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Triborate and pentaborate salts of non-metal cations derived from N-substituted piperazines: synthesis, structural (XRD) and thermal properties†

Michael A. Beckett,*a Peter N. Horton,b Michael B. Hursthouseb and James L. Timmisb

The synthesis and characterization of a triborate salt, \([\text{H}_2\text{N(CH}_2\text{CH}_2]_2\text{NH}_2][\text{B}_3\text{O}_5(\text{OH})_4]_2\) (1), and four pentaborate salts, \([\text{H}_2\text{N(CH}_2\text{CH}_2]_2\text{NH}][\text{B}_5\text{O}_6(\text{OH})_4]_2\) (2a), \([\text{MeHN(CH}_2\text{CH}_2]_2\text{NH}][\text{B}_5\text{O}_6(\text{OH})_4]_2\) (2b), \([\text{MeHN(CH}_2\text{CH}_2]_2\text{NMe}][\text{B}_5\text{O}_6(\text{OH})_4]_2\) (2c) and \([\text{Me}_2\text{N(CH}_2\text{CH}_2]_2\text{NMe}_2][\text{B}_5\text{O}_6(\text{OH})_4]_2\) (2d) are described. TGA and DSC analysis (in air, 25–1000 °C) indicate that triborate 1 decomposes to \(\text{B}_2\text{O}_3\) via a multistage process, with the first stage (<250 °C) being dehydration to condensed polymeric hexaborate of approximate composition: \([\text{H}_2\text{N(CH}_2\text{CH}_2]_2\text{NH}_2][\text{B}_6\text{O}_{10}]_2\). The pentaborates (2a–2d) are thermally decomposed to \(\text{B}_2\text{O}_3\) via a 2 stage process involving polymeric [NMC][\(\text{B}_5\text{O}_6\)]. The anhydrous polyborates were amorphous. BET analysis of materials derived from the thermolysis of 1 at 250, 400, 600, and 1000 °C were all non-porous (surface area <1.8 m² g⁻¹). A single-crystal X-ray diffraction study of 1 showed that it contains isolated triborate(1−) anions in a structure comprised of alternating cationic and anionic layers held together via extensive H-bonds. Single-crystal XRD structural studies on pentaborate salts 2c and 2d are also reported.

1. Introduction

There has been increased interest in recent years in non-metal cation (NMC) polyborate, notably pentaborate, salts as a result of their potential applications as porous1–5 or NLO⁶ piezoelectric or fluorescent⁷ materials. The chemistry of boric acid in aqueous solution is complicated with monomeric and various polymeric borate ions existing in equilibrium concentrations⁸ which are dependent upon B concentration, B/[OH⁻] ratio, and temperature. Despite this, pentaborate salts of NMCs are generally readily synthesized as crystalline solids from aqueous solution by the interaction of a free base, or its hydroxide salt, with \(\text{B(OH)}_3\), in a 1:5 ratio.⁹ Structurally, NMC pentaborates are best described as supramolecular networks of H-bonded isolated \([\text{B}_5\text{O}_6(\text{OH})_4]^{2−}\) anions, and the formation of this extended lattice is clearly a driving force in product formation. The NMCs occupy ‘cavities’ within the network, and usually (if possible) add further stabilizing H-bond cation-anion interactions.¹⁰,¹¹ Occasionally, NMC polyborate salts other than pentaborates have been obtained from aqueous solution e.g. \([\text{B}_2\text{O}_5(\text{OH})_4]^{2−}\),¹² \([\text{B}_2\text{O}_5(\text{OH})_3]^{2−}\),¹³ two \([\text{B}_2\text{O}_5(\text{OH})_4]^{2−}\) isomers,¹⁴,¹⁵ \([\text{B}_5\text{O}_6(\text{OH})_4]^{2−}\),¹⁶ \([\text{B}_5\text{O}_6(\text{OH})_4]^{2−}\),¹⁷ More forcing solvolithal methods have led to NMC salts of isolated or condensed polyborate sheets, which are formally derived from isolated anions.¹⁸ We are currently undergoing a research programme investigating the structure directing effects of NMCs in borate chemistry¹⁹,²⁰ and have recently isolated, by this method from aqueous solution, an unprecedented double salt of stoichiometry \([\text{H}_2\text{en}]_2[\text{Me}_2\text{N(CH}_2\text{CH}_2]_2\text{NMe}_2][\text{B}_5\text{O}_6(\text{OH})_4]_2\cdot 7\text{H}_2\text{O}\) which contains two isolated polyborate anions: \([\text{B}_5\text{O}_6(\text{OH})_4]^{2−}\) and \([\text{B}_5\text{O}_6(\text{OH})_4]^{2−}\). As a continuation of this study we have investigated substituted piperazine based NMCs and now report the synthesis of an unusual triborate salt, as well as further examples of pentaborate salts. The structures of the anions present are illustrated in Fig. 1. The thermal properties of the triborate salt (TGA/DSC) has been investigated in detail and results compared with those of the pentaborate derivatives. Porosity (BET surface area measurements) of materials derived from the thermal decomposition of the triborate salt are also

