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Pentaborate(1−) salts templated by substituted pyrrolidinium cations: synthesis, structural characterization, and modelling of solid-state H-bond interactions by DFT calculations†

Michael A. Beckett,*a Simon J. Coles,b R. Andrew Davies,a Peter N. Hortonb and Charlotte L. Jonesa

The synthesis and characterization of a series of pentaborate(1−) salts of substituted pyrrolidinium cations [C4H6NMe2][B5O6(OH)4] (1), [C4H6NMe][B5O6(OH)4] (2) [C4H6NMeH][B5O6(OH)4] (3), [(2-CH2OH)-C4H7NH2][B5O6(OH)4] (4) is reported. All compounds were characterized by single-crystal XRD studies with 3 (1/2CH3COCH3) and 4 (1/2H2O) solvated. TGA/DSC analysis of the pentaborates 1–4 showed that they thermally decomposed in air at 800 °C to 2.5 B2O3 in a 2 step process involving dehydration (<250 °C) and oxidative decomposition (250–600 °C). BET analysis of materials derived thermally from the pentaborates 1 and 2 had internal porosities of <1 m2 g−1, indicating they were non-porous. All compounds show extensive supramolecular H-bonded anionic lattices. H-bond interactions are described in detail and motifs found in these and in other pentaborate structures have been examined and modelled by DFT calculations. These calculations confirm that H-bonds interactions in pentaborates are moderately strong (ca. –10 to –21 kJ mol−1) and are likely to dominate the energetics of their templated syntheses.

1. Introduction

Many organic bases react with B(OH)3 in aqueous solution to yield pentaborate(1−) salts, [NMC][B5O6(OH)4]−, in which the protonated organic base is a non-metal cation (NMC).1 On rare occasions salts containing three,2 four,3 seven,4 eight,5 nine,6 fourteen7 and fifteen8 B atoms have been obtained. Variations arise since B(OH)3 in basic aqueous solution forms a dynamic combinatorial library9 (DCL) of polyborate anions whose concentrations are pH and boron concentration dependent.10 However, in mildly basic solutions it is estimated that <5% of the total boron is in the form of the [B2O4(OH)3]− anion, with [B3O3(OH)2]− and [B2O2(OH)3]2− the dominant species.11 We have recently performed DFT calculations (gas-phase)12 on the relative stabilities of the polyborate anions and concluded that in isolation the order of stability follows monoborate(1−) > triborate(1−) > pentaborate(1−) > triborate(2−) > tetraborate(2−). However, contrary to this order of stability, pentaborate(1−) salts are readily crystallized from aqueous solutions. The cations in these polyborate salts are structure directing and actively template the architecture of the NMC polyborate salts. The cations can influence the structures by their size, charge, and in some cases by their ability to form strong H-bond interactions. H-bonds are ranked high for intermolecular interaction energies in crystal engineering.13 H-bond interactions between hydrated polyborate anions are ubiquitous14 in polyborate salts, although cation–anion interactions will also play a significant role in the solid-state energetics. In this manuscript we prepare four (substituted) pyrrolidinium cation pentaborate salts, and confirm the structures by X-ray crystallography. We also examine their solid-state H-bond interactions and calculate (DFT) energies of the anion–anion interactions found in these structures. For completeness, we also calculate H-bond energies for anion–anion H-bonding motifs found in other pentaborate structures, and propose an explanation as to why pentaborate salts are so readily formed.

2. Results and discussion

2.1. Synthesis and characterization

The pyrrolidinium pentaborate salts were all prepared in high yields in MeOH–H2O solution from the reaction of the free base (1, 3, 4) or the quaternary amine hydroxide salt (2) with B(OH)3 in a 1 : 5 molar ratio (eqn (1)–(4)). The structures of the
organic cations and the pentaborate(1−) anions found in compounds 1–4 are shown in Fig. 1.

\[
\begin{align*}
\text{cyclo-C}_4\text{H}_8\text{NH}_2 + 5\text{B(OH)}_3 & \rightarrow [\text{C}_4\text{H}_8\text{NH}_2][\text{B}_5\text{O}_6\text{(OH)}_4]_4 \quad (1) \\
\text{cyclo-C}_4\text{H}_8\text{NMe}_2 + 5\text{B(OH)}_3 & \rightarrow [\text{cyclo-C}_4\text{H}_8\text{NMe}_2][\text{B}_5\text{O}_6\text{(OH)}_4]_4 + 6\text{H}_2\text{O} \quad (2) \\
\text{cyclo-C}_4\text{H}_8\text{NMe} + 5\text{B(OH)}_3 & \rightarrow [\text{C}_4\text{H}_8\text{NMeH}][\text{B}_5\text{O}_6\text{(OH)}_4]_4 + 5\text{H}_2\text{O} \quad (3) \\
2\text{HOCH}_2\text{cyclo-C}_4\text{H}_8\text{NH} + 5\text{B(OH)}_3 & \rightarrow 2\text{HOCH}_2\text{cyclo-C}_4\text{H}_8\text{NH}_2][\text{B}_5\text{O}_6\text{(OH)}_4]_4 + 4\text{H}_2\text{O} \quad (4)
\end{align*}
\]

