Synthesis and characterization of templated pentaborate(1-) salts: X-ray structure of [(2-HOCH₂CH₂)C₄H₇NMeH][B₅O₆(OH)₄]-0.3H₂O

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Synthesis and characterization of templated pentaborate(1-) salts: X-ray structure of $[(2\text{-HOCH}_2\text{CH}_2)\text{C}_4\text{H}_7\text{NMeH}][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 0.3\text{H}_2\text{O}$

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GRAPHICAL ABSTRACT

Abstract The synthesis of pyrrolidinium pentaborate(1-) and four substituted pyrrolidinium pentaborate(1-) salts from $\text{B}(\text{OH})_3$ in aqueous solution are reported. Characterization (IR, NMR, single-crystal XRD) of $[(2\text{-HOCH}_2\text{CH}_2)\text{C}_4\text{H}_7\text{NH}_2][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 0.3\text{H}_2\text{O}$ is described in detail. The cation is the largest of the five pyrrolidinium cations studied. A consequence of this is that its solid-state structure has anion-anion interactions ($\alpha\alpha\alpha\gamma$) which are different from the other four ($\alpha\alpha\alpha\beta$) structures. There are also stabilizing cation-anion H-bond interactions.

Keywords Pentaborate(1-); H-bonds; Pyrrolidinium; X-ray structure; Oxidoborate

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INTRODUCTION

Pentaborate(1-) salts, [NMC][B₅O₆(OH)₄], are often prepared from the reaction of organic bases with B(OH)₃ in aqueous solution, where the protonated organic base is a non-metal cation (NMC).¹ Occasionally, salts containing rarer anions e.g. three to fifteen B atoms, have also been obtained.²⁻⁹ In basic aqueous solutions, B(OH)₃ forms a dynamic combinatorial library (DCL) of polyborate anions whose concentrations are pH and boron concentration dependent.¹⁰⁻¹¹ Recently, we noted from DFT calculations (gas-phase)¹² on the relative stabilities of the polyborate anions that the pentaborate(1-) anion is not the most stable and yet despite this, [NMC][B₅O₆(OH)₄] salts are readily formed. Strong anion-anion H-bond interactions are present in [NMC][B₅O₆(OH)₄] salts and these we believe are responsible for their facile formation. Herein, we report the synthesis of several pentaborate(1-) salts partnered with substituted pyrrolidinium cations, explore steric effects of the cation, and describe in detail the synthesis of the salt [(2-HOCH₂CH₂)C₄H₇NMeH][B₅O₆(OH)₄] (**1**).

RESULTS AND DISCUSSION

Synthesis and characterization

The pyrrolidinium pentaborate salts [(2-HOCH₂CH₂)C₄H₇NMeH][B₅O₆(OH)₄]0.3H₂O (**1**), [(2-HOCH₂)C₄H₇NH₂][B₅O₆(OH)₄]0.5H₂O (**2**), [C₄H₈NMeH][B₅O₆(OH)₄]0.5CH₃COCH₃ (**3**), [C₄H₈NMe₂][B₅O₆(OH)₄] (**4**), and [C₄H₈NH₂][B₅O₆(OH)₄] (**5**), were all prepared in high yields from the reaction of the free base (**1-3**, **5**), or quaternary amine hydroxide salt (**4**), with B(OH)₃ in a 1:5 molar ratio. Characterization data including single-crystal XRD structural analyses for salts **2-5** have been recently been reported elsewhere.¹³

Characterization data¹⁴ (IR, NMR) obtained for **1** were in agreement with those previously reported for related pyrrolidinium and other non-metal cation pentaborate salts. ¹H and ¹³C NMR spectra (obtained in D₂O) were fully consistent with those expected for the cation, with the NH, OH and BOH protons overlapping and represented by a broad singlet at ~4.7 ppm due to rapid exchange. Three characteristic signals at ~17, 13 and 1 ppm were observed in ¹¹B NMR spectra, obtained in concentrated aqueous solutions (D₂O), which are assigned to B(OH)₃/[B(OH)₄]⁻, [B₃O₃(OH)₄]⁻ and the 4-coordinate centre of [B₅O₆(OH)₄]⁻, respectively.¹⁵ These species are

observed due to the complex borate equilibria observed in aqueous solution.^{11,16} The IR spectrum of **1** clearly shows the diagnostic band¹⁶ of pentaborate salts at $\sim 925\text{ cm}^{-1}$.

