SYNTHESIS, CHARACTERIZATION, AND THERMAL PROPERTIES OF BENZYLAMMONIUM PENTABORATE $[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$

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Dedicated to Professor Bohumil Štíbr on the occasion of his 70th birthday.

$[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$ was obtained as colourless crystals in high yield from a MeOH/H_2O (1:1) solution of benzylamine and boric acid (1:5). A single-crystal X-ray study confirmed that the solid-state structure was comprised of a supramolecular H-bonded pentaborate anion lattice, templated by the benzylammonium cations which occupy positions within the lattice cavities. Each pentaborate anion formed 4 H-bonds to 4 neighbouring pentaborate anions at α,α,α,β acceptor sites. Additionally, each cation H-bonds to 3 pentaborate anions. Crystals were monoclinic, $P2_1/c$, with a = 9.3511(2) Å, b = 14.5157(4) Å, c = 10.4670(2) Å, β = 90.778(2)°, T = 120 K, V = 1420.64(6) Å^3, and Z = 4. TGA/DSC analysis showed that $[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$ thermally decomposed in air at 800 °C to $2.5B_2O_3$, via a low-temperature (200–250 °C) dehydration step to a condensed pentaborate.

Keywords: Benzylammonium; Pentaborate; Supramolecular; Thermal decomposition; Hydrogen bonding.

Borate minerals are of great industrial importance due to the rich diversity in their intrinsic structures, their potential as precursors for inorganic porous materials[1]; their practical applications as fluorescence[2] or piezoelectric[3] materials, and their potential as second-harmonic-generation optical materials[4]. Many polyborate salts containing isolated anions have been synthesized and characterized using non-metal cations (NMCs) as structure directing templates, and salts containing the following isolated anions have been previously reported[5–10]: $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, $[B_5O_6(OH)_4]^-$,

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$[B_7O_9(OH)_5]^{2-}$, $[B_8O_{10}(OH)_6]^{2-}$, $[B_9O_{12}(OH)_6]^{3-}$, and $[B_{14}O_{20}(OH)_6]^{4-}$. We have been investigating the structure directing effects of innocent and non-innocent (e.g., H-bonding) NMCs, and have recently reported the synthesis and characterization of a number of such pentaborate and triborate derivatives[11]. This manuscript describes the synthesis of a new templated NMC pentaborate salt, $[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$ (**1**), its solid-state structure, and its thermal properties.

EXPERIMENTAL

General

Reagents and solvents were obtained from Aldrich Chemical Company or Lancaster Synthesis and were used without further purification. Multi-element NMR spectra were recorded at room temperature (298 K) in D_2O solution on a Bruker Avance 500 (11.7 T) spectrometer operating at 500 MHz for ^1H, 125 MHz for ^{13}C-{^1H} and 160 MHz for ^{11}B-{^1H} nuclei, and referenced to $SiMe_4$ or $BF_3{\cdot}OEt_2$. Chemical shifts (δ) are reported in ppm, and WIN-NMR or XWIN-NMR 3.5 were used for data analysis. IR spectra (450–4000 cm^{-1}) were obtained as KBr discs on a Perkin Elmer Spectrum 100 FTIR spectrometer. TGA-DSC analysis was performed in air between 10–800 °C with a ramp temperature of 10 °C min^{-1} on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles. CHN analyses were obtained at OEA laboratories Ltd (Callington, UK).

Preparation of $[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$ (**1**)

Boric acid (5.79 g, 93.33 mmol) was dissolved in a warm solution 1:1 methanol/water (100 ml). Benzylamine (2.00 g, 18.67 mmol) was added to the solution which was then heated for 1 h. The solvent was then removed by rotary evaporation, and the solid residue was further dried at 60 °C for 24 h (5.55 g, 92%). The compound was recrystallized from distilled water to yield colourless crystals of **1**. For **1** (325.26) calculated: 25.77% C, 4.33% H, 4.29% N; found: 25.41% C, 4.38% H, 4.05% N. ^1H NMR: 4.68 (–NH_3/HOD), 3.98 (s, 2 H, CH_2), 7.26 (s, 5 H, Ph). ^{11}B NMR: 1.11, 13.19, 19.06. ^{13}C NMR: 43.05 (CH_2), 128.71 (CH), 129.13 (CH), 132.54 (CH). IR (ν_{max}, cm^{-1}): 3387, 3183, 2342, 1631, 1411, 1303, 1203, 1111, 1010, 921, 782, 749, 695, 654, 487. Crystals of **1** suitable for X-ray crystallography were obtained by recrystallization of the salt from distilled water and dried using vacuum filtration.