Salts 1–4 were characterized by elemental composition, spectroscopy (NMR and IR), and thermal analysis. These data indicated that they were pentaborates and their structures were confirmed by single-crystal XRD studies. Spectroscopic measurements of 1–4 were in accord with previously reported non-metal cation pentaborates salts. 11B NMR spectra of moderately concentrated aqueous solutions (D2O) of these salts displayed the three characteristic signals at ~18, 13 and 1 ppm which are assigned to B(OH)3/2 [OH], [B_5O_6(OH)_4]− and the 4-coordinate centre of [B_5O_6(OH)_4]^−, respectively.15 These species arise due to the complex borate equilibria present in aqueous solution.10,16 11B NMR spectra obtained under very dilute conditions can give some diagnostic information. Under these conditions, the formation of polyborate species is suppressed, and a single peak is observed due to equilibrium monoborate (B(OH))_3/[B(OH)]^− species, and the observed chemical shift is dependent upon the relative proportions of B_{mag} and B_{art} in solution.17 Thus, the pentaborate(1−) anion should show, at infinite dilution, one peak at 16.1 ppm, and the pentaborate salts 1–4 all give a signal at this chemical shift when in dilute solution. The total B/charge ratio can be calculated from an observed chemical shift for dilute solutions (see experimental).

This chemical shift value is not often noted but may have utility in helping to formulate products of unknown composition. 1H and 13C spectra (in D2O) were fully consistent with those expected for pyrrolidinium cations, with the NH (1, 3, 4), OH (4) and BOH protons overlapping as represented by a broad signal at ~4.7 ppm due to rapid exchange. IR spectra of 1–4 clearly all show the diagnostic band of pentaborate salts at ~925 cm⁻¹.14 The recrystallized sample of 3 from acetone–H2O afforded a solvated species 3·1/2CH3COCH3 (confirmed by XRD, see below) with consistent analytical and spectroscopic data. Crystallisation of 4 from H2O–EtOH gave the solvated 4·1/2H2O, again confirmed by XRD.

2.2. Thermal properties

The thermal properties of the non-metal polyborate salts 1–4 were examined by TGA (in air) and DSC analysis. Previous studies on non-metal pentaborate salts has shown that they usually thermally dehydrate at temperatures up to 250 °C (via an endothermic process) to afford anhydrous non-metal cation pentaborate salts.1,19 At higher temperatures (up to 800 °C) in an exothermic processes occur (consistent with oxidation of the cation) and leaving B2O3 as a glassy residual solid, via an expanded intumesced material.5,20 B2O3 is also observed as the final product if the DSC thermolysis is recorded in an inert (Ar/N2) atmosphere.1,21 Compounds 1–4 all followed this expected path of decomposition, with observed weight losses for the dehydration, and residual masses of B2O3 after oxidation being consistent with calculated values (see experimental section). This is illustrated for 1 in eqn (5) and (6).

\[
\begin{align*}
1 & \rightarrow [\text{C}_4\text{H}_8\text{NH}_2][\text{B}_5\text{O}_6] + 2\text{H}_2\text{O} \quad (5) \\
[\text{C}_4\text{H}_8\text{NH}_2][\text{B}_5\text{O}_6] + \text{excess O}_2 & \rightarrow 2.5\text{B}_2\text{O}_3 \\
& + \text{volatile oxidation products} \quad (6)
\end{align*}
\]

Samples of 1 and 2 were each separately calcined in air at 250 °C, 500 °C and 750 °C for 24 h in order to obtained significant quantities of the ‘anhydrous’, ‘intumesced’, and ‘residual’ materials. BET analysis of the 6 calcined materials showed that they were all essentially non-porous with porosities of <1.0 m⁻² g⁻¹. These data are in agreement with BET analysis of thermal materials derived from other NMC pentaborates.20