X-ray structure of $[(2\text{-HOCH}_2\text{CH}_2)_4\text{C}_4\text{H}_7\text{NMeH}][\text{B}_5\text{O}_6(\text{OH})_4]$

The crystallographic data for compound **1** is given in a footnote¹⁷ with full details given in the supplementary data.¹⁸ The ionic salt is comprised of the expected (2-hydroxyethyl)-*N*-methylpyrrolidinium(1+) cation, partnered with a pentaborate(1-) anion, as shown in Figure 1. The cation was found to be disordered over multiple sites with three significant positions of occupancy identified (4:3:3 ratio) and one of which also included a solvated water molecule. All the disordered versions of the pyrrolidinium ring have an envelope conformation with both substituents equatorial. The bond lengths and internuclear angles observed within the boroxyl (B_3O_3) rings of the pentaborate anions of **1** are within the ranges observed for previously reported $[\text{NMC}][\text{B}_5\text{O}_6(\text{OH})_4]$ structures.^{1,6,15,16} The bond lengths and internuclear angles also lie within the ranges found in related boroxole (B_3O_3) structures containing both 3- and 4-coordinate B centres bound to O.¹⁹

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Figure 1 The structure of $[(2\text{-HOCH}_2\text{CH}_2)\text{-C}_4\text{H}_7\text{NMeH}][\text{B}_5\text{O}_6(\text{OH})_4]$ (**1**), showing the atomic numbering scheme.

Structure **1** possesses a giant H-bonded anionic lattice, with the substituted pyrrolidinium cations (and the H_2O) sitting within the cavities of the lattice. The anions arrange themselves in a series of ‘planes’ (Figure 2) H-bonded together *via* $\text{R}_2^2(8)$ reciprocal pair interactions²¹ to $\alpha\alpha\gamma$ acceptor sites, and the ‘planes’ are linked through further reciprocal- α $\text{R}_2^2(8)$ interactions.

Figure 2 Anionic lattice of **1** viewed along the a axis; the $[(2\text{-HOCH}_2\text{CH}_2)\text{C}_4\text{H}_7\text{NMeH}]^+$ cations sit H-bonded within the cavities of the lattice. The $\text{R}_2^2(8)$ reciprocal- α H-bond interactions are shown in blue.

The anions of the H-bonded lattice are in a different arrangement to that observed for **3-5** that have a familiar $\alpha\alpha\alpha\beta$ ‘brickwall’ structure.^{1,15} It is interesting to compare the structures of compounds **1** with **4** and **5**. The brickwall structure is sufficiently flexible to accommodate cations of variable sizes (within limits). *e.g.* the N,N -dimethylated pyrrolidinium cation in **4** has the same structure as the unsubstituted cation in **5**, despite a formula unit increase in volume of 13.3%.¹³ The formula unit volume of **1** has increased by a further 10.3% compared to **4**, as a consequence of the larger substituted cation. This, we believe, is responsible for switching the structure from the brickwall to the $\alpha\alpha\alpha\gamma$ arrangement. In this structure three strong reciprocal-

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α bonds (-21 kJ mol^{-1}) are maintained and the H-bond energy for a reciprocal- γ interaction is the same as that of a C(8) β -chain (-16 kJ mol^{-1}).¹³ The cation in **1** is also ‘non-innocent’ and cation-anion H-bond interactions *e.g.* N11H11...O4’, N11H11...O9’, and O11H11B...O8’, further stabilize the self-assembled crystal structure. Full details are available in the supplementary information.

