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# Supramolecular structures containing 'isolated' pentaborate anions and non-metal cations: Crystal structures of [Me₃NCH₂CH₂OH] [B₅O₆(OH)₄] and [4-MepyH, 4-Mepy][B₅O₆(OH)₄]

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## Abstract

The solid-state structures of two non-metal pentaborates $[Me_3NCH_2CH_2OH][B_5O_6(OH)_4]$ (**1**) and [4-MepyH, 4-Mepy]$[B_5O_6(OH)_4]$ (**2**) have been determined by single-crystal X-ray diffraction methods. Structures **1** and **2** both contain supramolecular pentaborate frameworks held together by extensive H-bond interactions. The framework of **1** exists essentially as planes of pentaborate anions linked via three pairwise 'planar' $\beta \rightarrow \alpha$ interactions, with a fourth $\beta \rightarrow \beta$ interaction crosslinking the planes. The framework of **2** is very similar except that one of the three pairwise linkages within the plane is replaced by pairwise 'step-like' bifurcated H-bonds to both $\alpha$ sites of a neighboring anion. The cations in **1** and the cations and neutral 4-Mepy ligands in **2** are present in the framework cavities and channels, with additional H-bond interactions existing between cations and anions.
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## 1. Introduction

Boron is always found in nature combined with oxygen as anhydrous mixed metal oxides or as hydrated metal borates, with more than 200 borate minerals known and more than 100 structurally characterized [1–3]. Some structures display 'isolated' borate or polyborate anions, but the vast majority display more condensed anions comprising infinite chains, sheets or networks. Generally, the boroxole $(B_3O_3)$ ring in various guises is a reoccurring structural motif, with the Lewis acidity of the metal counter-ions influencing the observed structures: strongly Lewis acidic metals being commonly found in structures with a high proportion of four-coordinate boron sites [4,5]. The only

minerals that do not contain metal counter-ions are ammonioborite, $[NH_4]_3[B_{15}O_{20}(OH)_8] \cdot 4H_2O$ [6] and larderellite $[NH_4][B_5O_7(OH)_2] \cdot H_2O$ [7] and these polyborate minerals have anionic structures exclusively paired with the ammonium cation. Non-metal cations differ from metal cations in their potential for interactions with borate anions: metal cations are spherical and primarily accept electron density from oxygen donors whilst non-metal cations may be nonspherical and may have H-bond donor sites [8]. These properties may lead to previously unobserved borate structural moieties and further offers the opportunity to explore structure directing H-bond relationships. Indeed, the guanidinium and imidizolium poyborate systems both display the isolated nonaborate anion, $[B_9O_{12}(OH)_6]^{3-}$, and this anion is only observed with these non-metal cations [9]. Quaternary ammonium, phosphonium and related nonmetal borate systems have also been studied and reviewed

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but few have been structurally characterized [8,10,11]. This manuscript reports the X-ray structural characterization of two novel non-metal pentaborate derivatives, [NR$_n$][B$_5$-O$_6$(OH)$_4$], containing 'isolated' pentaborate anions. The non-metal counter-ions used in this study, [NR$_n$], are the hydroxyl functionalized quaternary ammonium cation, choline [Me$_3$NCH$_2$CH$_2$OH]$^+$, and a substituted pyridinium cation, [4-MepyH]$^+$. The latter non-metal pentaborate crystallized with one neutral 4-Mepy ligand for each [4-MepyH]$^+$ cation. In both structures the pentaborate anions are H-bonded together to form unique layered supramolecular 3D frameworks, with the cations (and or ligands) located within the channels and cavities.

## 2. Results and discussion

### 2.1. Solid-state structure of [Me$_3$NCH$_2$CH$_2$OH]-[B$_5$O$_6$(OH)$_4$] (1)

Compound 1 was obtained in a low yield as crystals suitable for X-ray diffraction from an aqueous solution of choline hydroxide (50%) and boric acid in a ratio of 1:5, in a similar way to that reported by Schubert and co-workers for non-metal borate derived from α,ω-diamminoalkanes [12].

Crystals of 1 are triclinic and contains two independent [Me$_3$NCH$_2$CH$_2$OH][B$_5$O$_6$(OH)$_4$] formula units in the asymmetric unit as shown in Fig. 1. One of the choline cations is disordered but was successfully modelled based on three components with occupancy 0.522(3), N31; 0.263(4), N41; and 0.215, N51. The two pentaborate anions are structurally similar and are not notably different from other systems containing isolated [B$_5$O$_6$(OH)$_4$]$^-$ anions