2.3. Crystallographic studies on NMC pentaborate salts 1, 2, 3·1/2CH3COCH3, and 4·1/2H2O

Crystal data for compounds 1, 2, 3·1/2CH3COCH3 and 4·1/2H2O are given in Table 1. These four structures are free from disorder and are characterized by having discrete (substituted) pyrrolidinium cations and pentaborate anions. Diagrams of the cations and anions present, and their associated numbering schemes are shown in Fig. 2–5 respectively. Compound 4·1/2H2O has two independent cations and anions per unit cell. The bond lengths and internuclear angles observed within the pentaborate anions’ boroxyl (B=O) rings of 1–4 are within the ranges observed for previously reported [NMC]
Table 1  Crystal data and structural refinement data for 1, 2, 3·1/2CH₃COCH₃ and 4·1/2H₂O

<table>
<thead>
<tr>
<th>Crystal</th>
<th>1</th>
<th>2</th>
<th>3·1/2CH₃COCH₃</th>
<th>4·1/2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄H₈B₅NO₁₀</td>
<td>C₄H₁₁B₅NO₁₀</td>
<td>C₄H₈B₅NO₁₀,₅</td>
<td>C₄H₈B₅NO₁₁.₅</td>
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<tr>
<td>Formula wt/g mol⁻¹</td>
<td>290.21</td>
<td>318.26</td>
<td>333.28</td>
<td>329.24</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P ₁</td>
<td>Triclinic, P ₁</td>
<td>Monoclinic, C₂/c</td>
<td>Triclinic, P ₁</td>
</tr>
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<td>a/Å</td>
<td>8.8681(5)</td>
<td>9.166(4)</td>
<td>14.496(3)</td>
<td>9.1164(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>8.8820(6)</td>
<td>9.380(5)</td>
<td>11.640(2)</td>
<td>9.1691(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>9.6340(6)</td>
<td>9.883(4)</td>
<td>18.253(4)</td>
<td>9.5532(7)</td>
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<tr>
<td>α/°</td>
<td>77.006(5)</td>
<td>64.88(2)</td>
<td>90</td>
<td>90.02</td>
</tr>
<tr>
<td>β/°</td>
<td>75.896(5)</td>
<td>75.49(3)</td>
<td>107.200(4)</td>
<td>75.798(5)</td>
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<tr>
<td>γ/°</td>
<td>64.320(5)</td>
<td>84.73(4)</td>
<td>90</td>
<td>82.611(5)</td>
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<td>Vol/Å³</td>
<td>657.07(8)</td>
<td>744.7(6)</td>
<td>2942.5(10)</td>
<td>724.81(8)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>calc density (Mg m⁻³)</td>
<td>1.467</td>
<td>1.445</td>
<td>1.505</td>
<td>1.509</td>
</tr>
<tr>
<td>Abs coe (mm⁻¹)</td>
<td>0.132</td>
<td>0.125</td>
<td>0.131</td>
<td>0.136</td>
</tr>
<tr>
<td>F(000)</td>
<td>300</td>
<td>348</td>
<td>1392</td>
<td>342</td>
</tr>
<tr>
<td>Crystal Colour</td>
<td>Colourless block</td>
<td>Colourless plate</td>
<td>Colourless block</td>
<td>Colourless prism</td>
</tr>
<tr>
<td>Crystal dimensions/mm³</td>
<td>0.32 × 0.22 × 0.10</td>
<td>0.23 × 0.10 × 0.03</td>
<td>0.18 × 0.18 × 0.09</td>
<td>0.14 × 0.11 × 0.07</td>
</tr>
<tr>
<td>θ range (°)</td>
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<td>3.08–27.47</td>
<td>2.94–27.48</td>
<td>2.73–27.49</td>
</tr>
<tr>
<td>No. of reflections collected</td>
<td>7117</td>
<td>9366</td>
<td>13 841</td>
<td>724.81(8)</td>
</tr>
<tr>
<td>No. of data/restraints/parameters</td>
<td>2998/0/185</td>
<td>3355/0/205</td>
<td>3340/0/215</td>
<td>5960/3/419</td>
</tr>
<tr>
<td>R indices (all data):</td>
<td>R₁,w</td>
<td>R₂</td>
<td>R₂</td>
<td></td>
</tr>
<tr>
<td>R₁,w</td>
<td>0.0176</td>
<td>0.0428</td>
<td>0.0177</td>
<td>0.0239</td>
</tr>
<tr>
<td>R₂</td>
<td>0.0690, 0.1301</td>
<td>0.0595, 0.1549</td>
<td>0.0337, 0.0884</td>
<td>0.0360, 0.0960</td>
</tr>
<tr>
<td>Largest diff. peak and hole/e Å⁻³</td>
<td>0.782, −0.326</td>
<td>0.362, −0.314</td>
<td>0.241, −0.259</td>
<td>0.438, −0.238</td>
</tr>
</tbody>
</table>

Fig. 2  Drawing of the structure of [C₄H₈NH₂][B₅O₆(OH)₄] (1), showing the atomic numbering scheme.