Fig. 1 Schematic drawing of (i) triborate(1−) as observed in 1, and (ii) pentaborate(1−) as observed in 2a–2d.
2. Results and discussion

2.1 Synthesis and characterization

The triborate salt \([\text{H}_2\text{N(CH}_2\text{CH}_2\text{)}_2\text{NH}]\text{B}_3\text{O}_3(\text{OH})_4\) \(_2\) (1), and the pentaborate salts \([\text{H}_3\text{N(CH}_2\text{CH}_2\text{)}_3\text{NH}]\text{B}_5\text{O}_6(\text{OH})_4\) \(_2\) (2a), \([\text{MeHN(CH}_2\text{CH}_2\text{)}_2\text{NH}]\text{B}_5\text{O}_6(\text{OH})_4\) \(_2\) (2b), and \([\text{MeHN(CH}_2\text{CH}_2\text{)}_2\text{NMe}]\text{B}_5\text{O}_6(\text{OH})_4\) \(_2\) (2c) were conveniently prepared in \(\text{H}_2\text{O}/\text{MeOH}\) solution, from \(\text{B(OH)}_3\) and (substituted) piperazines according to eqn (1) and (2).

\[
\begin{align*}
\text{Me}_2\text{N(CH}_2\text{CH}_2\text{)}_2\text{NMe}_2 & + 12\text{B(OH)}_3 \rightarrow \text{Me}_2\text{N(CH}_2\text{CH}_2\text{)}_2\text{NMe}_2\text{B}_5\text{O}_6(\text{OH})_4\text{H}_2\text{O} \quad (1) \\
\text{Me}_2\text{N(CH}_2\text{CH}_2\text{)}_2\text{NMMe}_{2} & + 10\text{B(OH)}_3 \rightarrow \text{Me}_2\text{N(CH}_2\text{CH}_2\text{)}_2\text{NMMe}_2\text{B}_5\text{O}_6(\text{OH})_4\text{H}_2\text{O} \quad (2)
\end{align*}
\]

With the exception of 2d (obtained in 50%) products were readily obtained in high yield (86–97%) and were of good analytical purity by crystallization induced by removal of the solvents. Compounds 1 and 2a-d were characterized spectroscopically (NMR, IR) and X-ray diffraction (powder) techniques. Powder diffraction analysis showed that all samples were spectrally (NMR, IR) and X-ray diffraction (powder) techniques.

2.2 Thermal properties of 1

The thermal properties of NMC pentaborate salts, which contain intricate 3D H-bonded networks (section 2.3), have been well investigated and the thermal behaviour of 2a–2d are consistent with earlier reports on pentaborate salts.\(^{1-5}\) The layered structure for 1 (see section 2.3) might suggest that its thermal properties would be different and therefore was worthy of further and more detailed investigation.

Heating a sample of the triborate salt (1) in air resulted in thermal decomposition and the eventual formation of a glassy black solid. During this process the sample ‘chars’ and intumesces prior to collapsing down to the glass. This behaviour is similar to that observed for non-metal cation pentaborates.\(^{1-5}\) A thermal study of the one previously known NMC triborate, \([\text{HOCH}_2\text{CMe}_2\text{NH}_3]\text{B}_3\text{O}_3(\text{OH})_4\),\(^{11}\) suggested dehydration (2 mole equivalent per triborate) by 120 °C to a viscous liquid by either condensation of anions or anion/cation esterification. The process for 1 was followed in more detail by DSC/TGA (Fig. 3). Closer inspection of the TGA curve shows that the decomposition is a multistep process, with a series of endothermic processes occurring below 275 °C, and two exothermic processes occurring at 400 °C and 600 °C. The weight loss below 275 °C is consistent with dehydration as
shown in eqn (4). The final residue (55.4%) is in close agreement with that calculated (54.2%) for B₂O₃ according to eqn (5).

