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Synthesis and XRD study of an C_2-linked bis(quaternary ammonium) pentaborate: $[Me_3NCH_2CH_2NMe_3][B_5O_6(OH)_4]_2$

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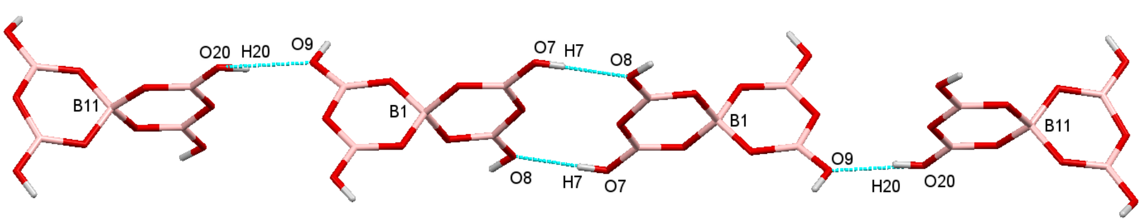
ABSTRACT The synthesis and characterization of a C2 (ethane) linked bis(trimethylammonium) pentaborate salt, [Me3NCH2CH2NMe3][B5O6(OH)4]2 (1), is reported . Compound 1 has been characterized by 1H, 11B, and 13C NMR Spectroscopy, IR spectroscopy, thermal (TGA/DSC) analysis, and single-crystal X-ray diffraction. There are two independent crystallographic pentaborate(1-) anions in the solid-state structure and these link by H-bonds at □-sites into a centrosymmetric tetrameric chain. These chains are crossed-linked by R22(8) H-bond motifs to □-sites of neighbouring pentaborate tetrameric units. The [Me3NCH2CH2NMe3]2+ cations are located between these tetrameric pentaborate(1-) units.

GRAPHICAL ABSTRACT



KEYWORDS Oxidoborate; Pentaborate(1-); Polyborate, 1,2-bis(trimethylammonium)ethane; X-ray structure

INTRODUCTION

We are interested in potential micronutrient and/or biostimulant properties of borates and silicate salts and are developing aspects of the chemistry of these salts with non-metal cations.[1] This work is in parallel with synthetic studies involving sterically hindering larger cations.[2] This work is now being expanded to include short chain cationic surfactants such as C_n-linked bis(imidazolium) and highly alkylated C_n-linked bis(quaternary ammonium) salts. There has been a previous report[3] on pentaborate(1-) salts partnered with protonated α,ω-diaminoalkanes and we anticipated that increasing the steric bulk of the cation may generate novel polyborate anions *via* self-assembly processes[4, 5] which occur in aqueous solution from the Dynamic Combinatorial Library[6, 7] of polyborate species present.[8, 9]

RESULTS AND DISCUSSION

Several pentaborate salts have been prepared from aqueous solution by self-templated reactions of $B(OH)_3$ with the appropriate cation hydroxide salt, obtained from the iodide salt by ion exchange. This is illustrated by the preparation of $[Me_3NCH_2CH_2NMe_3][B_5O_6(OH)_4]_2$ (**1**). Full details of other salts will be published elsewhere.

Compound **1** was obtained in excellent yield as a white crystalline solid, and was has characterized by ^1H, ^{11}B and ^{13}C NMR spectroscopy, IR spectroscopy, TGA analysis and by a single-crystal XRD study. Satisfactory elemental analysis data was obtained for **1**. ^1H and ^{13}C NMR were obtained for **1** in D_2O and data were fully consistent with the cation present. The ^{11}B NMR spectrum of **1** showed two signals in a pattern expected for a pentaborate(1-) anion undergoing rapid exchange with other polyborate species.[8] IR spectroscopy showed many strong bands in the B-O stretching region[10] and importantly one diagnostic[11] and strong band at 925 cm^{-1} attributed to a B_{trig}-O symmetric stretch. TGA data shows that **1** decomposes in air, *via* a two step process, involving (i) dehydration and condensation of pentaborate(1-)units, and (ii) oxidation of the organic cation, to leave $2.5B_2O_3$ as a glassy residue. This behaviour is consistent with other non-metal cation polyborates.[3, 12]

The formula unit of **1** is $C_8H_{30}B_{10}N_2O_{20}$ and it is an ionic compound comprised of the expected $[Me_3CH_2CH_2NMe_3]^{2+}$ cations and $[B_5O_6(OH)_4]^-$ anions. Crystallographically, the asymmetric unit contains two independent pentaborate(1-) anions (one contains B1 and the other contains B11) within the structure and two half independent centrosymmetric hexamethyldiaminoethane cations; one of these cations disordered over 3 sites, with occupancy 0.65, 0.175 and

0.175. The asymmetric unit of **1** is shown in Figure 1.

The pentaborate(1-) anions in **1** are comprised of two B_3O_3 (boroxole) rings fused together with a spiro B centre (B1 and B11) in common. The other four B centres on each pentaborate(1-) anion have a hydroxyl group attached to it. Pentaborate(1-) salts are well-known[3, 12-15] and B-O bond lengths and BOB and OBO bond angles in **1** are within normal ranges for two-coordinate O atoms and three- and four-coordinate B atoms in polyborate species. Likewise, structural parameters associated with the organic cations are unexceptional.

