-O angles are also in the ranges expected for oxidoborate species in general [19,22,29-33] and more specifically, the zwitterionic derivatives [41]. The B-O bond-lengths to tetrahedral B2 (bound to N1) in **2** range from 1.4418(16)-1.4706(16) Å (av.1.4564(16) Å) are slightly, but significantly, shorter than the B-O bond-lengths around the tetrahedral (spiro) B1 (1.4465(15)-1.4872(15) Å, av. 1.4705(16) Å). The B2-N1 bond length in **2** is 1.6078(16) Å and this is significantly shorter than in the other reported complexes where the boron acceptor atom is otherwise only bound to oxygen [48]. Angles about B2 range from 104.04(9)-114.89(10)° and indicate a tetrahedrally hybridized boron centre but the N-B-O angles are smaller (104.04(9)-108.92(10)°) than the O-B-O angles (111.65(10)-114.89(10)°) corresponding to tetrahedral character value (THC_{DA}, [48,49]) of 75.6%. This value is in the middle the broad range reported for other N→BO₃ sets (58.6 - 90.0) [49-53] and extends the narrower range (82.1 - 85.6) for the other three reported zwitterionic hydroxidooxidopentaborate derivatives [41]; the latter values were recalculated from the published bond angles [41].

There are potentially 3NH and 6OH H-bond donor sites within **2** and all are used in H-bonding interactions. Three of the hydroxidooxidopentaborate OH group partake in reciprocal R₂²(8) interactions: (O6-B5-O10-H10···O6'-B5'-O10'-H10'···, O3-B3-O8-H8···O3'-B3'-O8'-H8'···, and O4-B4-O9-H9···O4'-B4'-O9'-H9'···). Such interactions are strong (*ca.*- 21 kJ. mol⁻¹ / H-bond) and are a well-known influence in the stability of hydroxidooxidopentaborate structures [19]. The hydroxido group containing O7 is involved in an unusual R₂²(8) ring interaction (O7-H7···O10'-H10'···O6-B1-O1-B2); this includes the same O10', which is now the acceptor site, involved in the reciprocal donor interaction to O6-H6 (Figure 4). The Et₂NH-group is involved in an unusual S(7) intramolecular H-bond to O1 (B2-N1-C1-C2-N2-H2···O1-) (Figure 3) and the -NH₂B group H-bonds to two hydroxidooxidopentaborates at symmetry related O2 and O11 sites. The H₂O molecule (containing O11) bridges two hydroxidooxidopentaborate moieties at O9 and a symmetry related O7' acceptor sites (Figure 3).

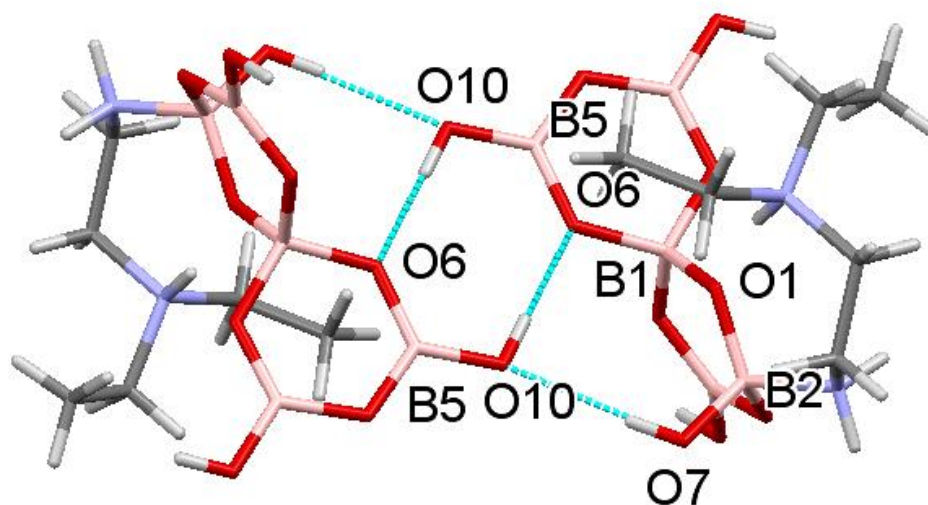


Figure 4. A view of the structure of **2** showing the reciprocal $R_2^2(8)$ interactions involving $O10H10\cdots O6$ and the unusual $R_2^2(8)$ interaction involving $O7H7\cdots O10$ and $O10H10\cdots O6$.

4. Conclusions

Two unusual organic-borate containing species, 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**) and B₅O₆(OH)₄(κN-NH₂CH₂CH₂NHEt₂)·H₂O (**2**) were obtained as crystalline solids from combinatorial library solutions containing B(OH)₃ and the organic fragments by self-selection processes. Compound **1** is a co-crystallized product and **2** is an internally condensed zwitterionic monoprotoneated diamine/tetrahydroxidohexaoxidopentaborate derivative (FBB = 5:2*T* + 2Δ). The plethora of H-bond interactions found in both solid-state structures are described in detail using Etter terminology and since these H-bond interactions are strongly stabilizing we conclude that they are a very important factor in directing the self-selection crystallization processes.

Credit authorship contribution statement

M.A. Altahan: synthesis and investigation of **2**, writing part of original draft. **M.A. Beckett:** conceptualization, methodology, supervision, writing original draft, review and editing final drafts. **S.J. Coles:** crystallographic fund holder, reviewing drafts. **P.N. Horton:** crystallographic experimental and structure determinations, reviewing drafts. **C.L. Jones:** synthesis and investigation of **1**, writing part of original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A Supplementary Materials

Crystallographic data for the structural analysis of compounds **1** and **2** are available as supplementary information and have also been deposited at the Cambridge Crystallographic Data Centre (CCDC numbers 2151130 and 2151131). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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