

Polyborate anions partnered with large non-metal cations: triborate(1-), pentaborate(1-), and heptaborate(2-) salts.

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Abstract: New polyborate salts containing bulky non-metal cations have been prepared from either the free organic base or the [non-metal cation][OH] in methanolic aqueous solution: 1-adamantylammonium pentaborate $[\text{C}_{10}\text{H}_{18}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4]$ (**1**), 2-adamantylammonium pentaborate dihydrate $[\text{C}_{10}\text{H}_{18}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (**2**), *N,N*-dimethyl-1-adamantylammonium pentaborate-boric acid monohydrate $[\text{C}_{12}\text{H}_{22}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot \text{B}(\text{OH})_3 \cdot \text{H}_2\text{O}$ (**3**), *N,N,N*-trimethyl-1-adamantylammonium pentaborate trihydrate $[\text{C}_{13}\text{H}_{24}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ (**4**), *N,N,N*-trimethyl-2-adamantylammonium pentaborate trihydrate $[\text{C}_{13}\text{H}_{24}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ (**5**), dibenzylammonium pentaborate sesquihydrate $[\text{C}_{14}\text{H}_{16}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 1.5\text{H}_2\text{O}$ (**6**), bis(triphenylphosphine)iminium pentaborate sesquihydrate $[\text{C}_{36}\text{H}_{30}\text{NP}_2][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 1.5\text{H}_2\text{O}$ (**7**), bis(triphenylphosphine)iminium triborate-2.5 hydrate $[\text{C}_{36}\text{H}_{30}\text{NP}_2][\text{B}_3\text{O}_3(\text{OH})_4] \cdot 2.5\text{H}_2\text{O}$ (**8**), 4,4'-bipiperidinium heptaborate dihydrate $[\text{C}_{10}\text{H}_{22}\text{N}_2][\text{B}_7\text{O}_9(\text{OH})_5] \cdot 2\text{H}_2\text{O}$ (**9**). All compounds were characterized by thermal (TGA/DSC), and spectroscopic analysis (NMR, IR). Compounds **3** - **5** and **9** have been characterized by single-crystal XRD studies. The waters of crystallization in **3** - **6** and the boric acid of crystallization in **3** play important structural roles in expanding the supramolecular pentaborate(1-) lattices to accommodate the bulkier cations.

Introduction

Boron-oxygen compounds have found many practical industrial applications^[1] and are also of academic interest due to their diverse structural chemistry.^[2] Non-metal cation polyborate salts are readily prepared from aqueous solution by the interaction of the organic free base or the [non-metal cation][OH] salt with $\text{B}(\text{OH})_3$.^[3] In aqueous solution $\text{B}(\text{OH})_3$ exists as a Dynamic Combinatorial Library^[4] of a variety of polyborate anions which are in rapid equilibrium^[5] and the polyborate salts that crystallize out of the solution are templated by the cations present. In the majority of cases salts containing the pentaborate(1-) anion, $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ (Figure 1(b)) are obtained as this is particularly the case when the organic cations are relatively 'innocent', carry a charge of 1+ and the reactants are mixed in a 1:5 ratio.^[2b,3a] Pentaborate(1-) salts invariably have giant supramolecular donor

structures comprised of anions H-bonded together, utilizing four donor interactions per pentaborate anion, with the cations filling the available 'cavities' within the lattice.^[2b,3b-e] Two very common structural motifs which involve $\alpha, \alpha, \alpha, \beta$ acceptor sites^[3d] on neighbouring pentaborates have been described as 'herringbone' or 'brickwall'.^[2b,3c,6] We have recently described work with substituted pyrrolidinium cation pentaborate(1-) salts^[7] with the brickwall structure and concluded that there is some flexibility in the pentaborate lattice which was noted to expand by 13.3% in the dimethylated salt $[\text{C}_4\text{H}_8\text{NMe}_2][\text{B}_5\text{O}_6(\text{OH})_4]$ compared to $[\text{C}_4\text{H}_8\text{NH}_2][\text{B}_5\text{O}_6(\text{OH})_4]$. The monomethylated salt, $[\text{C}_4\text{H}_8\text{NMeH}][\text{B}_5\text{O}_6(\text{OH})_4]$, co-crystallized as the 0.5 acetone solvate, again as a brickwall structure with the unit cell size comparable to that of the dimethylated salt and with the acetone innocently helping to space fill the cavity. The H-bond energies of the α anion-anion interactions are strong (-21 kJ mol^{-1})^[7] and these appear to dominate the solid-state energetics. In order to break the monopoly of pentaborate(1-) salts we have now investigated the synthesis of polyborate salts from aqueous solution with sterically more demanding 1+ cations and a sterically demanding 2+ cation. Using this strategy we now report the synthesis of a rare triborate(1-) salt (Figure 1(a)) and a rare heptaborate(2-) salt (Figure 1(c)) in addition to some new pentaborate(1-) derivatives. The heptaborate(2-) salt and three of the pentaborate(1-) salts were characterized crystallographically. In these pentaborate(1-) structures the brickwall motif has been expanded by 'spacer' molecules which have co-crystallized to accommodate the bulkier cations.

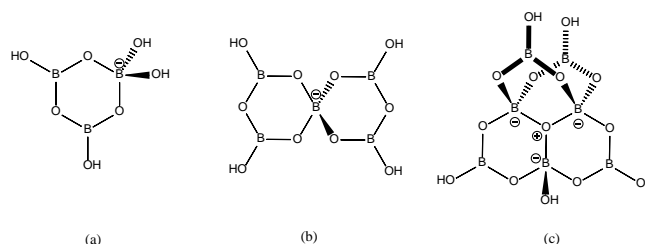


Figure 1. Polyborate anions in compounds **1-9**: (a) triborate(1-), $[\text{B}_3\text{O}_3(\text{OH})_4]^-$, (in **8**), (b) pentaborate(1-), $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ (in **1-7**), (c) heptaborate(2-), $[\text{B}_7\text{O}_9(\text{OH})_5]^{2-}$ (in **9**).

Results and Discussion

Synthesis and general discussion. Nine new polyborate salts containing bulky non-metal cations have been prepared in high yields (74-99%) from $\text{H}_2\text{O}/\text{MeOH}$ solution by reaction of the free

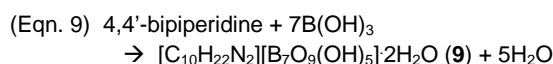
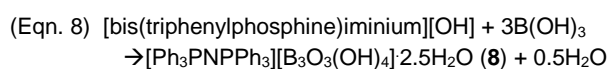
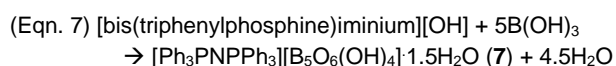
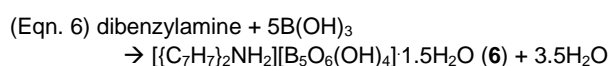
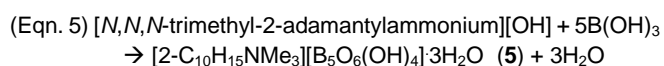
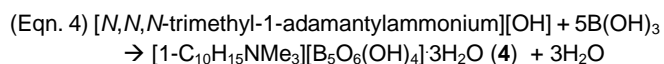
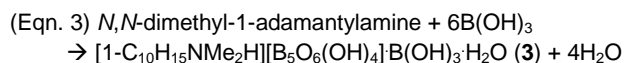
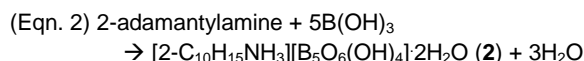
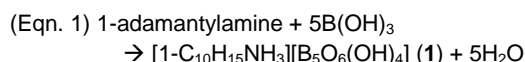
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base, or the non-metal cation hydroxide salt, with $B(OH)_3$ as shown in (idealized) Equations 1-9.