Fig. 4  Drawing of the structure of [C₄H₈NMeH][B₅O₆(OH)₄]·1/2C₃H₆O (3·1/2CH₃COCH₃), showing the atomic numbering scheme.

Fig. 3  Drawing of the structure of [C₄H₈NMe₂][B₅O₆(OH)₄] (2) showing the atomic numbering scheme.

Fig. 5  Drawing of the structure of [2-HOCH₂C₄H₇NHMe]-[B₅O₆(OH)₄]·1/2H₂O (4·1/2H₂O) showing the atomic numbering scheme.
[B\(_2\)O\(_3\)(OH)\(_3\)] structures.\(^{1}\,\,5\,\,15\,\,19\,\,22\) The bond lengths and inter-
uclear angles are also within ranges found in related boroxole
(B\(_2\)O\(_3\)) structures which also contain both 4-coordinate
and 3-coordinate B centres bound to O.\(^{23}\)

Structures 1–4 all possess giant H-bond anionic
natures, with cations (and co-crystallized species) situated within ‘cavi-
ties’ of the lattice. It is informative to compare the structures of
1 and 2. The unsubstituted cation (in 1) is smaller and able
to partake in H-bonding interactions whereas the dimethylated
cation (in 2) is larger and is unable to partake in H-bond inter-
actions. Despite these differences, 1 and 2 both crystallize in
the same space group with triclinic unit cells, and have very
similar supramolecular giant structures. Appropriately,
the unit cell of 2 is expanded by 13.3% to accommodate the larger
dimethylated cation. The anion–anion H-bond interactions in
both of these structures may be described\(^{5\,\,20\,\,24}\) as ‘brickwall’
with each pentaborate part of a C(8) chain (involving a β accep-
tor site) and 3 reciprocal pair R\(_2\)^2(8) interactions (involv-
ing α acceptor sites). The unsubstituted pyrrolidinium cation in
structure 2 is involved in H-bonding to both an α (O1) and a β (O8)
pentaborate acceptor site. Details of these H-bond interactions are
given in Table 2. The inferences from this are that whilst
additional H-bond interactions in 1 may further stabilize its
solid-state structure, the brickwall structure is sufficiently
flexible to accommodate larger cations, and that the pentaborate–
pentaborate H-bond interactions dominate the energetics.
These anion–anion H-bond interactions (and others
commonly encountered in pentaborate structures) are discussed in
section 2.4 in a computational study.

The structure of 4 is closely related to the ‘brickwall’ struc-
ture with each pentaborate forming a C(8) chain (involving a β
acceptor site) and 3 reciprocal pair R\(_2\)^2(8) interactions (involv-
ing α acceptor sites). The two independent cations each inter-
act \(\text{via} H\)-bonds to an O site on one or other of the two
independent pentaborate anions, at O9 (β) or O12 (γ) positions.
The co-crystallized H\(_2\)O molecule also forms additional
 donor H bonds to β sites of two pentaborates (O9 and O20)
and is an H-bond acceptor from the hydroxy group of one
cation (O21H) and the NH group (N31H) of the other cation.
The volume of the unit cell is only 2.7% smaller than that of 2.

### Table 2

<table>
<thead>
<tr>
<th>H-bond interactions</th>
<th>Lattice dimensions</th>
<th>DHA (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O7H7⋯O9 (β)</td>
<td>1.93, 2.7708 (18), 173.8</td>
<td>0.99 Å</td>
</tr>
<tr>
<td>O8H8⋯O3 (α)</td>
<td>1.86, 2.6939 (17), 175.9</td>
<td>0.99 Å</td>
</tr>
<tr>
<td>O10H10⋯O6 (α)</td>
<td>1.87, 2.7081 (17), 171.2</td>
<td>0.99 Å</td>
</tr>
<tr>
<td>O19H19⋯O18 (β)</td>
<td>2.05, 2.924 (2), 145.9</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O9H9⋯O12 (γ)</td>
<td>1.93, 2.763 (2), 170.7</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O8H8⋯O3 (α)</td>
<td>1.86, 2.6933 (18), 172.5</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O10H10⋯O6 (α)</td>
<td>1.87, 2.702 (2), 171.4</td>
<td>0.84 Å</td>
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<tr>
<td>O19H19⋯O18 (β)</td>
<td>2.05, 2.8275 (11), 155.7</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O9H9⋯O12 (γ)</td>
<td>1.93, 2.763 (2), 170.7</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O8H8⋯O3 (α)</td>
<td>1.88, 2.7199 (10), 173.4</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O10H10⋯O6 (α)</td>
<td>1.95, 2.7912 (10), 174.4</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O19H19⋯O18 (β)</td>
<td>2.04, 2.8275 (11), 155.7</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O9H9⋯O12 (γ)</td>
<td>1.81, 2.7968 (11), 170.3</td>
<td>0.84 Å</td>
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<tr>
<td>O7H7⋯O9 (β)</td>
<td>1.86, 2.688 (2), 171.1</td>
<td>0.84 Å</td>
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<tr>
<td>O8H8⋯O13 (α)</td>
<td>1.88, 2.712 (2), 169.2</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O9H9⋯O7 (β)</td>
<td>1.91, 2.701 (2), 156.4</td>
<td>0.84 Å</td>
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<tr>
<td>O10H10⋯O16 (α)</td>
<td>1.88, 2.717 (2), 175.0</td>
<td>0.84 Å</td>
</tr>
<tr>
<td>O19H19⋯O17 (β)</td>
<td>1.96, 2.736 (2), 153.4</td>
<td>0.84 Å</td>
</tr>
</tbody>
</table>