\[
\begin{align*}
[H₂N(CH₂CH₂)₂NH₂]B₂O₃(OH)_₄^{2-} & \rightarrow \quad \text{(4)} \\
[H₂N(CH₂CH₂)₂NH₂]B₂O₃ + 4H₂O \\
[H₂N(CH₂CH₂)₂NH₂]B₂O₃(OH)_₄^{2-} & \rightarrow \quad \text{(5)} \\
3B₂O₃ + \text{oxidation products}
\end{align*}
\]

It was of interest to examine the physical properties (crystallinity and porosity) of materials derived from the aerobic thermolysis of 1 and a furnace procedure was used to attempt to replicate the above TGA results on a small synthetic scale. Accordingly, samples (~1.0 g) were heated to 275 °C (1a), 500 °C (1b), 600 °C (1c), or 1000 °C (1d) and weighed and characterized. Elemental analytical data of 1a were consistent with the dehydrated product (eqn (4)) and the residual weight associated with formation of 1d was in good agreement with the residual weight calculated expected for formation of B₂O₃. Elemental analysis data for 1b and 1c demonstrated residual presence of C, H and N with lower amounts present in 1e indicating that the oxidation process was still incomplete at this temperature/time. All thermally produced samples were amorphous by powder XRD studies. and SEM pictures of ground samples were all remarkably similar (exemplified for 1b in Fig. 4) and were consistent with glassy shards.

The porosity of the thermally derived materials were determined by multipoint BET analysis. Essentially all samples were ‘non-porous’ with the isolated pentaborates having porosities of 0.12–0.85 m² g⁻¹, condensed pentaborates 0.04–0.86 m² g⁻¹, intumesced materials 0.12–1.59 m² g⁻¹, and the final glassy B₂O₃ 0.18 m² g⁻¹. The densities of 1b and 1c, determined as ‘tipped solids’, were extremely low (0.1, 0.2 g cm⁻³ respectively) and are consistent with the observation that the materials intumesced during oxidation to leave expanded materials. The low porosity of the final glassy black solid (~B₂O₃) was expected, but the porosity of the intumesced materials were lower than expected and indicated macroporous aerogel-like structures, in which gaseous decomposition products were trapped within the intumesced materials.²⁵

2.3 XRD structural studies on 1, 2c and 2d

The structure of 1 as a triborate salt of a dication was confirmed by single-crystal XRD studies. A drawing of 1 showing the ions present and the atomic numbering scheme is shown in Fig. 5. The structure contains two identical [B₃O₆(OH)₄]⁻ anions, as illustrated in Fig. 1(i), partnered by one [H₂N(CH₂CH₂)₂NH₂]⁺ cation which adopts the familiar chair conformation.²⁶ The [B₃O₆(OH)₄]⁻ anion appears in significant concentrations in aqueous solution at pH 5–12 but rarely is crystalized from such solutions by non-metal cations which generally favour partner pentaborate anions. As noted above, the solutions had excess base present, and the pH was higher than normal.⁵,¹⁵ Structurally characterized triborate[1-] salts are uncommon and are limited to two alkali metal salts Na[B₃O₆(OH)₄] [ref. 27] and K[B₃O₆(OH)₄]·H₂O,²⁸ and a NMC salt [HOCH₂C(Me)₂NH₂][B₃O₆(OH)₄]₁⁻ Interatomic distances and angles for the triborate anion of 1 are given in the caption to Fig. 5. The B₂O₃ ring in 1 deviates slightly from planarity and adopts an envelope conformation with 4-coordinate B1 0.034 Å from the plane containing B2B3O1O3. O2 is 0.008 Å below the same plane but this distance is not significant. Similar ring conformations are found for Na[B₃O₆(OH)₄] [ref. 27] and K[B₃O₆(OH)₄]·H₂O.²⁸ The anion in [HOCH₂C(Me)₂NH₂][B₃O₆(OH)₄] [ref. 11] adopts a half-chair conformation with the 4-coordinate B 0.206 Å out of the plane containing the 3 ring O atoms. The bond lengths and bond angles for 1 are not significantly different from those found for [HOCH₂C(Me)₂NH₂][B₃O₆(OH)₄] [ref. 11] with O–Btetra significantly longer than O–Btrig and vary systematically about the ring, as has been observed or related organotriboroxine adducts³⁹ and organotriboroxinates,³⁰ with B2–O1 and B3–O3 being significantly shorter.
Compound 1 has a giant H-bonded network involving both anion-anion and cation-anion interactions and where all four NH and all four OH groups participate as donors. For convenience, the O atom acceptor sites in 1 may be labelled, by analogy with pentaborate chemistry and distance from the 4 co-ordinate B1, α, β- or γ-sites. The OH sites on B1 can be labelled δ. The triborate anions form infinite zig-zag chains through alternating γ and x R₂2(8) rings (Etter31). The D−A distances/angle at H for the x and γ interactions are 2.7453(16) Å/165.0° and 2.7179(16) Å/163.3°, respectively. These chains are then stacked into layers by H-bond interactions from the two OH groups on B1 to β-sites as C(6) interactions with D−A distances/angle at H of 2.8312(17) Å/162.8° and 2.8258(16) Å/169.5°. The layers are separated by layers of [H₂N(CH₂CH₂)₂NH₂]⁺ cations which are H-bonded to δ acceptor sites of the triborate anion via unusual R₂2(10) rings. The D−A distances/angle at H for the cation−anion interactions are 2.7182(18) Å/165.0° and 2.6786(18) Å/163.3°.