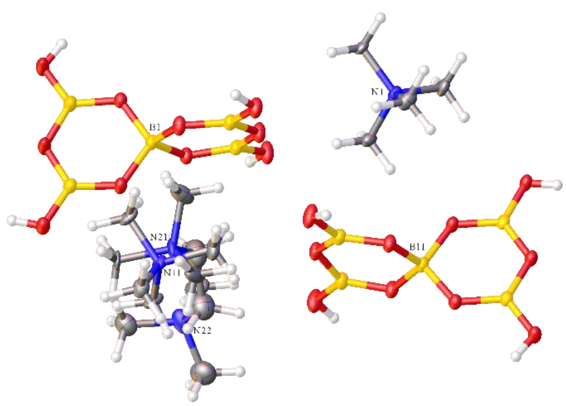


Figure 1. Asymmetric unit of $[Me_3NCH_2CH_2NMe_3]$ $[B_5O_6(OH)_4]_2$ (**1**) showing basic atomic numbering scheme.

Each pentaborate(1-) anion has four H-bond donor sites and ten potential H-bond acceptor sites, and in the solid-state pentaborate(1-) anions generally link together *via* H-bonds to form supramolecular lattices.[12] This is also the case for **1**. Since the $[Me_3CH_2CH_2NMe_3]^{2+}$ cations are unable to form any H-bond interactions the pentaborate(1-) anions have more acceptor sites than donor sites and some are not be used. Schubert introduced a nomenclature[3] to differentiate acceptor sites in pentaborate(1-) chemistry and using this nomenclature both of the crystallographically independent pentaborate(1-) anions in **1** form H-bonds to one β–site and three α–sites of four neighbouring pentaborate(1-) anions. These αααβ motifs are very common[12] in pentaborate(1-) chemistry but the structure adopted by **1**, with two independent pentaborate(1-) anions, is unique and is not typical of those often observed[12, 15] for αααβ systems (*e.g.* 'brickwall' or herringbone' structures) which contain only one crystallographic pentaborate(1-) anion.

The two crystallographically independent pentaborate(1-) anions are linked together by a simple β–link (O20H20···O9*) commonly encountered as a C(8) chain (Etter[16] nomenclature) in αααβ systems. These pairs are then linked *via* a centrosymmetric reciprocal $R_2^2(12)$ motif at β-centres (O7H7···O8*) generating a tetrameric pentaborate(1-) chain (Figure 2). Again, this ring motif is known in a number of αααβ systems[12, 17-20] but the combination is unique to this structure. Each pentaborate then cross links with three pentaborate(1-) centres *via* $R_2^2(8)$ interactions at α-centres to form a supramolecular structure, and the cations are able to sit within the 'voids' created at the end of the tetrameric blocks. All three $R_2^2(8)$ interactions originating from a particular crystallographic independent pentaborate(1-) anion within the tetramer are to three other crystallographically independent pentaborate(1-) anions. Full details of these H-bond interactions are available in the supplementary information.

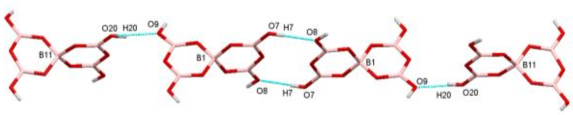


Figure 2 Tetrameric pentaborate(1-) chain comprised of both crystallographically independent pentaborate(1-) anions arranged centrosymmetrically. Each pentaborate(1-) partakes in three other $R_2^2(8)$ interactions (not shown) to complete a supramolecular structure.

EXPERIMENTAL

General. All chemical were obtained commercially and used as supplied. FTIR spectra were obtained (KBr pellets) on a Perkin-Elmer 100 FTIR spectrometer. TGA/DSC analysis (in air) were performed on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles, between 10-800 °C with a ramp temperature rate of 10 °C min^{-1}. NMR spectra were obtained on a Bruker Avance 400 spectrometer and reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of TMS (^{1}H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). CHN analysis was obtained from OEA laboratories Ltd in Callington, Cornwall.