Compound 3 also has a brickwall structure with ooβ penta-
borate acceptor sites, and R\(_2\)^2(8) and C(8) chains. There is an
additional cation–anion (NH·O) H-bond interaction to the
α-site (O6), and the co-crystallized acetone molecule simply
fills space within the lattice and is not involved in H-bonding.
Taking into account different Z numbers the volume of the
comparable unit of 3 is only 1.3% smaller than in 2.

The structure of 4 is closely related to the ‘brickwall’ struc-
ture with each pentaborate forming a C(8) chain (involving a β
acceptor site) and 3 reciprocal pair R\(_2\)^2(8) interactions (involv-
ing α acceptor sites). The two independent cations each inter-
act via H-bonds to an O site on one or other of the two
independent pentaborate anions, at O9 (β) or O12 (γ) positions.
The co-crystallized H\(_2\)O molecule also forms additional
donor H bonds to β sites of two pentaborates (O9 and O20)
and is an H-bond acceptor from the hydroxy group of one
cation (O21H) and the NH group (N31H) of the other cation.
The volume of the unit cell is only 2.7% smaller than that of 2.

### 2.4. DFT calculations on solid-state H-bonding motifs

observed in pentaborate salts

Given that pentaborate(1-) salts are most commonly crystal-
ized from the DCL of polyborate anions available in aqueous
solution, and that anion–anion H-bond interactions are found
in all pentaborate structures, the energetics of these inter-
actions have been examined computationally. Our QTAIM
studies on gas-phase polyborate anions\(^{25}\) noted that H atoms
are at a minimum energy when in the plane of a boroxole ring
and that the pentaborate(1-) anion has 4 low energy rotamers
which vary in energy by 22 kJ mol\(^{-1}\); the lowest energy rotamer
having all four H atoms directed inwards towards α-O atoms
(no bond critical points) and coplanar with the boroxole rings.
This rotamer has only been observed once in the solid-state
for [1,2,3-Me\(_3\)C\(_3\)N\(_2\)H\(_2\)][B\(_2\)O\(_3\)(OH)\(_3\)] which has significantly
non-planar boroxole rings.\(^{25}\) The rotamer which is most
commonly observed has one H-atom pointing away from the
4-coordinate B centre towards the γ-O atoms (coplanar with the
boroxole rings and no bond critical point) and 3 H atoms
pointing inwards. This rotamer is 4 kJ mol\(^{-1}\) higher energy\(^{12}\)
and is found as a basis for interanionic interactions in 1–4
and in most other reported pentaborate structures. The anion-
anion H-bond interactions found in 1–4 are illustrated in
Fig. 6. Each pentaborate is involved with three R\(_2\)^2(8) inter-
actions involving reciprocal-α sites and one C(8) interaction to a
β site.\(^{24}\) The ‘outward’ pointing H-atom is involved in this
chain interaction.

The gas-phase 3 ‘inward’/1 ‘outward’ rotamer (iiio) was used as
a starting geometry for DFT calculations involving pairing
of anions in the geometries appropriate for the R\(_2\)^2(8) and C(8)
interactions. Initially, attempts to pair the anions resulted in
endothermic rather than exothermic interactions, presumably
a result of unfavorable coulombic forces. We attempted to
solve this issue by protonating the pentaborate anions on γ-O
atoms on the boroxole rings not involved in H-bonding.
The interactions now became exothermic but minimised structures
were considered unrepresentative since they contained borox-