The structures of 2c and 2d were confirmed by single crystal XRD studies. Drawings of 2c and 2d are shown in Fig. 6 and 7, respectively. Both compounds contain isolated [B₃O₄(OH)₃]⁻ anions, as illustrated in Fig. 1(iii). B−O bond lengths and bond angles at B and O are not significantly different from those observed in other pentaborate structures containing non-metal cations, and related systems.1−4,14,19,32

The anions in both compounds form remarkably similar (despite the stoichiometry) extended H-bonded lattices, and the H-bond interactions for both 2c and 2d can be described as α,β,β,β. The α,β,β,β configuration is commonly found in ‘brickwall’ or ‘herringbone’ structures1−14 but the extended lattice found in 2c and 2d is not one of these types. Each pentaborate anion forms 3 reciprocal-pair R₂2(8) α-interactions with neighboring pentaborates, and 1 reciprocal-pair R₂2(12) β-interaction (Etter31). The R₂2(12) has not been previously observed in pentaborate systems and is responsible for the unusual extended lattices in 2c and 2d. The D−A distances/angle at H for these β interactions in 2c and 2d are 2.8508(10) Å/165.0° and 2.8182(19) Å/178.2°, respectively. Compound 2c has an additional H-bond contact between the cation and the α-position of a pentaborate (N12−H12···O4) with a N···O distance of 2.7548(11) Å and NHO angle of 169.2°.

### 3. Experimental

#### 3.1 General

Reagents were purchased from Aldrich Chemical company and used without purification. Multi-element NMR spectra were recorded at room temperature (298 K) on a Bruker Avance 500 (11.7 T) spectrometer operating at 500 MHz for ¹H, 125 MHz for ¹³C−¹H, and 160 MHz for ¹¹B−¹H) and referenced to SiMe₄ or BF₃·OEt₃ using D₂O as solvent. Chemical shifts (δ) are reported in ppm. Elemental analyses were performed at OEA Laboratories Ltd (Callington, UK). Powder XRD data were obtained on a Philips 1050/37 X-ray diffractometer, equipped with an iron filter, using Cu-Kα radiation (λ = 0.154056 nm) with a continuous scan between the range 2θ = 5–75°. Philips X’Pert System software was used to collect and manipulate the data. TGA and DSC analyses were obtained using a Netzsch TG 209 instrument. BET multipoint analyses were performed on a Micromeritics Gemini III 2375 instrument.

#### 3.2 Synthesis of [H₂N(CH₂CH₂)₂NH₂][B₅O₆(OH)₄]₂ (1)

B(OH)₃ (4.31 g, 69.67 mmol) was dissolved in 50 : 50 H₂O/MeOH (100 ml) with gentle warming. To this solution was added piperazine (2.00 g, 23.25 mmol) with stirring, and the solution was gently warmed (50 °C) for 1 h. The majority of the solvent (H₂O/MeOH) was removed under reduced pressure (rotary evaporator), and the remaining solid, obtained by filtration, was placed in an oven to dry for 4 h at 100 °C. The product 1 was obtained as a white crystalline solid was obtained 4.5 g (97%). Crystals were analytically pure and were suitable for X-ray diffraction studies. Elem. anal. (C₄H₁₂N₂B₅O₁₄). Calc: C 12.5, H 5.2, N 7.3%; Found: C 12.7, H 5.3, N 7.1%. Mpt > 260 °C (dec). NMR: δH/ppm 2.96 (8H, s), 4.27 (12H). δC/ppm 42.4 (CH₂), 138.9 ppm (1.1 (5%), 13.2 (20%) 18.8 (75%)). δB/ppm 1.15(5%).
XRD: d-spacing/Å (% rel. int.): 3.49 (100), 5.45 (81), 2.63 (78), 4.22 (71), 5.51 (53), 3.70 (37).