X-ray Crystallography

The crystallographic data collection of compound **1** (ref.[12]) was performed using a Nonius Kappa CCD diffractometer with MoKα radiation (λ = 0.71073 Å) controlled by the Collect[13] software package and an Oxford Cryosystem Cobra at 120(2) K. The data were processed using Denzo[14] and semi-empirical absorption corrections were applied using SADABS[15]. Crystallographic data are given in Table I. The structure was solved by direct methods and refined by full-matrix least-square procedures on F^2 using SHELXS97 and SHELXL97 (ref.[16]), respectively. All non-hydrogen atoms were refined anisotropically. Although the hydrogen

atoms could be located from the difference map, they were all placed geometrically using standard riding models.

RESULTS AND DISCUSSION

Compound **1**, an ionic salt comprised on benzylammonium cations and isolated pentaborate anions, was prepared in high yield as analytically pure colourless crystals from a $MeOH/H_2O$ (1:1) solution of benzylamine and bo-

TABLE I
Crystallographic data for **1**

Parameter	Compound **1**
Empirical formula	$C_7H_{14}B_5NO_{10}$
Formula weight	326.24
T, K	120
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.3511(2)
b, Å	14.5157(4)
c, Å	10.4670(2)
β, °	90.778(2)
V, Å^3	1420.64(6)
Z	4
D_c, g cm^{-1}	1.525
μ, mm^{-1}	0.131
F(000)	672
Crystal size, mm	0.16 × 0.16 × 0.14
$2\theta_{max}$, °	54.96
Reflections collected	15 637
Independed reflections [R_{int}]	3244 [0.0375]
Completeness, %	99.8
Data/restraints/parameters	3244/0/213
GOF on F^2	1.074
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0391, $wR2$ = 0.0874
R indices (all data)	$R1$ = 0.0457, $wR2$ = 0.0922
Maximal and minimal difference, e Å^{-3}	0.254, –0.240

ric acid (1:5). The salt was characterized by NMR (^{11}B, ^{13}C, and ^{1}H) and IR spectroscopies, and by a single-crystal XRD study. Spectroscopic data are in accord with the single-crystal XRD structure (see below) and with previously reported NMC pentaborates[11].

A perspective view of the **1** along with atom numbering scheme is shown in Fig. 1, and selected atomic distances and bond angles are presented in Table II. The pentaborate anions are H-bonded together in a supramolecular network, with benzylammonium cations filling the cavities and H-bonding to pentaborate anions. The bond angles and lengths of the $[C_6H_5CH_2NH_3]^+$ cation are not significantly different from those observed in other salts of this cation[17], e.g., $[C_6H_5CH_2NH_3][NO_3]$, $[C_6H_5CH_2NH_3]_2[SO_4]$, $[C_6H_5CH_2NH_3]_2[HAsO_4]\cdot H_2O$, $[C_6H_5CH_2NH_3]_4[Cu(ONO_2)_4][NO_3]_2$. The $-NH_3$ moiety of the cation interacts with three pentaborate anions by formation of hydrogen bonds (Table III). Schubert and co-workers[7] have designated pentaborate H-bond acceptor sites (O atoms) as either α, β, or γ and these three NH atoms form two strong H-bonds to α and β sites, with the third H atom forming a bifurcated H-bond interactions to γ and neighbouring β sites. The non-bifurcated H-bond interactions have an average NHO angle of 169.9° and an average (N···O) distance