Compounds **1 - 7** are obtained as pentaborate(1-) salts whilst **8** is a triborate(1-) salt and **9** is a heptaborate(2-) salt. The structures of these polyborate anions are shown in Figure 1 (a) – (c) and the structures of the non-metal cations are shown in Figure 2 (a) – (h). Compound **1** is a simple salt and **2 - 9** are simple salts with additional molecules of co-crystallization. Compounds **7** and **8** could also be prepared under solvothermal conditions ($H_2O / 145^\circ C / \text{autogenous pressure} / 24h$) from the same reagents. The new compounds have been formulated on the basis on elemental analysis, thermal (TGA/DSC) analysis, and spectroscopic analysis (IR, NMR - ^{11}B , 1H and ^{13}C). Powder-XRD measurements on crude samples indicated that all were crystalline except for **1** and **2** which were amorphous solids. The ionic compounds **1 - 6** and **9** were insoluble in organic solvents (toluene, CH_2Cl_2 , $CHCl_3$, acetone, MeOH, EtOH) but readily dissolved/reacted in H_2O . Single-crystal X-ray diffraction studies confirmed the above formulations for **3 - 5** and **9**.

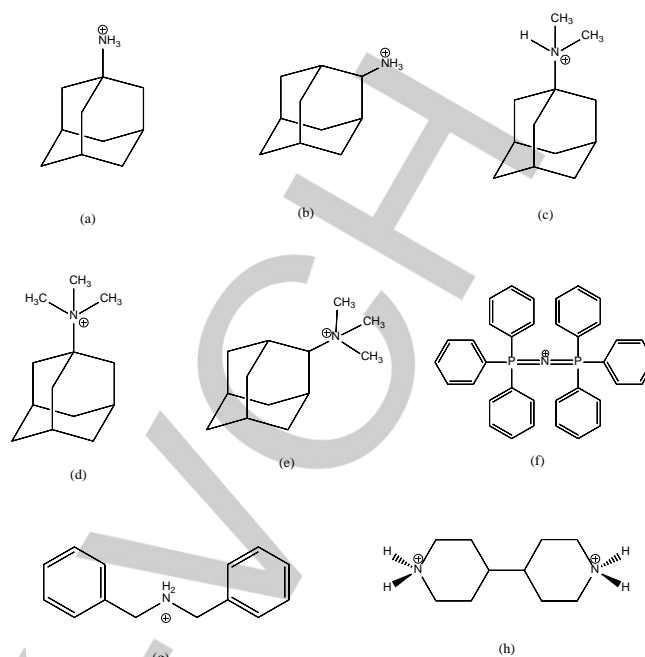


Figure 2. Cations in compounds **1 - 9**: (a) 1-adamantylammonium, (in **1**) (b) 2-adamantylammonium, (in **2**), (c) *N,N*-dimethyl-1-adamantylammonium (in **3**) (c) *N,N,N*-trimethyl-1-adamantylammonium (in **4**) (d) *N,N,N*-trimethyl-2-adamantylammonium (in **5**) (f) bis(triphenylphosphine)iminium (PPN) (in **7** and **8**) (g) dibenzylammonium (in **6**) (h) 4,4'-bipiperidinium (in **9**).

Thermal analysis. Non-metal polyborate salts are known to decompose under TGA conditions in air to afford B_2O_3 via multistep processes involving loss of interstitial H_2O ($100 - 150^\circ C$), further loss of H_2O by condensation of B-OH groups to form B-O-B ($150 - 270^\circ C$), and oxidation of the organic cation ($270 - 800^\circ C$); the DSC generally shows that the oxidation step is exothermic and the loss of H_2O is endothermic.^[3c,3d,6-8] The TGA/DSC plots for **1 - 9** (see Figure 3 for **9**, and supplementary information) could be assigned on this basis, with **1** not having H_2O of crystallization and **3** having a H_2O and a $B(OH)_3$ of co-crystallization. The dehydration steps for **9** are combined at $\sim 200^\circ C$. Boric acid has been found to co-crystallize in a number of other polyborate structures^[9,10] and its structural role will be discussed later. Elemental analysis data for **1 - 9** were in agreement with formulations based on thermal analysis data.

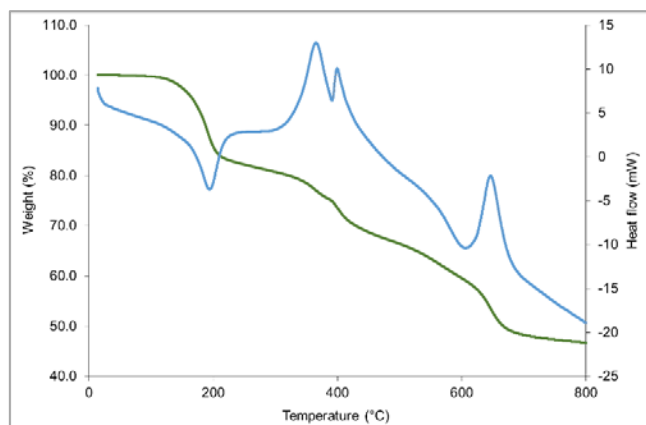


Figure 3. TGA (green, left scale) / DSC (blue, right scale) curves for **9**, showing dehydration at ~200 °C, followed by oxidation of the cation to leave residual B_2O_3 (>750 °C).

Spectroscopic analysis. 1H and ^{13}C NMR of the polyborate salts dissolved in D_2O gave spectra consistent with the cations present. ^{11}B spectra of **1-9** indicated that compounds were decomposed in aqueous solution due to facile polyborate equilibria which are boron-concentration dependent.^[5] Moderately concentrated aqueous solutions of pentaborate(1-) salts generally show three diagnostic signals at +1, +12 and +17 ppm with intensities 75%, 20%, 5% respectively and samples **1 - 7** all showed these characteristic signals.^[2b,3e,6,7,10a,11] It has been noted before that 'dilute' solutions show a single peak (due to rapid $B(OH)_3/[B(OH)_4]^-$ exchange) and it is possible to calculate the boron/charge ratio from the observed chemical shift.^[2b,7] The PPN salts **7** and **8**, were sparingly soluble in D_2O and gave single peaks at +16.4 and +13.7 ppm respectively corresponding to a B/charge ratio of 5.5 (pentaborate(1-), **7**) and 2.9 (triborate(1-), **8**). The heptaborate(2-) salt **9** gave a dilute ^{11}B spectrum with a single peak at 14.7 ppm, and a calculated B/charge ratio of 3.5 (*i.e.* **7/2**). It was found that the PPN salts **7** and **8** were soluble in chlorinated organic solvents, and it was possible to obtain their ^{11}B spectra in $CDCl_3$ and CD_2Cl_2 . This is the first time that such spectra have been obtained and signals for the 3-coordinate B atoms were observed (as expected) at +19.8 (**7**) and +19.7 (**8**) ppm in $CDCl_3$ (see supplementary information). Furthermore, their intensities were in correct proportion to the signals associated with four coordinate boron centres at +1.6 (**7**) and +1.3 (**8**) ppm. Similar data were obtained in CD_2Cl_2 . Compounds **7** and **8** were both insoluble in toluene and were decomposed by dissolution in DMSO, MeOH, EtOH, and acetone.