3.3 Synthesis of [NMC][B₂O₅(OH)₄] (2a–2d)

A similar procedure to that detailed in section 3.2 was used for 2a–c but with a B(OH)₃ ratio of 5 : 1.

2a. From B(OH)₃ (7.02 g, 113.6 mmol) and piperazine (2.00 g, 23.25 mmol). 5.84 g (86%). Elem anal. (C₆H₁₁B₂N₂O₁₀). Calc. C 15.7, H 4.9, N 9.2%; Found: C 14.3, H 5.4, N 8.9%. Mpt > 260 °C (dec). NMR: δH/ppm 2.95 (8H, s), 4.7 (7H). δC/ppm 42.7. δH/ppm 0.8 (15%), 12.0 (25%), 17.3 (60%). XRD: d-spacing/Å (% rel. int.): 3.50 (100), 3.72 (99), 5.55 (44), 7.00 (29), 3.30 (27), 4.25 (24).

2b. From B(OH)₃ (6.18 g, 100.0 mmol) and N-methylpiperazine (2.00 g, 20.00 mmol). 5.78 g (91%). Elem anal. (C₆H₁₃B₄N₂O₁₀). Calc. C 18.8, H 5.7, N 8.8%; Found: C 18.6, H 5.4, N 8.5%. Mpt > 260 °C (dec). NMR: δH/ppm 2.29 (3H, s), 2.68 (4H, s), 3.08 (4H) 4.7 (6H), δC/ppm 42.9 (2CH₂), 44.3 (CH₃), 51.2 (CH₂). δH/ppm 1.0 (5%), 12.5 (20%), 17.5 (75%). v max/cm⁻¹ 3380(s), 3054(s), 1431(s), 1362(s), 1252(m), 1162(m), 1101(m), 925(s), 782(m), 697(m), 591(m), 465(m). XRD: d-spacing/Å (% rel. int.): 3.71 (100), 4.84 (66), 3.45 (65), 7.33 (30), 2.76 (29), 3.50 (28).

2c. From B(OH)₃ (5.41 g, 87.7 mmol) and N,N,N′-trimethylpiperazine (2.00 g, 17.5 mmol). 5.35 g (92%). Elem anal. (C₆H₁₇B₅N₂O₁₀). Calc. C 21.5, H 6.3, N 8.4%; Found: C 20.9, H 5.7, N 7.9%. Mpt > 260 °C (dec). NMR: δH/ppm 2.45 (6H, s), 2.85 (8H, s), 4.70 (5H, s). δC/ppm 43.5 (4CH₂), 52.3 (2CH₃). δH/ppm 1.2 (15%, s), 13.3 (25%, s), 18.5 (60%, s). v max/cm⁻¹ 3313(s), 3035(s), 2810(m), 1433(s), 1308(s), 1192(m), 1142(m), 1025(s), 926(s), 774(m), 709(m), 471(m). XRD: d-spacing/Å (% rel. int.): 5.73 (100), 3.60 (96), 4.17 (88), 2.94 (84), 4.14 (84), 6.21 (49), 3.83 (28).

2d. N,N,N′,N′-tetramethylpiperazinium(2+) diiodide (4.0 g, 10.00 mmol) was dissolved in H₂O (50 ml) and Dowex 550A monosphere (OH⁻ form) was added and stirred for 24 h. The ion exchange resin was removed by filtration and MeOH (50 ml) was added to the filtrate. B(OH)₃ (3.09 g, 50.0 mmol) was added and the solution was heated for 1 h. The solvent was removed on a rotary evaporator to yield a white solid (3.08, 50%). Elem anal. (C₆H₂₅B₂O₁₀N₂O₂). Calc. C 16.6, H 4.9, N 4.8%; Found: C 17.1, H 5.8, N 2.4%. Mpt > 260 °C (dec). NMR: δH/ppm 3.60 (12H, s), 3.88 (8H, s), 4.70 (4H, s). δC/ppm 30.2 (4CH₃), 55.5 (8CH₂), δH/ppm 1.2 (15%), 13.5 (25%), 18.9 (60%). v max/cm⁻¹ 3386(s), 1409(s), 1321(s), 1201(m), 1142(m), 1040(s), 868(s), 775(m), 475(m). XRD: d-spacing/Å (% rel. int.): 5.07 (100), 5.67 (88), 3.66 (83), 4.08 (23), 3.41 (22), 6.09 (19).