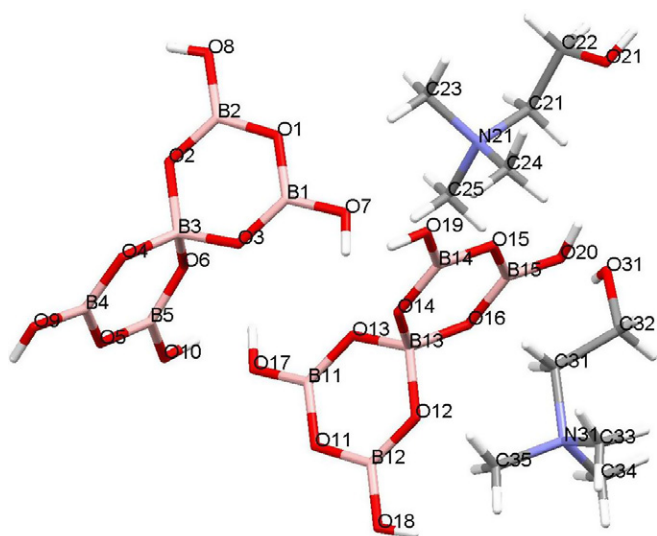[1,12–14] with B–O distances to the four-coordinate tetrahedral B3 centre [av. 1.471(2) Å] significantly longer than those involving the trigonal B centres which range from 1.357(2) to 1.385(2) Å. B–O bonds involving trigonal B atoms and terminal OH groups are at the shorter end of the range [av. 1.361(2) Å] whilst B–O bonds involving the O atoms distal (O1, O5) to the four-coordinate B3 centre are at the longer end of the range [av. 1.381(2) Å]. Bond angles at the B3 range from 108.68(14)° to 111.34(14)° and angles at the other ring atoms range from 116.65(16)° to 122.87(16)° for B centres consistent with sp$^3$ and sp$^2$ hybridization, respectively. The angles at the O ring centres range from 119.00(14)° to 123.73(14)°. The isolated pentaborate anions in 1 H-bond together to form a supramolecular framework, and the framework for this compound is discussed in detail, where it is compared and contrasted with that found for compound 2, in Section 2.3. The choline cations are situated in the cavities arising within the supramolecular pentaborate framework. The major component of the disordered choline acts as a H-bond acceptor to the other choline cation (O21–H21···O31) and a donor to a pentaborate anion (O31–H31···O4). However, the other two components show no H-bond interactions, perhaps suggesting the choline does not readily fit into the cavities. Hydrogen bond data for 1 is summarized in Table 1.

### 2.2. Solid-state structure of [4-MepyH, 4-Mepy]-[B$_5$O$_6$(OH)$_4$] (2)

Compound 2 was obtained in a low yield from a prolonged attempt of a re-crystallization of the orthoborate ester adduct (4-Mepy) · B(OCH$_2$CF$_3$)$_3$ [15]. It is believed that hydrolysis occurred by adventitious H$_2$O in the solvent, and that the hydrolysis was facilitated by the enhanced Lewis acidity of the tris(trifluoroethoxy)orthoborate moiety [16]. There is precedent for such a reaction since pre-mediated hydrolysis of the orthoborate ester B(OMe)$_3$ in the presence of organic bases (e.g. guanidine,



Fig. 1. Drawing of the structure of [Me$_3$NCH$_2$CH$_2$OH][B$_5$O$_6$(OH)$_4$] (1) showing two independent pentaborate anions and numbering scheme. One of the choline cations (containing N21) is ordered [S.o.f. = 1] whereas the other choline cation (containing N31) is disordered with the major component [S.o.f. = 0.522(3)] displayed.

Table 1
Hydrogen bond interactions for [Me$_3$NCH$_2$CH$_2$OH][B$_5$O$_6$(OH)$_4$] (1) (Å and °)

| D–H···A | $d$(D–H) | $d$(H···A) | $d$(D···A) | ∠(DHA) |
|---|---|---|---|---|
| O7–H7···O13 | 0.84 | 1.89 | 2.7266(18) | 173.5 |
| O8–H8···O2$^i$ | 0.84 | 1.86 | 2.6928(17) | 169.7 |
| O9–H9···O18$^{ii}$ | 0.84 | 1.94 | 2.7482(18) | 161.0 |
| O10–H10···O14$^{iii}$ | 0.84 | 1.89 | 2.7199(19) | 171.9 |
| O17–H17···O3 | 0.84 | 1.84 | 2.6761(18) | 172.3 |
| O18–H18···O12$^{iv}$ | 0.84 | 1.86 | 2.6941(18) | 173.9 |
| O19–H19···O6$^v$ | 0.84 | 1.86 | 2.6871(19) | 170.3 |
| O20–H20···O8$^{vi}$ | 0.84 | 1.94 | 2.7592(17) | 166.4 |
| O21–H21···O31$^{vii}$ | 0.84 | 1.86 | 2.699(3) | 174.1 |
| O31–H31···O4$^{viii}$ | 0.84 | 1.93 | 2.762(3) | 169.2 |