SUMMARY

The synthesis and crystal structures of pyrrolidinium pentaborate(1-) and 4 substituted pyrrolidinium pentaborates are reported. The larger cation present in **1** is unable to fit into the brickwall structure and as a result **1** adopts a similar but different anionic lattice of comparable energy. The solid-state structure of **1** is further stabilized by cation-anion H-bond interactions.

REFERENCES

1. (a) Freyhardt, C.C.; Felsche, J.; Engelhardt, G.; *Z. Naturforsch. B: Chem. Sci.*, **1993**, 48, 978-985. (b) Freyhardt, C.C.; Wiebcke, M.; Felsche, J.; Engelhardt, G.; *J. Inclusion Phenom. Mol. Recognit. Chem.*, **1994**, 18, 161-175.
2. (a) Schubert, D.M.; Visi, M.Z.; Knobler, C.B. *Inorg. Chem.* **2008**, 47, 2017-2023; (b) Beckett, M.A.; Horton, P.N.; Hursthouse, M.B.; Timmis, J.L. *RSC Adv.* **2013**, 3, 15185-15191.
3. (a) Wang, G.-M.; Sun Y.-Q.; Yang, G.-Y. *J. Solid State Chem.* 2004, 177, 4648-4654; (b) Weakley, T.J.R.; *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, **1985**, C41, 377-379; (c) Beckett, M.A.; Horton, P.N.; Coles, S.J.; Martin, D.W.; *Inorg. Chem.*, **2011**, 50, 12215-12218.
4. Liu, M.-C.; Zhou, P.; Yao, H.-G.; Ji, S.-H.; Zhang, R.-C.; Ji, M.; An, Y.-L.; *Eur. J. Inorg. Chem.*, **2009**, 4622-4624.
5. (a) Schubert, D.M.; Visi, M.Z.; Khan, S.; Knobler, C.B.; *Inorg. Chem.*, **2008**, 47, 4740-4745; (b) Beckett, M.A.; Horton, P.N.; Hursthouse, M.B.; Timmis, J.L.; Varma, K.S.; *Dalton Trans.*, **2012**, 41, 4396-4403.
6. Visi, M.Z.; Knobler, C.B.; Owen, J.J.; Khan, M.I.; Schubert, D.M.; *Cryst. Growth Des.*, **2006**, 6, 538-545.
7. (a) Schubert, D.M.; Smith, R.A.; Visi, M.Z.; *Glass Technol.*, **2003**, 44, 63-70; (b) Schubert, D.M.; Visi, M. Z.; Knobler, C.B.; *Inorg. Chem.*, **2000**, 39, 2250-2251.
8. Liu, Z.H.; Li, L.Q.; Zhang, W.J.; *Inorg. Chem.*, **2006**, 45, 1430-1432.
9. Merlino, S.; Sartori, F.; *Science*, **1971**, 171, 377-379.
10. Corbett, P.T.; Leclaire, J.; Vial, L.; West, K.R.; Wietor, J.-L.; Sanders, J.K.M.; Otto, S.; *Chem. Rev.*, **2006**, 106, 3652-3711.
11. (a) Farmer, J.B.; *Adv. Inorg. Chem.*, **1982**, 25, 187-237; (b) Salentine, C.G.; *Inorg. Chem.*, **1983**, 22, 3920-3924.