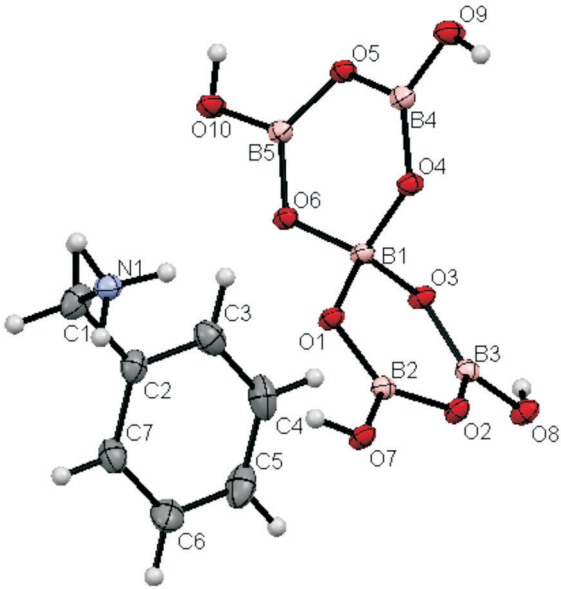

FIG. 1
Drawing of **1** with atom-labelling scheme

of 2.9955 Å. The bifurcated H-bonded interaction is unsymmetrical with an average NHO angle of 142.4° with the stronger interaction to the γ site (154.9°, 3.0162(15) Å), and a weaker interaction to a neighbouring β site (129.8°, 3.3024 Å). The three shortest contact interactions (<3.1 Å) are shown in Fig. 2. Bifurcated H-bond interactions to α,α sites have been previously observed in pentaborates[11a], but this we believed is the first example of a bifurcated β,γ interaction. The pentaborate anion consists of a central tetrahedral B atom with average B–O distances of 1.4686(17) Å; these are significantly longer than those to the four trigonal B atoms, which are in the range of 1.3506(18)–1.3944(18) Å, but shorter than those observed in O donor adducts of triarylboranes[18]. The B–O bonds of trigonal B centres to terminal hydroxyl group O atoms (av. 1.3575 Å) are generally

TABLE II
Selected interatomic distances and bond angles for **1**

Bond	Distance, Å	Bond	Distance, Å
B1–O6	1.4550(17)	O10–H10	0.8400
B1–O1	1.4706(17)	C1–C2	1.504(2)
B1–O4	1.4727(17)	C1–N1	1.5053(18)
B1–O3	1.4761(17)	C1–H1D	0.9900
B2–O7	1.3606(17)	C1–H1E	0.9900
B2–O1	1.3781(18)	C2–C3	1.391(2)
B2–O2	1.3556(17)	C2–C7	1.392(2)
B3–O3	1.3556(17)	C3–C4	1.388(2)
B3–O8	1.3680(18)	C3–H3	0.9500
B3–O2	1.3897(17)	C4–C5	1.382(3)
B4–O9	1.3508(18)	C4–H4	0.9500
B4–O4	1.3615(17)	C5–C6	1.378(3)
B4–O5	1.3944(18)	C5–H5	0.9500
B5–O10	1.3506(18)	C6–C7	1.387(2)
B5–O6	1.3649(17)	C6–H6	0.9500
B5–O5	1.3938(18)	C7–H7A	0.9500
O7–H7	0.8400	N1–H1A	0.9100
O8–H8	0.8400	N1–H1B	0.9100
O9–H9	0.8400	N1–H1C	0.9100

TABLE II
(*Continued*)

Bonds	Angle, °	Bonds	Angle, °
O6–B1–O1	108.36(11)	C2–C1–H1D	109.5
O6–B1–O4	111.15(10)	N1–C1–H1D	109.5
O1–B1–O4	107.45(10)	C2–C1–H1E	109.5
O6–B1–O3	109.91(10)	N1–C1–H1E	109.5
O1–B1–O3	109.78(10)	H1D–C1–H1E	108.1
O4–B1–O3	110.13(11)	C3–C2–C7	119.39(14)
O7–B2–O1	120.22(13)	C3–C2–C1	120.14(14)
O7–B2–O2	118.81(12)	C7–C2–C1	120.47(14)
O1–B2–O2	120.96(12)	C4–C3–C2	120.04(15)
O3–B3–O8	122.59(12)	C4–C3–H3	120.0
O3–B3–O2	121.29(12)	C2–C3–H3	120.0
O8–B3–O2	116.11(12)	C5–C4–C3	120.05(16)
O9–B4–O4	123.06(13)	C5–C4–H4	120.0
O9–B4–O5	116.32(12)	C3–C4–H4	120.0
O4–B4–O5	120.61(12)	C6–C5–C4	120.29(16)
O10–B5–O6	117.88(13)	C6–C5–H5	119.9
O10–B5–O5	121.51(12)	C4–C5–H5	119.9
O6–B5–O5	120.59(12)	C5–C6–C7	120.02(16)
B2–O1–B1	120.68(11)	C5–C6–H6	120.0
B2–O2–B3	117.75(11)	C7–C6–H6	120.0
B3–O3–B1	121.00(11)	C6–C7–C2	120.16(16)
B4–O4–B1	121.77(11)	C6–C7–H7A	119.9
B5–O5–B4	118.50(11)	C2–C7–H7A	119.9
B5–O6–B1	121.94(11)	C1–N1–H1A	109.5
B2–O7–H7	109.5	C1–N1–H1B	109.5
B3–O8–H8	109.5	H1A–N1–H1B	109.5
B4–O9–H9	109.5	C1–N1–H1C	109.5
B5–O10–H10	109.5	H1A–N1–H1C	109.5
C2–C1–N1	110.87(12)	H1B–N1–H1C	109.5