Symmetry transformations used to generate equivalent atoms: (i) −x + 2, −y, −z; (ii) −x + 1, −y, −z + 1; (iii) x + 1, y, z; (iv) −x, −y + 1, −z + 1; (v) x − 1, y, z; (vi) −x + 1, −y + 1, −z; (vii) −x + 1, −y + 2, −z; (viii) x, y + 1, z.
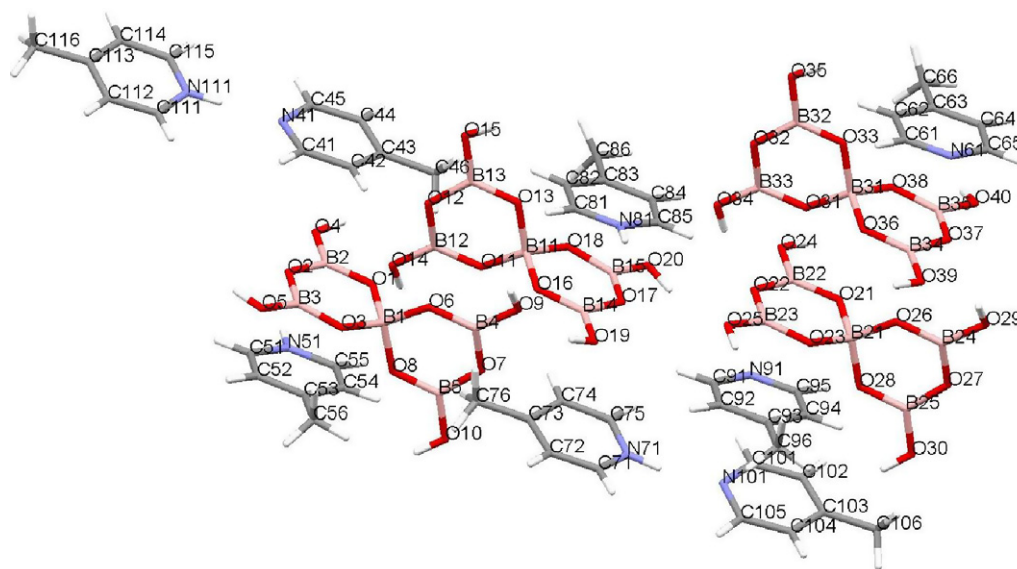
Fig. 2. Drawing of the structure of [4-MepyH, 4-Mepy][$B_5O_6(OH)_4$] (**2**) showing four independent pentaborate anions and numbering scheme.

piperidine, $Bu_3N$, [$Me_4N$][OH], [$Et_4N$][OH]) in organic solvents has been employed as a synthetic route to polyborate (triborate, tetraborate, pentaborate and heptaborate) salts [10]. In particular, [X][$B_5O_6(OH)_4$] (X = [$C(NH_2)_3$], [$C_5$-$NH_{12}$], [$Me_4N$], [$Et_4N$]) have been isolated using this methodology [10]. A possible mechanism for such hydrolysis/condensation reactions has been described [17].

Crystals of **2** are triclinic and the unit cell contains four independent pentaborate anions, four independent 4-methylpyridinium cations and four independent neutral 4-methylpyridine molecules as shown in Fig. 2. Compound **2** was solved in *P*1 since the final *R*-factor was half of that which could be obtained in *P$\bar{1}$*. The suggested reason for this was that there were only pseudo-inversion centres for which two of the methylpyridinium cations did not fit. In this structure all the hydrogen atoms were initially found using a difference map to determine which atom they were bonded to. They were than constrained to those atoms using appropriate standard riding models. Half of the [4-MepyH]$^+$ cations are H-bonded to neutral 4-Mepy ligands, whilst the remainder, together with the remaining neutral 4-Mepy molecules, H-bond to hydroxy sites on the pentaborate anions. All four pentaborate anions are structurally very similar and not notably different from other systems containing isolated [$B_5O_6(OH)_4$]$^-$ anions [1,12–14] and the pentaborate anions observed for **1**. B–O distances to the four-coordinate tetrahedral B1 centre range from 1.446(6) to 1.497(6) Å and are significantly longer than those involving the trigonal B centres which range from 1.327(7) to 1.415(6) Å. These ranges are larger than corresponding ranges observed for **1** and the systematic variations of bond-lengths observed in **1** were apparent but not significant in **2**. Bond angles at the B1 range from 107.7(4)° to 111.7(4)° [av. 109.48°] and angles at the other ring atoms range from 115.6(4)° to 122.9(4)° [av. 120.0°] for B centres consistent with sp$^3$ and sp$^2$ hybridization,

respectively. Distal O to terminal O angles at three-coordinate B centres, 115.6(4)–117.7(4) [av. 116.6°] are significantly smaller than the other angles at the three-coordinate ring borons. The angles at the O ring centres range from 117.5(4)° to 125.4(4)°, with angles at distal O2 and O7 significantly smaller. The isolated pentaborate anions in **2** H-bond together to form a supramolecular framework. This framework is discussed in detail in Section 2.3. The [4-Mepy]$^+$ cations and the neutral 4-Mepy ligands are also involved in H-bonding interactions. Half of the [4-Mepy]$^+$ cations (pryridinium rings that include N101 and N111) interact with half of the neutral 4-Mepy ligands (pyridine rings to include N71 and N41, respectively) to form extended dimeric planar adducts which stack within the cavities of the supramolecular pentaborate anion framework. These N–H···N interactions are non-symmetric with D···A distances averaging 2.64 Å and ∠DHA angles averaging 174.5°, indicative of strong H-bonds. The remaining [4-Mepy]$^+$ cations (pyridinium rings that include N51 and N81) are H-bond donors to pentaborate anions (to O5 and O20, respectively) at β-sites (see Fig. 3 for nomenclature), and the remaining neutral 4-Mepy ligands (pyridine rings to include N91 and N61) are H-bond acceptors from pentaborate β-sites (O25 and O40, respectively). Detailed hydrogen bond data for **2** are given in Table 2.