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12. Beckett, M.A.; Davies, R.A.; Thomas, C.D.; *Comput. Theor. Chem.*, **2014**, 1044, 74–79.
13. Beckett, M.A.; Coles, S.J.; Davies, R.A.; Horton, P.N.; Jones, C.L. *Dalton Trans.* **2015**, 44, 7032–7040.
14. Characterization data for **1**: C₇H_{20.60}B₅NO_{11.30}. Elem. Anal Calc: C, 23.8; H 5.9; N, 4.0. Found: C, 23.8; H 5.7; N, 3.9%. Mp >300 °C. IR (KBr/cm⁻¹): 3399(br,s), 2973(m), 2893(m), 1639(m), 1432(m), 1315(s), 1100(s), 1027(s), 923(vs), 776(s) 707(s). NMR (400 MHz, D₂O) δ¹H/ppm: 3.82–3.76 1H (m), 3.72–3.61 2H (m), 3.46–3.38 1H (m), 3.18–3.12 1H (q, 8 Hz) 2.90 3H (s), 2.41–2.32 1H (m), 2.19–2.01 3H (m), 1.86–1.76 2H (m). δ¹¹B/ppm: 16.8, 13.2, 1.2. δ¹³C/ppm: 66.8 (CH), 58.2 (CH₂), 55.9 (CH₂), 38.9 (CH₃), 32.0 (CH₂), 28.8 (CH₂), 21.1 (CH₂).
15. Beckett, M.A.; Horton, P.N.; Hursthouse, M.B.; Knox, D.A.; Timmis, J.L.; *Dalton Trans.*, **2010**, 39, 3944–3951.
16. (a) Beckett, M.A.; Horton, P.N.; Coles, S.J.; Kose, D.A.; Kreuziger, A.-M.; *Polyhedron*, **2012**, 38, 157–161; (b) Beckett, M.A.; Horton, P.N.; Hursthouse, M.B.; Timmis, J.L.; Varma, K.S.; *Collect. Czech. Chem. Commun.*, **2010**, 75, 971–980.
17. A Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (70μm focus) was used. X-ray data for **1**: C₇H_{20.60}B₅NO_{11.30}, M = 353.69; monoclinic space group P21/c, a = 10.0014(7) Å, b = 11.4193(8) Å, c = 14.8649(10) Å, α = 90°, β = 104.6400(10)°, γ = 90°; U = 1642.6(2) Å³; Z = 4; T = 100(2) K; Wavelength = 0.71075 Å; density (calc) = 1.430 Mg/m³; Absorption coefficient 0.125 mm⁻¹; Crystal: colourless prism, 0.110 x 0.100 x 0.080 mm³; F(000) 740; θ range for data collection 3.073 – 27.484°; Index ranges –12 ≤ h ≤ 12, –14 ≤ k ≤ 14, –19 ≤ l ≤ 18; 22146 reflections collected with 3746 independent reflections [R_{int} = 0.0321]; Completeness to θ = 25.242°: 99.7%; absorption correction: semi-empirical from equivalents; refinement method: full-matrix least squares on F²; data/restraints/parameters 3746/244/261; goodness-of-fit on F², 1.103; Final R indices [F² > 2σ(F²)] R1 = 0.0787, wR2 = 0.2322; R indices (all data) R1 = 0.0944, wR2 = 0.2484; extinction coefficient n/a; largest diff. peak and hole 0.743 and -0.509 e Å⁻³.
18. (a) Coles, S.J.; Gale, P.A. *Chem. Sci.* **2012**, 3, 683–689; (b) Rigaku, CrystalClear-SM Expert 3.1 **2013**, b27; (c) Sheldrick, G.M. *Acta Crystallogr.* **2015**, C71, 3; (d) Farrugia, L.J.; *J. Appl. Crystallogr.* **1997**, 30, 565; (e) Palatinus, L.; Chapuis, G.; *J. Appl. Crystallogr.* **2007**, 40, 786–790.
19. (a) Beckett, M.A.; Coles, S.J.; Light, M.E.; Fischer, L.; Stiefvater-Thomas, B.M.; Varma, K.S. *Polyhedron* **2006**, 25, 1011–1016; (b) Beckett, M.A.; Hibbs, D.E.; Hursthouse, M.B.; Owen, P.; Malik, K.M.A.; Varma, K.S. *Main Group Chem.* **1998**, 2, 251–258; (c) Beckett, M.A.; Strickland, G.C.; Varma, K.S.; Hibbs, D.E.; Hursthouse, M.B.; Malik, K.M.A. *J. Organomet. Chem.* **1997**, 535, 33–41.
20. Etter, M.C.; *Acc. Chem. Res.*, **1990**, 23, 120–126.

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