3.4 Thermolysis experiments of 1

Samples of 1 were individually placed within open topped ceramic bowls and positioned within a furnace (air atmosphere). The furnace temperature was set to increase from room temperature to either 250 °C (1a), 500 °C (1b) or 600 °C (1c) at 10 °C per minute. After the samples had reached the required temperature, isolated and powdered in a mortar and pestle.

Sample 1a was pale yellow. Samples 1b and 1c were black and had increased their volume ~10 fold. 1a: 0.70 g obtained from 1.02 g 74% residue; Elem anal. (C₆H₁₃B₂N₂O₁₀). Calc. C 15.4, H 3.9, N 8.9%; Found: C 15.1, H 4.0, N 8.6%. IR: v max/cm⁻¹: 3488(s), 3255(s), 1637(m), 1506(m), 1383(s), 1140(m), 1063(s), 864(s), 809(m), 701(m). Density: 0.690 g cm⁻³. BET: surface area 0.21 m² g⁻¹. 1b: (0.70 g from 1.03 g, 68% residue). Elem anal. Found: C 5.3, H 2.6, N 1.9%. IR: v max/cm⁻¹: 3692(s), 3209(s), 1727(w), 1627(w), 1437(s), 1195(m), 883(w), 721(m), 644 (m), 547(w). Density: 0.096 g cm⁻³. BET: surface area 1.90 m² g⁻¹. 1c: (0.61 g from 1.02 g, 59% residue). Elem anal. Found: C 2.4, H 4.7, N 0.8%. IR: v max/cm⁻¹: 3600(m), 3220(s), 1449(s), 1196(s), 883(w), 795(m), 720(m), 644(m), 547(m). Density: 0.214 g cm⁻³. BET: surface area 1.85 m² g⁻¹. In a similar experiment 1 (0.499 g) was placed within open topped Ni crucible and positioned within the furnace (air atmos-
sphere). The furnace temperature was set to increase from room temperature to 1000 °C at 10 °C per minute, and then held at 1000 °C for 3 h, and then allowed to cool to room temperature, yielding a glassy black solid (1d), which was powdered in a mortar and pestle and weighed (0.2759 g, 44.2% weight loss). 1d: Elem anal. Found: C 0.1, H 0.4, N 0.1%. IR: v\text{max}/\text{cm}^{-1}: 3200(s), 1445(s), 1194(s), 795(m), 720(m), 550(m). BET: surface area 0.16 m\textsuperscript{2} g\textsuperscript{-1}.

3.5 X-ray crystallography

The crystallographic data collection of compounds 1, 2c and 2d were performed using a Nonius Kappa CCD diffractometer with Mo-K\textalpha radiation (\lambda = 0.71073 Å) controlled by the Collect\textsuperscript{35} software package and an Oxford Cryosystem N\textsubscript{2} open flow cryostat at 120(2) K. The data were processed using Denzo\textsuperscript{34} and absorption corrections were applied using SORTAV.\textsuperscript{35} Crystallographic data are in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures on \textit{F}\textsuperscript{2} using SHELXS-97 and SHELXL-97 respectively.\textsuperscript{36} All non-hydrogen atoms were fixed using a standard riding model.

Crystallographic data for 1, 2c, 2d have been deposited with the Cambridge Crystallographic Data Centre with CCDC 930889–930891. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44 1223 336033) or email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

3.6 Conclusion

Salts containing cations derived from N-substituted piperazines, partnered with either triborate(1−) or pentaborate(1−) anions have been prepared. The triborate salt 1 possesses an alternating cationic/anionic layered solid-state structure and contains extensively H-bonded triborate sheets. Compound 1 is thermally decomposed in air via a multistage process to glassy B\textsubscript{2}O\textsubscript{3}. Materials thermally derived from 1 were amorphous and non-porous. Similar thermal behaviour was observed for the pentaborate salts (2a–2d) which possess three dimensional H-bonded lattices.

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