### 2.3. Supramolecular H-bonded pentaborate frameworks of 1 and 2

An isolated [$B_5O_6(OH)_4$]$^-$ anion has four potential H-bond donor sites and 10 potential H-bond acceptor sites. The [$B_5O_6(OH)_4$]$^-$ anions in **1** and **2** interact with one-another via H-bonds to form a supramolecular network. Schubert and co-workers [12] have introduced a nomenclature, as shown in Fig. 3a, to differentiate between the avail-
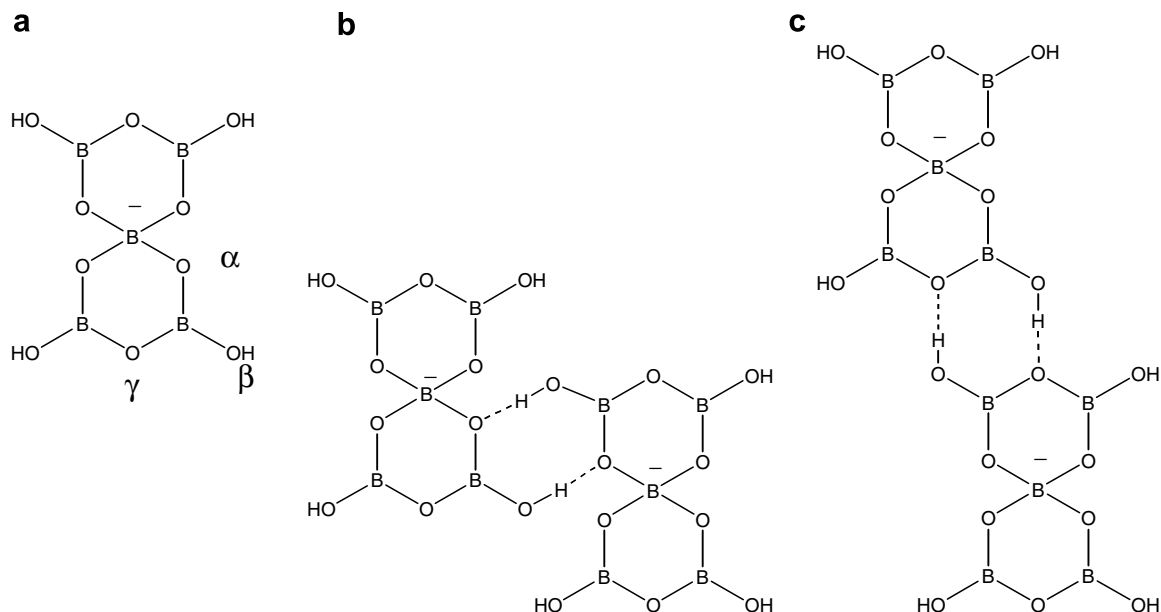
Fig. 3. Schematic diagrams of pentaborate anions showing (a) α, β, and γ nomenclature, (b) a pairwise β → α dimeric interaction between two pentaborates and (c) a pairwise β → γ dimeric interaction between two pentaborates.

able sites and classify H-bond interactions between neighbouring pentaborate anions. Interactions which have been previously observed [1,12–14] include pairwise (β → α) interactions between two neighbouring anions, as shown in Fig. 3b, with formation of dimers. A similar dimeric

Table 2
Hydrogen bond interactions for [4-MepyH, 4-Mepy][B_5O_6(OH)_4] (**2**) (Å and °)

| D–H⋯A | $d$(D–H) | $d$(H⋯A) | $d$(D⋯A) | ∠(DHA) |
|---|---|---|---|---|
| O4–H4⋯O16[i] | 0.84 | 1.94 | 2.748(5) | 160.3 |
| O5–H5⋯O40[ii] | 0.84 | 1.82 | 2.626(5) | 159.5 |
| O9–H9⋯O11 | 0.84 | 2.00 | 2.801(6) | 158.9 |
| O9–H9⋯O18 | 0.84 | 2.45 | 3.031(6) | 127.2 |
| O10–H10⋯O13[iii] | 0.84 | 1.94 | 2.737(6) | 157.0 |
| O14–H14⋯O6 | 0.84 | 2.02 | 2.837(6) | 166.4 |
| O14–H14⋯O3 | 0.84 | 2.48 | 3.065(6) | 127.7 |
| O15–H15⋯O8[iv] | 0.84 | 1.92 | 2.741(6) | 166.4 |
| O19–H19⋯O1[v] | 0.84 | 1.94 | 2.742(6) | 159.3 |
| O20–H20⋯O25 | 0.84 | 1.82 | 2.633(5) | 163.6 |
| O24–H24⋯O36 | 0.84 | 1.93 | 2.764(5) | 174.6 |
| O25–H25⋯N91[v] | 0.84 | 1.84 | 2.652(7) | 162.3 |
| O29–H29⋯O31[v] | 0.84 | 2.10 | 2.916(6) | 163.9 |
| O29–H29⋯O38[v] | 0.84 | 2.42 | 3.029(6) | 130.2 |
| O30–H30⋯O33[vi] | 0.84 | 1.97 | 2.761(6) | 156.7 |
| O34–H34⋯O26[i] | 0.84 | 2.19 | 2.898(6) | 141.7 |
| O34–H34⋯O23[i] | 0.84 | 2.47 | 3.056(6) | 127.7 |
| O35–H35⋯O28[vii] | 0.84 | 1.90 | 2.736(6) | 172.1 |
| O39–H39⋯O21 | 0.84 | 1.94 | 2.773(6) | 172.4 |
| O40–H40⋯N61[viii] | 0.84 | 1.85 | 2.664(6) | 162.6 |
| N51–H51A⋯O5 | 0.88 | 1.84 | 2.704(7) | 168.5 |
| N81–H81A⋯O20 | 0.88 | 1.83 | 2.702(7) | 168.8 |
| N101–H10D⋯N71[vii] | 0.88 | 1.78 | 2.656(6) | 172.9 |
| N111–H11D⋯N41[ix] | 0.88 | 1.75 | 2.632(6) | 176.3 |