Synthesis of 1. $Me_2NCH_2CH_2NMe_2$ (3.32g, 3.0 ml, 20 mmol) was added to acetonitrile (50 ml). MeI (11.4 g, 5 ml, 80 mmol) was added and the resulting solution was heated to reflux for 4 hours. The white solid $[Me_3NCH_2CH_2NMe_3]I_2$ which formed was isolated by filtration and washed with Et_2O (7.0g, 87 %). NMR (D_2O): ^{1}H (400 MHz)/ppm: 3.34 (t), 18H; 4.07(t) 4H; ^{13}C (100 MHz)/ppm: 54.02 (CH_3), 59.93 (CH_2). IR (KBr/cm^{-1}): 3434 (br), 3012 (s), 3003 (s), 2971 (s), 1487 (s), 1471 (s), 1447 (m), 1403 (s), 1221 (m), 954 (vs), 921 (s), 815 (s). This was used in the next step without further purification. Excess Dowex 550A monosphere ion exchange resin (OH^- form, 15 g) was added to a solution of $[Me_3NCH_2CH_2NMe_3]I_2$ (0.65 g, 1.62 mmol) in H_2O (20 ml). The solution was stirred for

24h, the resin removed by filtration. $B(OH)_3$ (1.0 g, 16.2 mmol) was added to the filtrate which was allowed to stand for 4h and then reduced to dryness to yield a the crude product (1) (0.75 g, 80 %). $C_8H_{30}B_{10}N_2O_{20}$ Anal. Calc.: C = 16.5%, H = 5.2 %, N = 4.8 %. Found: C = 16.8 %, H = 5.2 %, N = 4.8 %. M.p. >250°C. NMR (D_2O): ^1H (400 MHz) /ppm: 3.20(t), 18H, (CH_3); 3.92(t), 4H, (CH_2); ^{11}B (128 MHz)/ppm: 17.1 (84 %), 13.2 (16 %); ^{13}C (100 MHz)/ppm: 53.77 (CH_3), 57.82 (CH_2). IR (KBr/cm^{-1}): 3437(br), 3052(m), 1651(m), 1434(m), 1361(m), 1252(s), 1103(s), 102 (s), 925(vs), 782(vs), 696(s), 591(m), 509(m), 455(s). TGA: 100-250 °C, condensation of pentaborate with loss of four H_2O 12.0 % (12.4 % calc.); 150-700 °C, oxidation of organic residue leaving residual B_2O_3 61.8% (59.8 % calc.).

X-ray crystallography. Single colourless plate-shaped crystals of **1** were recrystallised from water. Single-crystal X-ray crystallography was carried out at the EPSRC National Crystallography service at the University of Southampton. A suitable crystal (0.160 × 0.100 × 0.030) mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using Olex2[21] the structure was solved with the ShelXT[22] structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of ShelXL[23] using Least Squares minimisation.

Crystal data. $C_8H_{30}B_{10}N_2O_{20}$, Mr = 582.44, triclinic, P-1 (No. 2), a = 8.5098(2) Å, b = 9.3293(2) Å, c = 16.7816(5) Å, α = 88.937(2)°, β = 78.940(2)°, γ = 80.430(2)°, V = 1289.24(6) $Å^3$, T = 100(2) K, Z = 2, Z' = 1, $\mu(MoK_\alpha)$ = 0.134 mm^{-1}, 26740 reflections measured, 5854 unique (R_{int} = 0.0493) which were used in all calculations. The final wR_2 was 0.1145 (all data) and R_1 was 0.0438 (I > 2σ(I)).

CONCLUSIONS

Pentaborate(1-) salts, exemplified by $[Me_3NCH_2CH_2NMe_3][B_5O_6(OH)_4]_2$ (**1**), have been synthesised in aqueous solution from self-assembly reaction. A single-crystal X-ray diffraction study reveals interesting H-bonding motifs in the solid-state structure of **1**. There are two independent crystallographic pentaborate(1-) anions in the solid-state structure and these link by H-bonds at β-sites into a centrosymmetric tetrameric chain. These chains are crossed-linked by $R_2^2(8)$ H-bond motifs to α-sites of neighbouring pentaborate tetrameric units. The $[Me_3NCH_2CH_2NMe_3]^{2+}$ cations are situated between these tetrameric pentaborate(1-) units.

Acknowledgements.

We thank the EPSRC for the NCS X-ray crystallographic service (Southampton).

Supplemental Materials

Crystallographic data for the structural analysis of compound **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC number 1881704. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: + 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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A BIS(QUATERNARY AMMONIUM) PENTABORATE(1-) SALT