IR spectra of the pentaborate(1-) salts **1 - 7** all displayed the characteristically^[10a] strong band at $\sim 925\text{ cm}^{-1}$ which can be assigned with reference to Li *et al.*^[12] to a symmetric $B_{\text{trig}}-O$ stretch. The trisborate(1-) salt, **8**, showed strong/medium bands centered at 1437, 1296, 997, and 855 cm^{-1} . These values are in reasonable agreement to those reported for $[NH_2(CH_2CH_2)_2NH_2][B_3O_4(OH)_4]_2$ ($1414, 1305, 985, \text{ and } 862\text{ cm}^{-1}$) and can be considered diagnostic for trisborate(1-) salts.^[13] The heptaborate(2-) anion in **9** has been described as the 'O+' isomer^[14] and IR spectra for cycloalkylammonium heptaborates^[15] of this isomer have been

reported with bands at 905 cm^{-1} and 863 cm^{-1} tentatively assigned as diagnostic for this anion. The IR spectrum of **9**, showed a band of medium intensity band at 854 cm^{-1} , but only a weak band at 909 cm^{-1} , indicating that the band at 905 cm^{-1} in the cycloalkylammonium salts may be organic related. The band at $\sim 860\text{ cm}^{-1}$ may be diagnostic of this heptaborate(2-) anion.

Structural studies. Crystallographic data for compounds **3 - 5** and **9** are given in Table 1. Compounds **3 - 5** possess the expected (substituted) adamantyl cations and pentaborate(1-) anions with either one (**3, 4**) or two (**5**) crystallographically independent pentaborate(1-) anions partnered with one (**3, 4**) or two (**5**) crystallographically independent cations. In addition all three compounds are found co-crystallized with H_2O (**3 - 5**) or $B(OH)_3$ (**3**). As expected, the average $B_{\text{trig}}-O$ bond lengths (1.369 \AA , **3**; 1.370 \AA , **4**; 1.367 \AA , **5**) are significantly shorter than $B_{\text{tet}}-O$ bonds (1.470 \AA , **3**; 1.473 \AA , **4**; 1.472 \AA , 1.471 \AA , **5**) and in general the bond lengths and bond angles are all within ranges typically observed for pentaborate(1-) anions^[3,6,7,10a,11,13,15,16] and for other boroxole ring systems^[17] containing both 3- and 4-coordinate boron centers bound to oxygen.

The solid-state structures of **3 - 5** possess giant anionic lattices held together by H-bonds, with the cations sitting within the 'cavities' of the lattice and the co-crystallized molecules part of the anionic lattice. Structurally all three compounds are related to the brickwall^[2b,3c,6] structure where six pentaborate(1-) anions H-bond to one another to form rectangular bricks which link in a plane to form the brickwall, *via* three reciprocal- α interactions. α -, β -, and γ -Positions of pentaborate(1-) anions are used as described in the literature.^[3d,3e] The brickwall structure has an $\alpha, \alpha, \alpha, \beta$ H-bond distribution (the β H-bond interaction links the planes) and three of these linkages (α, α, β) are retained in structures **3 - 5** (see Figures 4, 5, and 6 for **3, 4**, and **5**, respectively). Since each of the six pentaborates of a rectangle contribute to three rectangles, each cavity requires two $1+$ cations to balance the charge. The molar volumes of the cations in **3, 4**, and **5** can be calculated^[3b,18] as $169, 242, \text{ and } 247\text{ \AA}^3$ respectively, and these are significantly larger than that calculated for the cation in a typical brickwall structure, *e.g.* $[(CH_2)_4NH_2][B_5O_6(OH)_4]$ (75 \AA^3).^[7] It was anticipated that such large cations would not be able to template the brickwall structure and that polyborates other than pentaborates might be templated from aqueous solution. However, inclusion of the spacer molecules $B(OH)_3/H_2O$ for **3**, H_2O for **4** and **5**) has enabled much of the brickwall structure to be retained with the cavities enlarged to accommodate the bulkier cations. The 'spacer' molecules bridge and are H-bonded to two pentaborate moieties. In essence the long sides of the rectangle bricks are extended by the co-crystallized molecules so that the rectangle now becomes $14.9 \times 6.1\text{ \AA}$ (**3**), $16.2 \times 7.5\text{ \AA}$ (**4**), $13.5 \times 6.3\text{ \AA}$ (**5**) rather than the $11.5 \times 6.1\text{ \AA}$ observed in a typical brickwall structure, $[(CH_2)_4NH_2][B_5O_6(OH)_4]$.^[7] Boric acid expanded lattices have been observed previously for $[NR_4][B_5O_6(OH)_4] \cdot 2B(OH)_3$ ($R = ^nPr, ^nBu$)^[3b] and $[HPS][B_5O_6(OH)_4] \cdot B(OH)_3$ ($PS = 1,8$ -bis(dimethylamino)naphthalene)^[10a] although neither appear to be brickwall. Boric acid 'spacers' are also observed in $[H_3N(CH_2)_8NH_3][B_5O_6(OH)_4(NH_2(CH_2)_2NH_2)B_5O_6(OH)_4] \cdot 2B(OH)_3 \cdot 2H_2O$.^[10b]

Table 1. Crystallographic data for **3**, **4**, **5** and **9**.

	3	4	5	9
Empirical formula	C ₁₂ H ₃₁ B ₆ NO ₁₄	C ₁₃ H ₃₄ B ₅ NO ₁₃	C ₁₃ H ₃₄ B ₅ NO ₁₃	C ₁₀ H ₃₁ BrN ₂ O ₁₆
Formula Weight	478.24	466.46	466.46	511.04
Crystal size (mm ³)	0.240 x 0.120 x 0.020	0.330 x 0.300 x 0.120	0.220 x 0.110 x 0.040	0.110 x 0.060 x 0.050
Crystal description	Plate; Colourless	Block; Colourless	Block; Colourless	Block; Colourless
Crystal System	Triclinic	Triclinic	Triclinic	Monoclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.0399(5)	9.4233(7)	9.9476(7)	16.7630(11)
<i>b</i> (Å)	9.9064(7)	9.7856(7)	13.5559(10)	8.3895(5)
<i>c</i> (Å)	12.8523(9)	13.7629(10)	17.4648(11)	0.945(2)
α (°)	80.858(4)	104.170(4)	76.989(4)	90
β (°)	81.545(4)	93.306(4)	81.620(4)	96.1990(10)
γ (°)	83.654(4)	115.301(4)	74.968(4)	90
Volume (Å ³)	1119.50(13)	1093.23(14)	2206.6(3)	4326.4(5)
<i>Z</i>	2	2	4	8
ρ_{calcd} (mg m ⁻³)	1.419	1.417	1.404	1.569
Absorption coefficient (mm ⁻¹)	0.120	0.118	0.117	0.137
<i>F</i> (100)	504	496	992	2144
θ range (°)	2.958 – 27.480°	2.412 – 27.491°	2.129 – 27.541°	2.444 – 27.507°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -16 ≤ <i>l</i> ≤ 14	-12 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -17 ≤ <i>l</i> ≤ 16	-12 ≤ <i>h</i> ≤ 12, -17 ≤ <i>k</i> ≤ 17, -22 ≤ <i>l</i> ≤ 22	-21 ≤ <i>h</i> ≤ 21, -8 ≤ <i>k</i> ≤ 10, -40 ≤ <i>l</i> ≤ 37
Reflections collected	15617	17415	40086	31232
Independent reflections	5107 [<i>R</i> _{int} = 0.0380]	4999 [<i>R</i> _{int} = 0.0314]	10129 [<i>R</i> _{int} = 0.0383]	4953 [<i>R</i> _{int} = 0.0387]
Goodness of fit on <i>F</i> ²	1.030	1.073	1.075	1.046
Final <i>R</i> indices [<i>F</i> ² > 2 σ (<i>F</i> ²)]	<i>R</i> 1 = 0.0341, <i>wR</i> 2 = 0.0876	<i>R</i> 1 = 0.0373, <i>wR</i> 2 = 0.1019	<i>R</i> 1 = 0.0396, <i>wR</i> 2 = 0.1263	<i>R</i> 1 = 0.0497, <i>wR</i> 2 = 0.1350
<i>R</i> indices (All data)	<i>R</i> 1 = 0.0422, <i>wR</i> 2 = 0.0919	<i>R</i> 1 = 0.0396, <i>wR</i> 2 = 0.1040	<i>R</i> 1 = 0.0751, <i>wR</i> 2 = 0.1454	<i>R</i> 1 = 0.0547, <i>wR</i> 2 = 0.1398
Largest diff. peak/hole (e Å ⁻³)	0.271/-0.226	0.360/-0.346	0.505/-0.539	0.370/-0.547