Symmetry transformations used to generate equivalent atoms: (i) $x$, $y + 1$, $z$; (ii) $x$, $y$, $z - 1$; (iii) $x + 1$, $y + 1$, $z$; (iv) $x - 1$, $y - 1$, $z$; (v) $x$, $y - 1$, $z$; (vi) $x + 1$, $y$, $z$; (vii) $x - 1$, $y$, $z$; (viii) $x$, $y + 1$, $z + 1$; (xi) $x$, $y$, $z + 1$.

interaction is shown in Fig. 3c where pairwise (β → γ) interactions are shown. Both of these interactions are almost 'planar' with two boroxyl (B_3O_3) rings on neighbouring pentaborates bridged by two hydroxyl groups, affording a central B_2O_4 heavy atom ring. Each pentaborate is able to interact in principle with four neighbouring borate anions and supramolecular structures result. Schubert and co-workers have noted β-OH donation to the four neighbouring anions as 2(β → α) and 2(β → β), 3(β → α) and 1(β → β), and 1(β → α), 1(β → β) and 1(β → γ) in the structures of the diammonium complexes [H_3N(CH_2)_6-NH_3][B_5O_6(OH)_4]_2, [H_3N(CH_2)_8NH_3][B_5O_6(OH)_4]_2, and [H_3N(CH_2)_12NH_3][B_5O_6(OH)_4]_2 · 4H_2O, respectively. The mineral Na[B_5O_6(OH)_4] · 2H_2O has a ribbon structure with alternating pairs of 1(β → α) and 1(β → γ) interactions; the H_2O molecules and the Na$^+$ cations also interact with the pentaborate anions in this structure to link the ribbons.

A view of the supramolecular layered structure of the pentaborate anions of **1** is shown Fig. 4. Here each pentaborate anion is linked to three neighbouring pentaborates within the plane via pairwise β → α interactions. Detailed inspection of Fig. 4 reveals that ribbons of pentaborates are linked (horizontally) by two pairwise interactions from the same boroxyl (B_3O_3) ring of a pentaborate anion whereas the other boroxyl ring of the pentaborate cross-linking (vertically) the ribbons via a third pairwise β → α interaction. Typical structural data for such a paired planar β → α interaction (e.g. O7–H7⋯O13 and O17–H17⋯O3) are averaged at a O⋯O distance of 2.70 Å and a ∠OHO angle of 172.9°. The fourth hydroxyl group of each pentaborate anion serves to crosslinks the planes via a strong β → β interaction. There are two independent β → β interactions in **1** (O9–H9⋯O18 and O20–H20⋯O8) and these interactions are relatively short (av. 2.728 Å) with ∠OHO
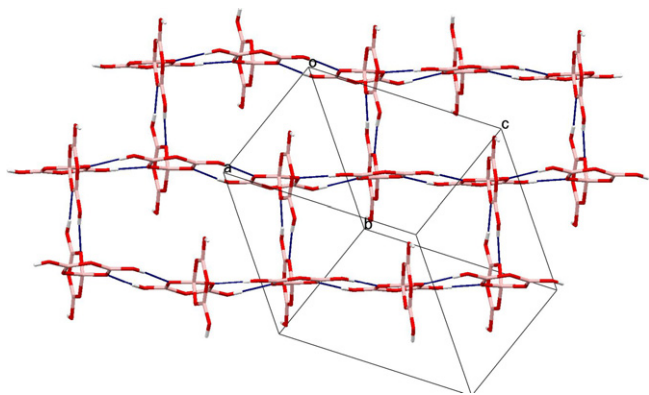
Fig. 4. View of a plane of pentaborate anions in **1** with each pentaborate anion linked through 3(β → α) pairwise dimeric 'planar' H-bond interactions.



Fig. 6. View of a plane of pentaborate anions in **2** with each pentaborate anion linked through 2(β → α) pairwise dimeric 'planar' H-bond interactions and a dimeric 'stepped' β → 2α interaction with bifurcated H-bonds.

of av. 163.7°. Thus each pentaborate partakes in the supramolecular architecture by 1(β → β) and 3(β → α) H-bond interactions.