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ole rings which were distorted away from their idealised planar conformations. An alternative procedure, which we believe was successful, involved using ‘solvated’ rather than ‘gas-phase’ DFT energies in the calculations. Fang and co-workers have recently calculated solvated energies of the pentaborate anion (but did not specify the rotamer) at a lower computational level. Our data for the solvated ‘brick’ isomer was similar to their calculated value but not directly comparable since different basis sets were used. The solvated rotamers were dimerized and exothermic energies were computed, without boroxole distortions. The data for these two interactions are given in Table 3. The $R_2^2(8)$ $\alpha$-reciprocal dimer is considerably more favoured per H-bond ($-21$ kJ mol$^{-1}$) than the $\beta$-chain ($-16$ kJ mol$^{-1}$). Durka et al. have calculated H-bond energies for boronic acid dimers, which also contains a $R_2^2(8)$ ring, and have reported an energy of $-23.7$ kJ mol$^{-1}$. Our calculated structural data for the $R_2^2(8)$ system for D–A, angle OHO, H–O and H–O are 2.78 Å, 178.1°, 1.77 Å and 0.98 Å and these agree well with Durka’s values (2.73 Å, 176.8°, 1.73 Å, 0.99 Å) which were computed at a lower level. It is difficult to compare the calculated values with those observed by X-ray crystallographically since the O–H distance in structures 1–4 was crystallographically fixed at 0.84 Å. Despite this, the calculated data does agree (with the exception for the OHO angle which is 1.6° larger than the range) within the observed range for the structural data available for 1–4 (Table 2). However, this OHO angle is within the range of structures published elsewhere. This leads us to conclude that our approach is valid and that the reciprocal-$\alpha$ H-bonds in these systems are relatively strong, and strongly influence the structure.

Two other H-bond motifs which have been less frequently observed in pentaborate structures are $R_2^2(8)$ reciprocal-$\gamma$ interactions$^{5,18,20}$ and $R_2^2(12)$ reciprocal-$\beta$ interactions$^{25,28}$ (Fig. 7). For completeness these were calculated by the same methods and their data are included in Table 3. The H-bond strengths for the $R_2^2(8)$ reciprocal-$\gamma$ interaction is comparable to that of a C(8) $\beta$-chain, and is favoured over that of the $R_2^2(12)$ reciprocal-$\beta$ interaction. QTAIM calculations (Fig. 8 and ES1†) on all H-bonded systems show that the H-bonds have bond critical points, with the energies of the H-bonds mirroring the electron density ($\rho_b$) at their bond critical points. There is also a red-shift in calculated O–H (donor) stretching vibrational frequencies of up to 450 cm$^{-1}$, which correlates with the relative energies of the H-bonds. The calculated $R_2^2(12)$ reciprocal-$\beta$ interaction has a close O–O contact (3.04 Å) which is similar to that observed in [2′-PrN$_2$C$_3$H$_4$][B$_5$O$_6$(OH)$_4$] (2.98 Å)$^{25}$ and QTAIM analysis indicates that in addition to the two H-bonds, there exists a further bond critical point between these two O atoms. $\rho_b$ for these H-bonds are the lowest of the 4 calculated H-bond interactions and this is in agreement with less favourable H-bond energies.

Table 3 DFT calculated energies for H-bond motifs commonly found in solid-state structures containing pentaborate(1−) anions. Relative energy is calculated energy of dimer – (2 x energy of $i$io monomer)

<table>
<thead>
<tr>
<th>Species</th>
<th>Abs energy (10$^3$ kJ mol$^{-1}$)</th>
<th>Rel. energy (kJ mol$^{-1}$)</th>
<th>H-bond energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{B}_2\text{O}_5(\text{OH})_4]^-$ ($i$io)</td>
<td>-2310.943</td>
<td>0</td>
<td>-21</td>
</tr>
<tr>
<td>$R_2^2(8)$ ($\alpha$)</td>
<td>-4621.927</td>
<td>-42</td>
<td>-16</td>
</tr>
<tr>
<td>$R_2^2(12)$ ($\beta$)</td>
<td>-4621.905</td>
<td>-19</td>
<td>-10</td>
</tr>
<tr>
<td>$R_2^2(8)$ ($\gamma$)</td>
<td>-4621.917</td>
<td>-32</td>
<td>-16</td>
</tr>
<tr>
<td>C(8) ($\beta$-chain)</td>
<td>-4621.901</td>
<td>-16</td>
<td>-16</td>
</tr>
</tbody>
</table>

3. Conclusion

As noted in sections 1 and 2.3 the majority of polyborate salts are pentaborates and the majority of pentaborate salts crystalize with either a ‘brickwall’ or a ‘herringbone’ giant H-bonded
lattice with cations in the cavities. Both of these common structural types contain ααβ acceptor sites H-bond interactions in the guise of three energetically favourable R2^2(8) reciprocal-α interactions and one C(8) β-chain. The ability for pentaborate anions to form strong 3D networks is an important driving force behind the facile syntheses of these salts. As shown in section 2.3 there is sufficient flexibility in the lattice to accommodate (within limits) cations of various sizes. Cation–anion interactions (as observed in 1, 3 and 4) can further stabilize the structure but do not necessarily outweigh the anion–anion contributions, which primarily arise through the reciprocal-α H-bonds. We surmise that given the energetically favoured pentaborate lattice, polyborates other than pentaborates would only be formed when the lattice cannot be stretched to accommodate the cations, and/or when there is sufficient cation–anion interactions to dominate the energetics.