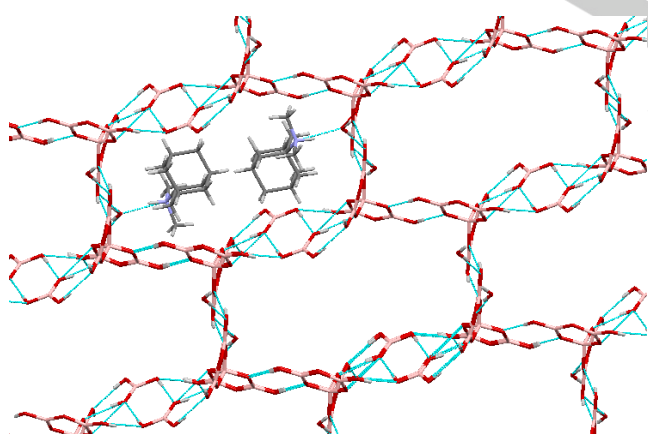


Figure 4. The expanded brickwall anionic supramolecular structure as observed in **3**. Two B(OH)₃ molecules are inserted as 'spacers' along the long edges of each hexa(pentaborate) rectangle. Two cations (shown in one rectangle only) occupy each rectangular cavity.

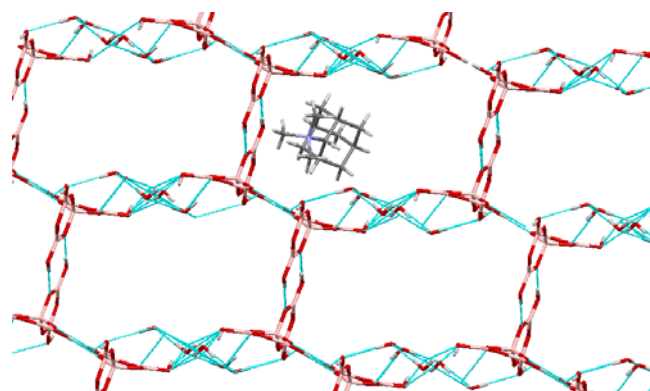


Figure 5. The expanded brickwall anionic supramolecular structure as observed in **4**. Two H₂O molecules are inserted as 'spacers' along the long edges of each hexa(pentaborate) rectangle. Two cations (one shown in one rectangle only) occupy each rectangular cavity.

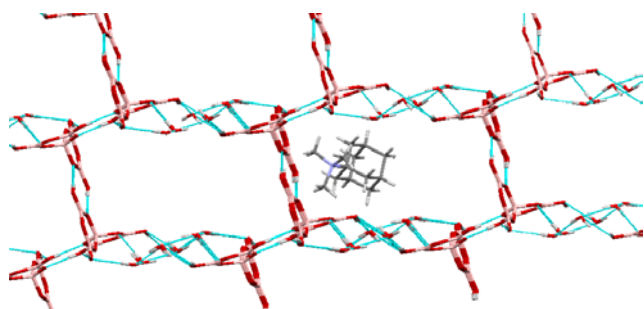


Figure 6. The expanded brickwall anionic supramolecular structure as observed in **5**. Three H₂O molecules are inserted as 'spacers' along the long edges of each hexa(pentaborate) rectangle. Two cations (one shown in one rectangle only) occupy each rectangular cavity.

The regular brickwall structure in **3**, which should have reciprocal- α $R_2^2(8)$ interactions (Etter nomenclature^[19]) between $O7OH \cdots O1^*$, is broken up by the inclusion of two $B(OH)_3$ moieties (Figure 7). The $R_2^2(8)$ interactions are now present in three places, forming a chain, and there is an additional $R_3^3(10)$ linking *via* the α -position of the other boroxole ring of the pentaborate(1-) anion. The brickwall structure of **4** and **5** is expanded by the inclusion of six H₂O molecules in an hexagonal $R_6^6(12)$ ring, illustrated for compound **4** in Figure 8.

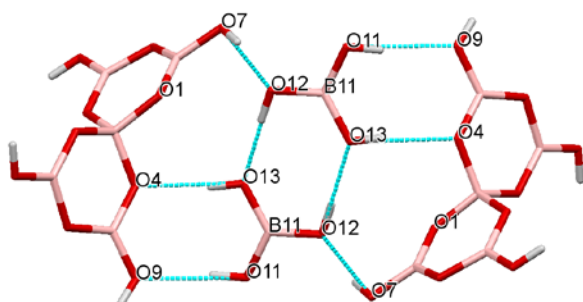


Figure 7. Two $B(OH)_3$ molecules bridge two pentaborate(1-) anions by three $R_2^2(8)$ and two $R_3^3(10)$ H-bond interactions.

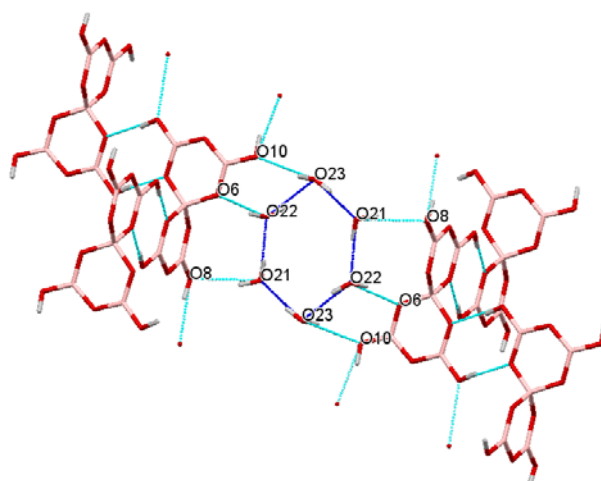


Figure 8. Six H₂O molecules bridge two pentaborate(1-) anions in a hexagonal $R_6^6(12)$ arrangement. The linkages to the pentaborates are $R_2^2(8)$ and $R_3^3(10)$.