Anion–anion pentaborate interactions for **2** are shown for the structural unit in Fig. 5 where three types of H-bond interactions are observed. The 'planar' pairwise β → α interaction is shown on the left and a β → β interaction is shown in the centre of the diagram, and these interactions are similar to those observed for **1**. An additional interaction is shown on the right of the diagram which has not been previously observed. Here we see a novel non-planar 'stepwise' dimer involving pairwise bifurcated H-bond interactions from the β → 2α sites. There are two independent bifurcated H-bond interactions within the unit cell and these involve O9–H9 to O11 and O18, and O14–H14 to O6 and O3. In both cases the bifurcated H-bonds are asymmetrical with a shorter almost linear H-bond (av. O···O 2.82 Å, ∠OHO 161.95°), and a longer more angled interaction (av. O···O 3.05 Å, ∠OHO 127.4°). A view of a plane of the supramolecular framework of **2** is shown in Fig. 6. This plane is similar to that observed in **1** with each pentaborate anion H-bonded to three neighbourouring anions within the plane. However, each pentaborate anion is now linked to three neighbouring pentaborates within
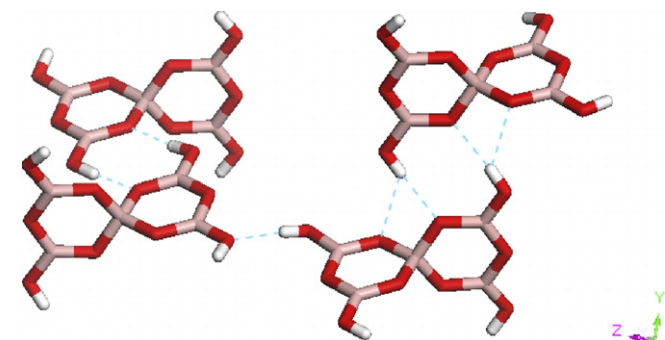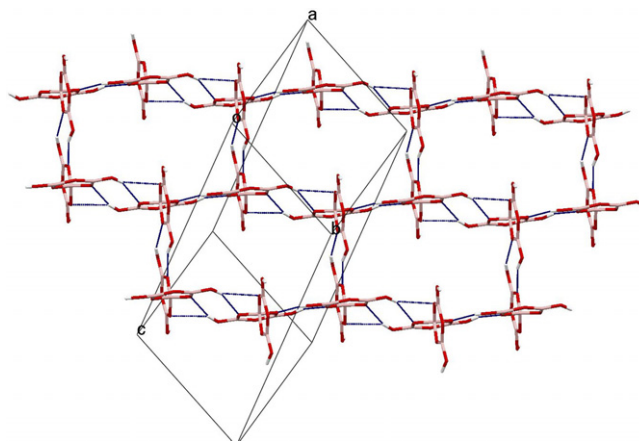
the plane via three pairwise H-bond interactions with one of these pairwise interactions involving 'stepped' boroxyl rings and bifurcated H-bonds (β → 2α). Detailed inspection of Fig. 6 reveals that ribbons of pentaborates are linked (horizontally) by alternating 'planar' (β → α) and 'stepwise' (β → 2α) pairwise interactions from the same boroxyl ($B_3O_3$) ring of a pentaborate anion with the other boroxyl ring of the pentaborate serving to crosslink (vertically) the ribbons via a third 'planar' pairwise β → α interaction. The fourth hydroxyl group of each pentaborate anion of **2** serves to crosslink the planes via a strong β → β interaction. There are two independent β → β interactions in **2** (O5–H5···O40 and O20–H20···O25) and again these interactions are relatively short (both at 2.629 Å) with ∠OHO of av. 161.7°. Thus each pentaborate partakes in the supramolecular architecture by 1(β → 2α), 1(β → β) and 2(β → α) H-bond interactions. Fig. 7 is a view of **2** looking into the



Fig. 5. Pentaborate anions in **2** showing three types of H-bond interactions: pairwise 2(β → α), β → β, and pairwise 2(β → 2α).
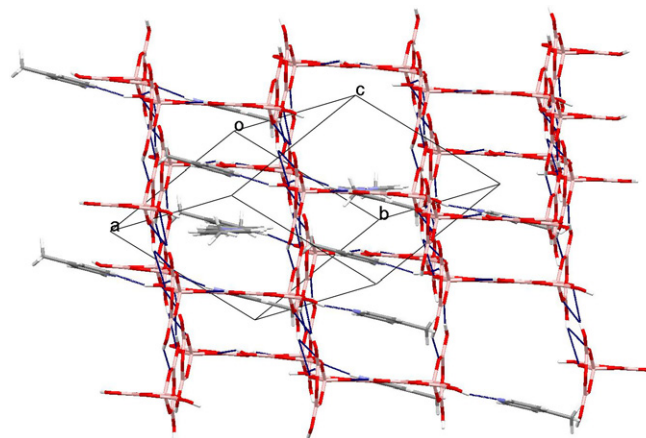