at the shorter end of this range, whilst B–O bonds which involve the O atoms distal to the tetrahedral B are longer (av. 1.3833 Å). These bond length variations are in accord with the expected bond orders as described elsewhere[11a,18,19].

TABLE III
Hydrogen bonds for **1**

D–H···A	*d*(D–H), Å	*d*(H···A), Å	*d*(D···A), Å	(DHA), °
O7–H7···O1^{i}	0.84	1.85	2.6855(14)	174.5
O8–H8···O4^{ii}	0.84	1.97	2.8030(13)	169.1
O9–H9···O3iii	0.84	1.94	2.7812(13)	173.8
O10–H10···O7^{iv}	0.84	1.92	2.7513(13)	168.9
NI–H1A···O8^{v}	0.91	2.20	3.1019(15)	171.0
N1–H1B···O5^{vi}	0.91	2.17	3.0162(15)	154.9
N1–H1B···O9^{vi}	0.91	2.64	3.3024(16)	129.8
N1–H1C···O6^{vii}	0.91	1.99	2.8892(16)	168.8

Symmetry transformations used to generate equivalent atoms: (i) $-x$, $-y$, $-z + 2$; (ii) x, $-y + 1/2$, $z - 1/2$; (iii) x, $-y + 1/2$, $z + 1/2$; (iv) $x + 1$, y, z; (v) $x + 1$, $-y + 1/2$, $z - 1/2$; (vi) x, y, $z - 1$; (vii) $-x + 1$, $-y$, $-z + 1$.

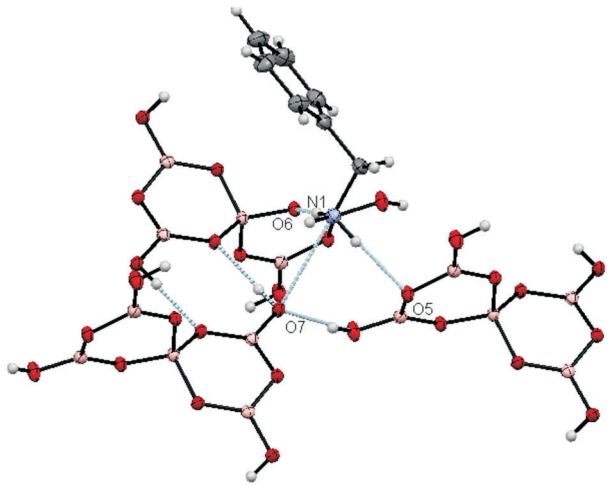

FIG. 2
H-bonding interactions in **1**: the three shortest cation–anion hydrogen are shown together with one $R_2^2(8)$ anion–anion and the C(8) anion–anion interaction[20]

In addition to the cation–anion H-bond interactions, each $[B_5O_6(OH)_4]^-$ anion forms four donor H-bonds to adjacent pentaborate anions (three at α sites and one at a β site) forming a supramolecular network. The α interactions are arranged as reciprocal pairs, forming 'layers' (Fig. 3) and these layers are connected through the β interactions. The three α interactions may be described in Etter nomenclature[20] as $R_2^2(8)$ with the β interaction C(8).