There are two independent bipiperdinium(2+) cations in the structure of **9** and these are partnered by two crystallographically identical heptaborate(2-) anions and four waters of crystallization. The heptaborate(2-) anion is relatively rare in polyborate chemistry but is known to exist in two isomeric forms.^[14] The isomer present in this salt is a further example of the 'O⁺' isomer (Figure 1(c)) with previous reports^[15,20] of nonmetal cation salts containing this heptaborate(2-) anion limited to three examples: $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5] \cdot H_2O$, $[cyclo-C_6H_{11}NH_3]_2[B_7O_9(OH)_5] \cdot 3H_2O \cdot B(OH)_3$ and $[cyclo-C_7H_{13}NH_3]_2[B_7O_9(OH)_5] \cdot 2H_2O \cdot 2B(OH)_3$. The 2- anion has a 3-coordinate oxygen atom, carrying a formal 1+ charge, and three 4-coordinate boron atoms, carrying formal 1- charges. QTAIM analysis^[14] of this anion has shown that the real charges for this anion are in accord with electronegativity values with the 3-coordinate oxygen centre carrying a charge of -1.53 and the 4-coordinate boron centres carry a charge of +2.30 each. The atomic labelling for the heptaborate(2-) anion is given in Figure 9. The 3-coordinate oxygen centre is pyramidal and sits out of the plane of B1, B2, B3 by 0.3 Å, with ΣBOB at 349.2°. Bond lengths involving O1 are given in the legend to Figure 9 and average 1.51 Å. These long B-O bonds have been noted before^[15,20] in the other related non-metal cation heptaborate(2-) structures. Excluding bonds to the pyramidal O1 (which are exceptionally long) the remaining $B_{tet}-O$ bond lengths range from 1.438(3) Å to 1.4725(18) Å, (av. 1.4575 Å) and these are significantly longer than the $B_{rig}-O$ bonds which range from 1.355(2) Å to 1.377(4) Å, (av. 1.370 Å). Bond angles for the 4 coordinate boron centres range from 104.18° to 112.52° and those at 3-coordinate boron centres range from 115.85° to 124.08° consistent with tetrahedral and trigonal planar geometries and similar to other reported data.^[15,20]

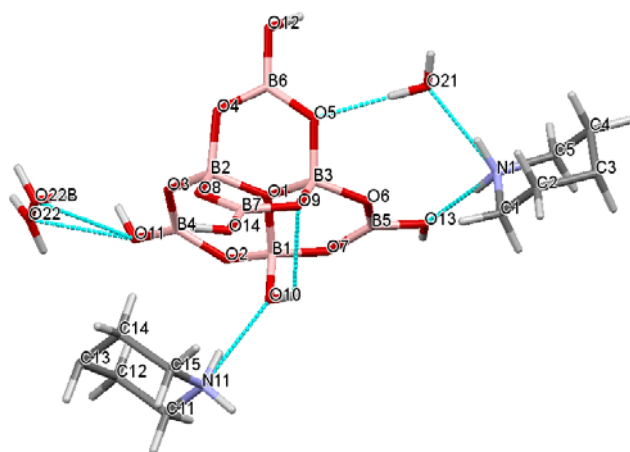


Figure 9. The heptaborate(2-) anion as found in compound **9**. Selected bond distances (Å) and angles (°) are: O1-B1, 1.515(2); O1-B2, 1.504(2); O1-B, 1.520(2); B1-O10, 1.450(2); B1-O1-B2, 121.12(12); B1-O1-B3, 117.06(14); B2-O1-B3, 111.03(13). Selected H-bond data: O10H...O9, $d(\text{H}\cdots\text{O}9)$ 2.54; $d(\text{O}10\cdots\text{O}9)$ 3.0652(18); $\angle\text{O}10\text{H}\text{O}9$, 121.7; N11H...O10, $d(\text{H}\cdots\text{O}10)$ 1.83; $d(\text{O}10\cdots\text{O}9)$ 2.715(2); $\angle\text{N}11\text{H}\text{O}10$ 164.0; N1H...O13, $d(\text{H}\cdots\text{O}13)$ 2.00; $d(\text{N}1\cdots\text{O}13)$ 2.9026(17); $\angle\text{N}1\text{H}\text{O}13$ 172.5; N1H...O21, $d(\text{H}\cdots\text{O}21)$ 1.85; $d(\text{N}1\cdots\text{O}21)$ 2.7488(18); $\angle\text{N}1\text{H}\text{O}21$ 169.7; O12H...O5, $d(\text{H}\cdots\text{O}5)$ 1.95; $d(\text{O}12\cdots\text{O}5)$ 2.8058(16); $\angle\text{O}12\text{H}\text{O}5$ 168.9.

Compound **9** is able to form numerous H-bond interactions. Both independent cations show two H-bond donor interactions (see Figure 10) with amino hydrogen atoms on N1 interacting with a heptaborate(1-) anion (O13 acceptor) and a H₂O molecule (O21 acceptor) whilst amino hydrogen atoms on N11 interact with two different heptaborate(2-) anions at O4 and O10 sites. The heptaborate(2-) anion has five potential H-bond donor sites and three of these are involved with interactions to three neighboring heptaborate(2-) anions (O12H...O11*, O13H...O7*, O14H...O8*). In addition, there is one intramolecular H-bond (O10H10...O9). This intramolecular H-bond has been observed in computational studies.^[21] Details of these H-bond interactions are given in the legend to Figure 9. Surprisingly, with O11H is not involved as a H-bond donor, although O11 is a H-bond acceptor from O12H (heptaborate) and O21H (H₂O). The heptaborate(2-) anions link together via H-bonds and the co-crystallized H₂O molecules to form a giant lattice with the 4,4'-bipiperidinium cations sitting within the cavities. Each dianion forms two R₂²(8) rings at O7 and O8 acceptor sites and one C(8) chain at an O11 acceptor site (Figure 10). The H₂O molecules also form many H-bond interactions and facilitate the formation of the anionic lattice.

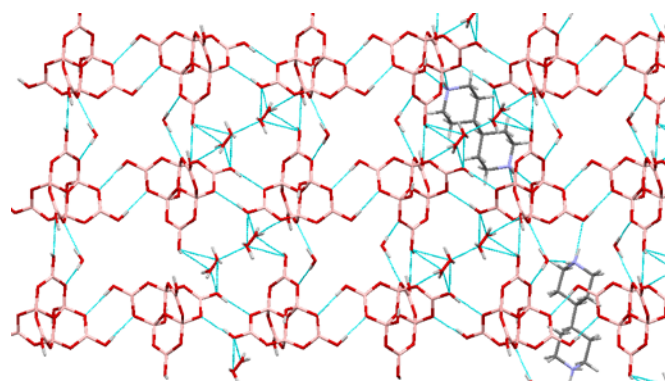


Figure 10. The H-bonded anionic lattice of **9** as viewed along the b axis. The positions of the two independent cations are also indicated. Each heptaborate(2-) anion is linked to others via two R₂²(8) interactions (horizontal) and is part of a C(8) chain (vertical).

Conclusions

Polyborate salts containing bulkier non-metal cations have been prepared and these cations influence the structure and stoichiometry of the observed products. In particular, further examples of rare triborate(1-) and heptaborate(2-) anions have been templated by the PPN(1+) and bipiperidinium(2+) cations in **8** and **9**, respectively. The three crystallographically characterized pentaborate(1-) salts (**3** - **5**) co-crystallized with additional molecules (H₂O/B(OH)₃). In these salts the co-crystallized molecules function as 'spacer' entities enabling the supramolecular H-bonded anionic pentaborate(1-) lattice to expand in order to accommodate the larger cations.