Fig. 7. Pentaborate anionic framework of **2** viewed perpendicular to that of Fig. 6. The vertical planes are linked through a series of β → β H-bonds. Some of the [4-MepyH]⁺ cations and 4-Mepy neutral molecules are shown, and these all reside within the cavitie of the framework and form H-bonds with themselves or with pentaborate anions.

planes depicted in Fig. 6, where the interplane crosslinking β → β interactions are readily apparent. Some of the [4-MepyH]$^+$ cations and neutral 4-Mepy molecules are also included within this diagram to illustrate their occupancy of the cavities present within the framework. As noted in Section 2.2 there are four neutral 4-Mepy molecules and four [4-MepyH]$^+$ cations per unit cell, with half of each structurally bound together as planar dimers (see above), while the remaining [4-MepyH]$^+$ cations and neutral 4-MePy molecules are involved in H-bonding to pentaborate anions. Thus, the two remaining neutral 4-Mepy molecules function as H-bond acceptors from pentaborate β-OH groups (O40–H40···N61; O25–H25···N91; av. D···A 2.659 Å) with av. ∠OHN 163.1° from 'planar' pentaborate dimers whereas the two remaining [4-MepyH]$^+$ cations act as H-bond donors to β-OH groups (N51–H51···O5; N81–H81···O20; av. D···A 2.702 Å) with av. ∠NHO 168.6° of 'stepped' pentaborate dimers. It is likely that such H-bond interactions, along with size effects associated with the cations/encapsulated neutral molecules, are involved in determining the supramolecular pentaborate architecture, and may be responsible for the switching some of the pentaborate pairwise interactions from 'planar' to 'stepwise'.

## 3. Experimental

### 3.1. General

Choline hydroxide (50% w/w), B(OH)$_3$, and 4-Mepy were all obtained commercially and were used without further purification. B(OCH$_2$CF$_3$)$_3$ was prepared by a published procedure [15,16]. $^{11}$B and $^{13}$C NMR spectra were recorded on a Bruker 500 AVANCE spectrometer operating at 160 and 125 MHz, respectively. $^1$H NMR spectra were recorded at 250 MHz on a Bruker AC 250 CP/MAS instrument. Chemical shifts are given in ppm with positive values towards high frequency of BF$_3$ · OEt$_2$ ($^{11}$B) or SiMe$_4$ ($^{13}$C, $^1$H). Elemental analyses data were obtained on a Carla Erba MOD-1106 instrument using He carrier gas.

### 3.2. Synthesis of [Me$_3$NCH$_2$CH$_2$OH][B$_5$O$_6$(OH)$_4$] (1)

B(OH)$_3$ (0.31 g, 5 mmol) was dissolved in an aqueous solution of [Me$_3$NCH$_2$CH$_2$OH][OH] (0.26 g of a 50% w/w containing 1 mmol) diluted with additional H$_2$O (0.50 ml). $^{11}$B NMR analysis of this solution was in agreement [18] with equilibrium concentrations of pentaborate anion [B$_5$O$_6$(OH)$_4$]$^-$ (15%), triborate anion [B$_3$O$_3$(OH)$_4$]$^-$ (53%), and monoborate species B(OH)$_3$/[B(OH)$_4$]$^-$ (32%) at 1.08, 13.71, and 18.69 ppm, respectively. After several weeks a few colourless crystals had formed (1) and these were isolated by filtration (0.005 g); m.p. ∼316 °C (dec.). Anal. Calc. for C$_5$H$_{18}$B$_5$NO$_{11}$:C, 18.64; H, 5.63; N, 4.35. Found: C, 18.38; H, 5.81; N 4.24. These crystals were used in the X-ray diffraction study described below.

### 3.3. Synthesis of 4-Mepy · B(OCH$_2$CF$_3$)$_3$ and its subsequent crystallization as [4-MepyH, 4-Mepy][B$_5$O$_6$(OH)$_4$] (2)

B(OCH$_2$CF$_3$)$_3$ (0.18 g, 0.57 mmol) was added to 4-Mepy (0.06 ml, 0.57 mmol) in Et$_2$O (10 ml) with stirring under an N$_2$ atmosphere. After 20 min the solvent was removed under reduced pressure to produce a colourless liquid adduct 4-Mepy · B(OCH$_2$CF$_3$)$_3$ (0.20 g, 84%), confirmed by NMR analysis {CDCl$_3$, $^{11}$B: +5.65 ppm; $^{13}$C: 21.19 (CH$_3$), 60.88q (CH$_2$, $^2J_{CF}$ = 35 Hz), 125.34 (CH), 125.79q (CF$_3$, $^1J_{CF}$ = 278 Hz), 150.13 (CH), 147.18 (ipso C); $^1$H: 2.43 (s, 3H), 3.97 (q, 6H, $^3J_{FH}$ = 8.85 Hz), 7.26 (d 2H), 8.49 (d, 2H)}. A prolonged attempted crystallization at room temperature of this adduct from CDCl$_3$ yielded a small crop of colourless crystals (2) which used in the X-ray analysis described below.