The average O···O distance for the α interactions is 2.7566 Å at an average angle OH···O angle of 172.47°, and for the β interaction 2.7513(13) Å at an angle of 168.9° (Table III). Two structural variations (herringbone and brickwall) of the H-bonding α,α,α,β motif have been previously noted[11c,19], and **1** is a further example of this 'herringbone' pattern (Fig. 3).

Non-metal cation salts of isolated pentaborate anions have been reported to undergo a two stage thermal decomposition in air[5,7,11c,21,22]. The first stage of the decomposition is the cross linking of the isolated pentaborate anions with the release of two equivalents of water per pentaborate anion. The second stage of decomposition is the pyrolysis of the organic compound. Thermal gravimetric analysis (TGA) of **1** (Fig. 4) shows a series of weightloss events. The first weightloss event is associated with the loss of two water molecules. This occurs in the temperature range of 200–250 °C and results in a weightloss of ~12% (calc. 11.04%). The DSC trace shows

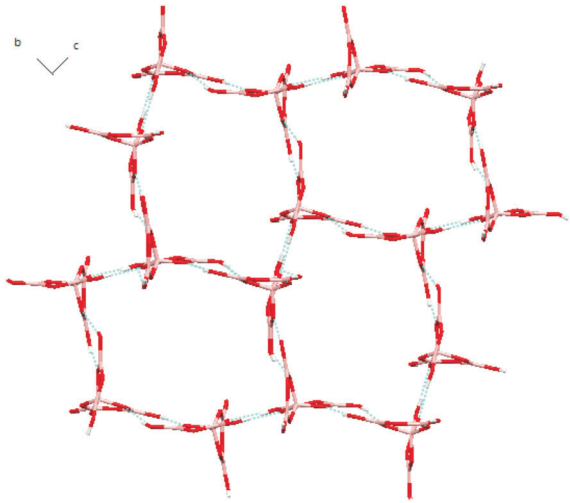

FIG. 3
Supramolecular structure of pentaborate anions in **1**, viewed along the along the *a* axis

that the dehydration step is endothermic whilst further steps are exothermic. The second series of weightloss events starts at ~250 °C and continues to >800 °C, leaving two and half equivalents of boron oxide (B_2O_3) as the final residue, weightloss of 43% (calc. 46.65%).

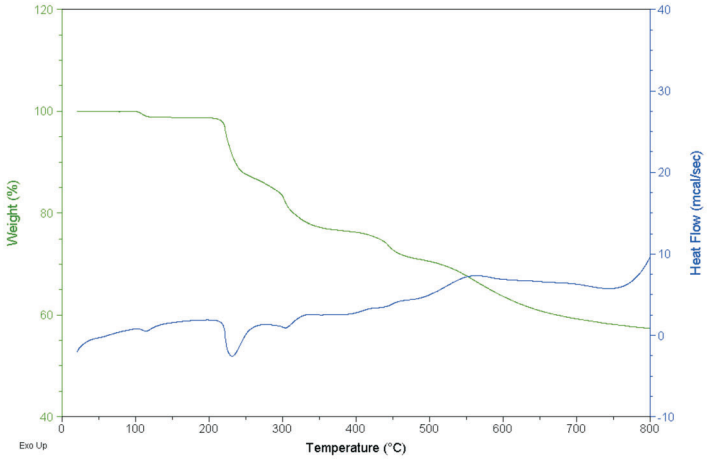

FIG. 4
TGA and DSC curves for **1**

CONCLUSIONS

Benzylammonium pentaborate $[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$ crystallized in high yield from an aqueous methanol solution containing benzylamine and boric acid (1:5). The anions of **1** are H-bonded into a supramolecular network through α and β interactions, into a herringbone motif. The cation H-bonds to the lattice through α, β and γ sites. TGA/DSC analysis showed that $[C_6H_5CH_2NH_3][B_5O_6(OH)_4]$ is thermally decomposed in air at 800 °C to 2.5 B_2O_3, with a clean low temperature dehydration step to $[C_6H_5CH_2NH_3][B_5O_8]$ at 250 °C.

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12. CCDC 776543 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 336033; or deposit@ccdc.cam.ac.uk).
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