Experimental Section

General. NMR spectra were obtained on a Bruker Avance-400 spectrometer with samples dissolved in D₂O unless otherwise stated. ¹H, ¹³C, ¹¹B, and ³¹P spectra were obtained at 400, 101, 128 and 162 MHz respectively and were referenced ($\delta = 0$) to TMS (¹H, ¹³C), BF₃·OEt₂ (¹¹B) and H₃PO₄ (³¹P). ¹¹B NMR spectra were obtained on samples dissolved in D₂O with **7** and **8** obtained in CDCl₃. FTIR spectra were obtained as KBr pellets on a Perkin-Elmer 100FTIR spectrometer. TGA and DSC were performed on an SDT Q600 instrument using Al₂O₃ crucibles with a ramp rate of 10 °C per minute (RT to 1000 °C in air). Powder X-ray diffraction was carried out on a Phillips X'Pert 2040/60 XRD diffractometer with spectra obtained using the Phillips X'Pert Data Collector software. CHN analyses were obtained from OEA Laboratories (Callingham, Cornwall). 1-adamantylamine, 2-adamantylamine-hydrochloride, dibenzylamine, 4,4'-bipiperidine-hydrochloride, and [PPN]Cl were purchased and used as obtained. *N,N*-dimethyl-1-adamantylamine, *N,N,N*-trimethyl-1-adamantylammonium iodide and *N,N,N*-trimethyl-2-adamantylammonium iodide were prepared according to a literature procedure.^[22] 2-adamantylamine was obtained from 2-adamantylamine-hydrochloride by neutralisation with NaOH.

X-ray crystallography. Crystallographic data for **3** - **5** and **9** are given in Table 1. All the crystallographic data collection of compounds were performed using a standard method^[23] on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity HG Saturn 724+ detector mounted

at the window on an FR-E+ SuperBright molybdenum rotating anode generator with HF Varimax optics ($\lambda = 0.71075 \text{ \AA}$) at 100(2) K. Cell determinations and data collections were carried out using CrystalClear,^[24] with the data reduction, cell refinement and absorption correction using either CrystalClear (3, 4) or CrysAlisPro^[25] (5, 9). Using Olex2^[26] the structures were solved using Superflip^[27] and models refined against all data by full-matrix least squares on F^2 using SHELXL.^[28] CCDC1547669-1547672 contains supplementary data for 3-5 and 9 respectively. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/retrieving.html> or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk.

Synthetic procedures.

Preparation of 1-adamantylammonium pentaborate $[\text{C}_{10}\text{H}_{18}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4]$ (1). $\text{B}(\text{OH})_3$ (2.04 g, 33 mmol) was dissolved in 1:1 MeOH:H₂O (100 ml). 1-adamantylamine (1.0 g, 6.6 mmol) was added with stirring. The solvent was removed under reduced pressure after 1 h, resulting in the formation of the product (2.44 g, 99%) as a white solid. NMR. $\delta_{\text{H}}/\text{ppm}$: 1.60 – 1.72 (m, 6H), 1.83 (s, 6H), 2.12 (br s, 3H, 3CH), 4.79 (DOH, NH and OH rapidly exchanging in D₂O). $\delta_{\text{C}}/\text{ppm}$: 28.63 (CH), 34.71 (CH₂), 39.87 (CH₂), 52.16 (C). $\delta_{\text{B}}/\text{ppm}$: 1.2, 13.3, 17.5. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3393 (br, m), 3248 (br, m), 2916 (s), 2856 (m), 1633 (m), 1422 (br, s), 1381 (m), 1314 (br, m), 1163 (m), 1086 (br), 918 (s), 861 (m), 821 (m), 781 (m), 706 (m), 670 (w), 547 (w), 459 (w), 424 (w). Elemental Anal. Calc. (%) for 1, C₁₀H₂₂NB₅O₁₀: C, 32.5; H, 6.0; N, 3.8. Found (%): C, 32.7; H, 6.1; N, 3.6. p-XRD: amorphous solid. TGA: Loss of 2H₂O (210 – 250 °C): 9.7% (9.7% calc.); residual 2.5B₂O₃ (>750 °C): 46.6% (47.0% calc.).

Preparation of 2-adamantylammonium pentaborate dihydrate $[\text{C}_{10}\text{H}_{18}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (2). Method as for 1. 1.80 g (94%) from 1.60 g $\text{B}(\text{OH})_3$. NMR. $\delta_{\text{H}}/\text{ppm}$: 1.73 – 1.97 (m, 12H, 2CH and 5CH₂), 2.05 (s, 2H, 2CH), 3.53 (s, 1H, CH), 4.79 (HOD, NH and OH rapidly exchanging in D₂O). $\delta_{\text{C}}/\text{ppm}$: 26.32 (CH), 26.47 (CH), 29.58 (2CH₂), 30.40 (2CH), 36.15 (2CH₂), 36.49 (CH₂), 55.91 (CH). $\delta_{\text{B}}/\text{ppm}$: 13.1, 16.8. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3381 (br, s), 3223 (br, s), 2916 (m), 1619, 1427 (br, m), 1361 (br, m), 1101 (m), 1028 (m), 923 (s), 783 (s), 702 (s). Elemental Anal. Calc. (%) for 4, C₁₀H₂₆NB₅O₁₂: C, 29.6; H, 6.4; N, 3.4. Found (%): C, 29.7; H, 6.2; N, 3.3. p-XRD: amorphous solid. TGA: Loss of interstitial 2H₂O (90 – 110 °C): 9.0 % (8.9% calc.); further loss of 2H₂O (260 – 290 °C): 18.8 % (17.7% calc.); residual B₂O₃ (>750 °C): 42.9% (42.8% calc.).

Preparation of *N,N*-dimethyl-1-adamantylammonium pentaborateboric acid monohydrate $[\text{C}_{12}\text{H}_{22}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot \text{B}(\text{OH})_3 \cdot \text{H}_2\text{O}$ (3). Method as for 1. 4.46 g (80% yield) from 3.61 g $\text{B}(\text{OH})_3$. NMR. $\delta_{\text{H}}/\text{ppm}$: 1.63 – 1.74 (m, 6H), 1.91 (s, 6H), 2.23 (s, 3H, 3CH), 2.76 (s, 6H, 2CH₃), 4.79 (DOH, NH and OH rapidly exchanging in D₂O). $\delta_{\text{C}}/\text{ppm}$: 29.13 (CH), 34.77 (CH₂), 35.75 (CH₂), 35.87 (CH₃), 63.20 (C). $\delta_{\text{B}}/\text{ppm}$: 1.2, 13.1, 17.1. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3403 (br, m), 2916 (s), 2853 (m), 1635 (w), 1421 (br, m), 1316 (m), 1159 (m), 1075 (m), 1054 (m), 912 (s), 865 (m), 842 (m), 809 (s), 778 (s), 707 (s), 672 (w), 561 (w), 527 (w), 485 (w), 463 (w). Elemental Anal. Calc. (%) for 2 C₁₂H₃₁NB₅O₁₄: C, 30.1; H, 6.5; N, 2.9. Found (%): C, 33.1; H, 6.9; N, 3.0. p-XRD: d spacing/Å (% rel. int.): 4.51 (100.00), 12.57 (71.74), 4.97 (67.33), 4.87 (50.12), 4.47 (50.09), 7.79 (44.49). TGA: Loss of interstitial H₂O (110 – 130 °C): 5.4% (3.8% calc.); loss of further interstitial H₂O (140 – 150 °C): 12.1% (11.4% calc.); loss of further H₂O (180 – 210 °C): 18.1% (17.0% calc.); residual 3.0B₂O₃ (>800 °C): 45.8% (43.7 % calc.). Recrystallization of H₂O yielded crystals suitable for single-crystal XRD studies.