### 3.4. X-ray structure determinations of [Me$_3$NCH$_2$CH$_2$OH][B$_5$O$_6$(OH)$_4$] (1) and [4-MepyH, 4-Mepy][B$_5$O$_6$(OH)$_4$] (2)

Suitable crystals were selected and data for 1 and 2 were measured on a Bruker Nonius KappaCCD Area Detector at the window of a Bruker Nonius FR591 rotating anode (Mo Kα, λ = 0.71073 Å) driven by COLLECT [19] and processed by DENZO [20]software at 120 K. The structures were determined in SHELXS-97 and refined using SHELXL-97 [21]. Crystal data and refinement results for both samples are collated in Table 3.

Table 3
Crystallographic data for 1 and 2

| Crystal | 1 | 2 |
|---|---|---|
| Empirical formula | C$_5$H$_{18}$B$_5$NO$_{11}$ | C$_{12}$H$_{19}$B$_5$N$_2$O$_{10}$ |
| Formula weight (g mol$^{-1}$) | 322.25 | 405.34 |
| Crystal system | Triclinic | Triclinic |
| Space group | P1̄ | P1 |
| a (Å) | 9.2241(2) | 9.2049(13) |
| b (Å) | 10.2941(2) | 10.0699(15) |
| c (Å) | 16.1534(2) | 22.266(3) |
| α (°) | 86.048(1) | 91.965(12) |
| β (°) | 76.418(1) | 100.722(13) |
| γ (°) | 81.765(1) | 110.640(15) |
| V (Å$^3$) | 1474.57(5) | 1886.4(5) |
| Z | 4 | 4 |
| D$_{calc}$ (Mg m$^{-3}$) | 1.452 | 1.427 |
| Absorption coefficient (mm$^{-1}$) | 0.130 | 0.116 |
| F(000) | 672 | 840 |
| Crystal | Colourless slab | Colourless slab |
| Crystal dimensions (mm) | 0.46 × 0.42 × 0.12 | 0.24 × 0.20 × 0.08 |
| θ Range (°) | 3.05–27.48 | 3.02–27.48 |
| Number of reflections collected | 33958 | 33978 |
| R$_{int}$ | 0.0331 | 0.0410 |
| Number of data/restraints/parameters | 6735/518/550 | 8582/3/1069 |
| Final R indices [F$^2$ > 2σ(F$^2$)]: R$_1$, wR$_2$ | 0.0553, 0.1453 | 0.0463, 0.1203 |
| R indices (all data): R$_1$, wR$_2$ | 0.0723, 0.1605 | 0.0744, 0.1398 |
| Largest difference in peak and hole (e Å$^{-3}$) | 0.864 and −0.561 | 0.226 and −0.236 |

## Acknowledgements

## Appendix A. Supplementary material

CCDC 622144 and 622145 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.038.

## References

[1] G. Heller, Top. Current Chem. 131 (1986) 39–98.
[2] M. Schubert, R.J. Brotherton, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, second ed., Wiley, New York, 2005, pp. 499–524.
[3] M. Schubert, Struct. Bond. 105 (2003) 1–40.
[4] M. Schindler, F.C. Hawthorne, Can. Mineral. 39 (2001) 1243–1256.
[5] I.D. Brown, in: M. O'Keeffe, A. Navrotsky (Eds.), Structure and Bonding in Crystals, vol. 2, Academic Press, New York, 1981, pp. 1–30 (Chapter 14).
[6] S. Merlino, F. Sartori, Science 171 (1971) 377–379.
[7] S. Merlino, F. Sartori, Acta Crystallogr., Sect. B 25 (1969) 2264–2270.
[8] D.M. Schubert, R.A. Smith, M.Z. Visi, Glass Technol. 44 (2003) 63–70.
[9] D.M. Schubert, M.Z. Visi, C.B. Knobler, Inorg. Chem. 39 (2000) 2250–2251.
[10] G. Heller, J. Inorg. Nucl. Chem. 30 (1968) 2743–2754.
[11] G.H. Bowden, Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical ChemistryBoron. Part A. Boron–Oxygen Compounds, vol. V, Longman, London, 1980, pp. 694–702.
[12] M.Z. Visi, C.B. Knobler, J.J. Owen, M.I. Khan, D.M. Schubert, Cryst. Growth Des. 6 (2006) 538–545.
[13] M. Wiebcke, C.C. Freyhardt, J. Felsche, G. Engelhardt, Z. Naturforsch. B 48 (1993) 978–985.
[14] S. Merlino, F. Sartori, Acta Crystallogr., Sect. B 28 (1972) 3559.
[15] M.P. Rugen-Hankey, Ph.D. Thesis, University of Wales, Bangor, 2002.
[16] M.A. Beckett, M.P. Rugen-Hankey, G.C. Strickland, K.S. Varma, Phosphorus, Sulfur Silicon 168 (2001) 437–440.
[17] G. Heller, A. Giebelhausen, Z. Anorg. Allg. Chem. 460 (1980) 228–234.
[18] C.G. Salentine, Inorg. Chem. 22 (1983) 3920–3924.
[19] R. Hooft, COLLECT: Data Collection Software, Nonius B.V., 1998.
[20] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
[21] G.M. Sheldrick, SHELX-97: Programs for Crystal Structure Determination (SHELXS) and Refinement (SHELXL), University of Göttingen, Göttingen, Germany, 1997.