4. Experimental

4.1. General

All chemicals were obtained commercially from Sigma Aldrich (UK) or Lancaster Synthesis (UK) and were used as supplied. N,N,N-Dimethyl pyrrolidinium iodide was prepared from N-methyl-pyrrolidine by use of MeI following standard procedures. NMR spectra were recorded at room temperature (298 K) on a Bruker Ultrasound™ Plus 400, using TopSpin™ 3.2 software package; spectra were further analysed using MestReNova v6.0.2–5475. ^11B, ^13C and ^1H NMR spectra were obtained at 400 MHz (^1H), 128 MHz (^11B), 100 MHz (^13C), with samples dissolved in D2O. Fourier transform Infrared spectra (FTIR) were obtained using KBr pellets on a Perkin-Elmer 100 FTIR spectrometer over 450–4000 cm⁻¹. TGA and DSC analysis was performed between 25–100 °C (in air) on an SDT Q600 V4.1 Build 59 instrument using Al2O3 crucibles, with a ramp temperature rate of 2 °C min⁻¹. Powder X-ray diffraction (p-XRD) was carried out on a Phillips X-Pert 3040/60 XRD diffractometer, with spectra obtained using the Phillips X’Pert Data Collector software package. X-ray crystallography was carried out at the EPSRC National Crystallography service at the University of Southampton. BET multipoint analyses were performed on a Micromeritics Gemini III 2375 instrument. CHN analysis was carried out at OEA laboratories Ltd in Callington, Cornwall. The chemical shift (δcalc) for equilibrium ratio of Btet and Bβet at infinite dilution was calculated from δcalc = [δ(B(OH)3) + ([Btet + Btrig] - Btet)]/[Btet + Btrig] = δ(B(OH)3) - δ(B(OH)4⁻) where δ(B(OH)3) and δ(B(OH)4⁻) are +19.48 and +2.48 ppm, respectively. The total B/charge ratio (B/1) was calculated from B/1 = 17.0/ (δobs +19.48), i.e., δobs of 16.1 ppm gives a ratio of 5.02/1.

4.2. Preparation pyrrolidinium pentaborate(1–) salts (1–4)

Compounds 1, 3 and 4 were prepared by a general procedure as described below for 1.

[C4H8NH2][B5O6(OH)4] (1). B(OH)3, (5.01 g, 81.0 mmol), was dissolved in 1:1 MeOH–H2O (100 ml), cyclo-C4H8NH2 (1.15 g, 16.2 mmol) was added with stirring. The solvent was removed under reduced pressure resulting in the formation of the product as a white solid, which was oven-dried at 60 °C for 24 hours (4.683 g, 99% yield). Recrystallisation from water yielded colourless crystals suitable for single-crystal XRD. NMR: δ (ppm): 1.95–1.99 (4H, m, CH2, J = 6.8 Hz), 3.24–3.27 (4H, m, CH2, J = 6.8 Hz), 4.79 (HOD, OH and NH rapidly exchanging in the D2O). δC (ppm): 23.58 (CH3), 45.44 (CH2N). δ1H (ppm): 1.1, 13.0, 18.1. IR (KBr) (vmax/cm−¹): 3738, 2360, 1425, 1320, 1185 (m), 1120 (m), 1017 (m), 923 (vs), 777 (s), 697 (s), 485 (m). p-XRD: d-spacing/Å (% rel. int.): 5.66 (100.00), 4.39 (80.35), 6.78 (72.38), 3.39 (68.51), 4.33 (49.10), 9.38 (46.36). TGA: Loss of H2O: 12.3% (12.4% calc.); oxidation of cation: 26.8% (28.9% calc.); residual B2O3: 60.5% (60.0% calc.).
Elemental Anal. Calc. (%) for 1, C4H8NO14B3; C, 16.55; H, 4.86; N, 4.82. Found (%): C, 16.78; H, 4.87; N, 4.92. 