Preparation of *N,N,N*-trimethyl-1-adamantylammonium pentaborate trihydrate $[\text{C}_{13}\text{H}_{24}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ (4). *N,N,N*-trimethyl-1-adamantylammonium iodide (1.97 g, 6 mmol) was converted to the hydroxide salt by stirring with activated DOWEXTM ion-exchange resin for

24 h prior to reaction with $\text{B}(\text{OH})_3$. 2.11 g (85% yield) from 1.86 g $\text{B}(\text{OH})_3$. NMR. $\delta_{\text{H}}/\text{ppm}$: 1.64 – 1.75 (m, 6H, 3CH₂), 2.07 (s, 6H, 3CH₂), 2.31 (brs, 3H, 3CH), 2.99 (s, 9H, 3CH₃), 4.79 (DOH and OH rapidly exchanging in D₂O). $\delta_{\text{C}}/\text{ppm}$: 29.95 (CH), 34.13 (CH₂), 34.47 (CH₂), 47.48 – 47.56 (3CH₃). $\delta_{\text{B}}/\text{ppm}$: 1.2, 13.1, 17.1. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3437 (br, m), 3261 (br, m) 2922 (s), 2860 (m), 1656 (w), 1422 (br, m), 1409 (m), 1306 (m), 1152 (s), 1072 (m), 1025 (m), 1008 (s), 916 (s), 841 (m), 771 (s), 708 (s), 573 (w), 462 (m). Elemental Anal. Calc. (%) for 3 C₁₃H₃₄NB₅O₁₃: C, 33.5; H, 7.4; N, 3.0. Found (%): C, 33.2; H, 6.9; N, 3.0. p-XRD: d spacing/Å (% rel. int.): 3.18 (100), 5.20 (34), 4.56 (30), 4.52 (18), 7.79 (17); 3.87 (17). TGA: Loss of interstitial 3H₂O (100 – 150 °C): 8.3% (11.6% calc.); loss of further 2H₂O (250 – 270 °C): 17.4% (19.3% calc.) residual 2.5B₂O₃ (>750 °C): 49.2% (37.3% calc.). Recrystallization from H₂O yielded crystals suitable for single-crystal XRD studies.

Preparation of *N,N,N*-trimethyl-2-adamantylammonium pentaborate trihydrate $[\text{C}_{13}\text{H}_{24}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ (5). *N,N,N*-trimethyl-2-adamantylammonium iodide (0.5 g, 1.56 mmol) was converted to the hydroxide salt by stirring with activated DOWEXTM ion-exchange resin for 24 h prior to reaction with $\text{B}(\text{OH})_3$. 0.59 g (92% yield) from 0.48 g $\text{B}(\text{OH})_3$. NMR. $\delta_{\text{H}}/\text{ppm}$: 1.78 – 2.12 (m, 12H), 2.61 (s, 2H), 3.19 (s, 9H, 3CH₃), 3.53 (s, 1H, CH), 4.79 (HOD, NH and OH rapidly exchanging in D₂O). $\delta_{\text{C}}/\text{ppm}$: 25.87 (CH), 26.87 (CH), 28.67 (2CH), 30.20 (CH), 30.73 (2CH₂), 36.84 (CH₂), 39.49 (CH₂), 53.46 (3CH₃), 79.68 (CH). $\delta_{\text{B}}/\text{ppm}$: 13.3, 17.6. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3436 (m), 3378 (m), 3220 (br, s), 2909 (m), 2496 (w), 2385 (w), 2260 (m), 1649 (w), 1439 (br, m), 1361 (br, m), 1252 (s), 1197 (m), 1102 (s), 1026 (s), 926 (s), 782 (m), 696 (m), 650 (m). Elemental Anal. Calc. (%) for 5, C₁₃H₃₄NB₅O₁₃: C, 33.5; H, 7.3; N, 3.0. Found (%): C, 33.6; H, 7.4; N, 2.9. p-XRD: d spacing/Å (% rel. int.): 4.59 (100), 4.43 (37), 4.24 (32), 3.05 (27), 5.42 (27), 8.86 (21). TGA: Loss of interstitial 3H₂O (100 – 140 °C): 12.0% (11.6% calc.); further loss of H₂O (220 – 260 °C): 19.0 % (19.3% calc.) residual 2.5B₂O₃: 40.7% (37.3% calc.). Recrystallization from H₂O yielded crystals suitable for single-crystal XRD studies.

Preparation of dibenzylammonium pentaborate sesquihydrate $[\text{C}_{14}\text{H}_{18}\text{N}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 1.5\text{H}_2\text{O}$ (6). Method as for 1. 6.63 g (98%) from 5.02 g $\text{B}(\text{OH})_3$. NMR. $\delta_{\text{H}}/\text{ppm}$: 4.24 (s, 4H, 2CH₂), 4.79 (HOD and OH rapidly exchanging in D₂O), (7.45 – 7.50 (m, 10H, arom.). $\delta_{\text{C}}/\text{ppm}$: 50.57 (2CH₂), 129.21 (4CH), 129.52 (2CH), 129.73 (4CH), 131.02 (2C). $\delta_{\text{B}}/\text{ppm}$: 1.2, 13.1, 19.0. IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3552 (s), 3271 (br, s), 3062 (br, m), 2818 (m), 2632 (w), 2472 (w), 1995, 1929, 1602 (w), 1447 (m), 1423 (m), 1305 (s), 1154 (m), 1093 (m), 1055 (m), 1024 (m), 1009 (m), 916 (vs), 834 (m), 781 (s), 764 (m), 700 (s), 571 (w), 531 (m), 486 (m). Elemental Anal. Calc. (%) for C₁₄H₂₃NB₅O_{11.5}: C, 37.9; H, 5.2; N, 3.2. Found (%): C, 37.7; H, 5.0; N, 3.0. p-XRD: d spacing/Å (% rel. int.): 3.67 (100), 4.56 (94), 4.26 (92), 4.79 (65), 4.46 (46), 4.04 (35). TGA: Loss of interstitial 1.5H₂O (150 – 160 °C): 5.2 % (6.1 % calc.); further loss of 2H₂O (220 – 250 °C): 14.1 % (14.2% calc.) residual 2.5B₂O₃ (>750 °C): 43.4% (39.3% calc.).

Preparation of bis(triphenylphosphine)iminium pentaborate sesquihydrate $[\text{C}_{36}\text{H}_{30}\text{NP}_2][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 1.5\text{H}_2\text{O}$ (7). Method as for 4 starting with [PPN]Cl (1.00 g, 1.74 mmol). 1.26 g (95 % yield) from 0.54 g (8.8 mmol) $\text{B}(\text{OH})_3$. The product was also prepared under solvothermal conditions. [PPN]Cl (1.02 g, 1.76 mmol) was dissolved in H₂O (50 mL) and was stirred for 24 h with activated DOWEXTM anion exchange resin (OH⁻) form. The resin was filtered off and the filtrate concentrated to ~3 mL. $\text{B}(\text{OH})_3$ (0.54 g, 8.8 mmol) was added and was sealed in a Teflon-lined stainless steel autoclave, which was heated to 145 °C, at autogenous pressure, for 24 h. The autoclave was allowed to cool to room temperature before opening to yield the product as fragile needle-like crystals (1.10 g, 83%). NMR. $\delta_{\text{H}}/\text{ppm}$: 4.79 (HOD and OH rapidly exchanging in D₂O), 7.31 – 7.35 (m, 12H), 7.47 – 7.57 (m, 18H). $\delta_{\text{C}}/\text{ppm}$: 126.83 (dd, ¹J_{PC} = 108.1 Hz, ³J_{PC} = 2.0 Hz, *ipso*, 6C, arom.), 129.14 (m, *meta*, 12C, CH arom.), 132.13 (m, *ortho*, 12C, CH arom.), 133.49 (brs, *para*, 6C, CH arom.). $\delta_{\text{B}}/\text{ppm}$: 16.4

(D₂O); 19.8 (4B), 1.3 (1B) (CDCl₃); 19.3 (4B), 1.5 (1B) (CD₂Cl₂); δ_P/ppm: 21.2. IR (ν_{max}/cm⁻¹): 3372 (br, m), 3227 (br, m), 3058 (w), 2261 (w), 1976 (w), 1909 (w), 1827 (w), 1630 (w), 1589 (w), 1437 (s), 1303 (br, m), 1265 (m), 1184 (w), 1159 (w), 1115 (vs), 1026 (m), 922 (s), 781 (m), 748 (m), 723 (vs), 692 (vs), 534 (s), 500 (s). Elemental Anal. Calc. (%) for C₃₆H₃₇B₅NO_{11.5}P₂: C, 55.7; H, 4.8; N, 1.8. Found (%): C, 55.4; H, 4.7; N, 1.9. p-XRD: d spacing/Å (% rel. int.): 3.89 (100), 3.74 (95), 7.38 (91), 3.71 (98), 7.85 (67), 10.65 (63). TGA: Loss of interstitial 3.5H₂O (120 – 150 °C): 7.1 % (8.1 % calc.); residual 2.5B₂O₃ (>650 °C): 22.9% (22.4% calc.).

Preparation of bis(triphenylphosphine)iminium tetraborate 2.5 hydrate [C₃₆H₃₀NP₂][B₄O₃(OH)₄].2.5H₂O (**8**). Method as for **4**. 1.25 g (94 % yield) from 0.33 g (5.3 mmol) B(OH)₃. The product was also prepared under solvothermal conditions (0.4 g, 31 % yield from 1.09 g (1.9 mmol) [PPN]Cl, 0.24 g (3.8 mmol) B(OH)₃) with method as for **7**. NMR. δ_H/ppm: 4.79 (HOD and OH rapidly exchanging in D₂O), 7.26 – 7.29 (m, 12H), 7.42 – 7.52 (m, 18H). δ_C/ppm: 126.78 (dd, ¹J_{PC} = 108.7 Hz, ³J_{PC} = 2.0 Hz, *ipso*, 6C), 129.15 (m, *meta*, 12H, CH arom.), 132.08 (m, *ortho*, 12C, CH arom.), 133.52 (brs, *para*, 6C, CH arom.). δ_B/ppm: 13.7 (D₂O); 19.7 (2B), 1.6 (1B) (CDCl₃); 19.7 (2B), 1.4 (1B) (CD₂Cl₂); δ_P/ppm: 21.1. IR (KBr) (ν_{max}/cm⁻¹): 3286 (br, m), 3058 (m), 1975 (w), 1907 (w), 1827 (w), 1643 (w), 1589 (m), 1482 (w), 1437 (s), 1296 (m), 1261 (m), 1185 (w), 1159 (w), 1115 (vs), 1025 (m), 997 (m), 918 (m), 855 (m), 801 (m), 779 (m), 747 (s), 723 (vs), 691 (vs), 532 (s), 500 (s). Elemental Anal. Calc. (%) for C₃₆H₃₃B₃NO_{9.5}P₂: C, 59.1; H, 5.4; N, 1.9. Found (%): C, 58.8; H, 5.1; N, 1.9. p-XRD: d spacing/Å (% rel. int.): 4.41 (100), 3.68 (57), 4.17 (43), 3.56 (34), 6.62 (34), 8.95 (30). TGA: Loss of interstitial 2.5H₂O (90 – 100 °C): 6.0% (6.2% calc.); further loss of 2H₂O 190 – 220 °C): 10.5% (11.1% calc.); residual 1.5B₂O₃ (>750 °C): 17.8% (14.3% calc.).

Preparation of 4,4'-bipiperidinium heptaborate dihydrate [C₁₀H₂₂N₂][B₇O₉(OH)₅].2H₂O (**9**). Method as for **3**. 1.57 g (74% yield) from 1.0 g 4,4'-bipiperidyl hydrochloride and 1.01 g B(OH)₃. NMR. δ_H/ppm: 1.39 – 1.54 (m, 6H, 2CH₂ and 2CH), 2.0 (d, 4H, ³J = 12.0 Hz, 2CH₂), 2.97 (t, 4H, ³J = 12.0 Hz, 2CH₂), 3.45 (d, 4H, ³J = 12.0 Hz, 2CH₂), 4.79 (HOD and OH rapidly exchanging in D₂O). δ_C/ppm: 25.37 (4CH₂), 37.33 (2CH), 44.09 (4CH₂). δ_B/ppm: 14.7. IR (KBr) (ν_{max}/cm⁻¹): 3602 (w), 3436 (br, m), 3265 (m), 3022 (br, m), 2921 (m), 2863 (m), 2822 (m), 2761 (m), 2551 (s), 1650 (m), 1636 (m), 1448 (m), 1437 (m), 1419 (m), 1356 (s), 1165 (br, m), 1078 (m), 1044 (m), 986 (m), 919 (w), 909 (w), 855 (m), 810 (s), 719 (w), 689 (w), 670 (w), 622 (w), 489 (w), 469 (w), 440 (w), 420 (w). Elemental Anal. Calc. (%) for C₁₀H₃₁B₇N₂O₁₆: C, 23.5; H, 6.1; N, 5.5. Found (%): C, 23.5; H, 6.3; N, 5.8. TGA: Loss of 4.5H₂O (160 – 220 °C): 15.7% (15.9% calc.); residual 3.5B₂O₃ (>750 °C): 47.9% (47.7% calc.) Recrystallization from H₂O yielded crystals suitable for single-crystal XRD studies.

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Keywords: bulky cations • heptaborate(2-) • pentaborate(1-) • tetraborate(1-) • X-ray structure

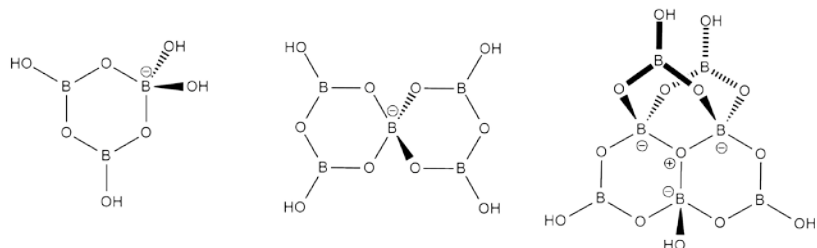
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Polyborate self-assembly*

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**Polyborate anions partnered with
large non-metal cations: triborate(1-),
pentaborate(1-), and heptaborate(2-)
salts.**

Sterically demanding non-metal cations influence the structure and stoichiometry of polyborate salts. Triborate(1-) and heptaborate(2-) anions have been templated by the PPN(1+) and biperdinium(2+) cations, respectively, and pentaborate(1-) salts co-crystallized with additional molecules of (H₂O/B(OH)₃). The co-crystallized molecules function as 'spacer' entities enabling the supramolecular H-bonded anionic lattice to expand in order to accommodate the large cations.