\[ \text{C}_{4} \text{H}_{8} \text{NMeH}[\text{B}_{5}\text{O}_{6}(\text{OH})_{4}] \cdot 4.5\text{H}_{2}\text{O} \] (3). Yield 4.853 g from 5.01 g B(OH)₃ (98%). NMR: δ(H) (ppm): 2.08 (4H, s, CH₂), 2.90 (3H, s, CH₃), 3.05 (s, 2H, CH₂), 3.61 (2H, s, CH₂), 4.79 (s, HOD, OH and NH rapidly exchanging in the D₂O). δ(C) (ppm): 22.80 (CH₃), 40.55 (CH₃), 55.72 (CH₃). δ(B) (ppm): 1.2, 13.2, 18.8. IR (KBr) (νmax/cm⁻¹): 3381, 2775, 2360, 1426, 1182 (m), 1087 (m), 1026 (m), 922 (s), 778 (s), 480 (m). p-XRD: d-spacing/Å (% rel. int.): 3.54 (100.00), 5.09 (97.66), 6.32 (82.79), 4.05 (56.23), 6.00 (47.83), 8.36 (36.23). TGA: Loss of interstitial H₂O: 8.2% (8.2% calc.); loss of H₃O: 16.6% (19.0% calc.); oxidation of cation: 26.3% (28.3% calc.); residual B₂O₃: 56.7% (52.5% calc.). Elemental Anal. Calc. (%) for 2·1·1/2H₂O, C₅H₁₇NB₅O₁₀.5; C, 18.05; H, 5.05; N, 4.14. Recrystallisation of 2·1·1/2H₂O from 3.2365 g (45.54% loss). BET: surface area 0.4842 m² g⁻¹. 750 °C: 1.5189 g (B₂O₃) obtained from 2.5741 g (40.9% loss). BET: surface area 0.7157 m² g⁻¹.

4.3. Thermolysis experiments on 1 and 2 at 250 °C, 500 °C and 750 °C

Compounds of 1 and 2 (1–3 g, per experiment) were subjected to the following thermal treatments at 250 °C, 500 °C and 750 °C (detailed for 250 °C) and BET analyses were performed on the thermally produced materials. Samples of each were placed in open top Vitreosil (SiO₂) crucibles and positioned within the furnace (air atmosphere). The furnace temperature was set to increase from room temperature to 250 °C at a ramp rate of 10 °C min⁻¹. After reaching 250 °C, the samples were held at a constant temperature for 24 hours, before being allowed to cool to room temperature. Samples obtained from thermolysis at 500 °C had intumesced, and increased their volume ~3 fold; the samples at 750 °C yielded glassy black solids. Samples were then removed from the furnace, ground using a mortar and pestle, and then used for BET analysis.

1. 250 °C: 1.1709 g obtained from 1.3686 g. 14.45% weight loss (−2.3 H₂O per unit formula). BET: surface area 0.3875 m² g⁻¹. 500 °C: 1.0642 g obtained from 1.7843 g (40.36% loss). BET: surface area 0.4842 m² g⁻¹. 750 °C: 1.5189 g (B₂O₃) obtained from 2.5741 g (40.9% loss). BET: surface area 0.7157 m² g⁻¹.

2. 250 °C: 1.1430 g obtained from 1.3024 g. 12.24% weight loss (−2.2 H₂O per unit formula). BET: surface area 0.7517 m² g⁻¹. 500 °C: 0.8426 g obtained from 1.5223 g (44.65% loss). BET: surface area 0.5591 m² g⁻¹. 750 °C: 1.7625 g (B₂O₃) obtained from 3.2365 g (45.54% loss). BET: surface area 0.6605 m² g⁻¹.

4.4. Computational studies

Density Functional Theory (DFT) calculations were performed using Gaussian09 at the B3LYP/6-311+G(d,p) level of theory and analysed using GaussView 5.0 and WebMO visualization packages. Implicit water (ε = 78.3553) solvation was performed using the Polarizable Continuum Model (PCM) Self-Consistent Reaction Field (SCRF) approach. QTAIM (Quantum Theory of Atoms in Molecules) analyses were performed using AIM2000. Data and diagrams are supplied as ESI†.

4.5. X-ray crystallography

Suitable crystals were selected and data collected following a standard method. For compound 1 on a Rigaku SPIDER RAPID diffractometer at 120 K with an image plate detector. For compounds 2–4 on a Rigaku AFC12 goniometer at 100 K equipped with an enhanced sensitivity (HG) Saturn724+ detector.
mounted at the window of an FR-E-Superbright molybdenum anode generator with VHF Varimax optics (70 mm focus). Cell determination and data collection, data reduction, cell refinement and absorption correction were carried out using CrystalClear, structure solution and refinement using SHELX programs.14

Acknowledgements

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Notes and references


33 Rigaku, CrystalClear- SM Expert 2.0 r1 or 3.1 b18 or 3.1 b27, 2013.