



Note

Tetraphenylboroxinate(1-) salts of monoborate cations: Synthesis and single-crystal X-ray structures of $[\text{Ph}_2\text{B}\{\text{OCH}_2\text{CH}_2\text{N}(\text{Me})(\text{CH}_2)_n\}_2][\text{Ph}_4\text{B}_3\text{O}_3]$ ($n = 4, 5$)

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ARTICLE INFO

Article history:

Received 8 July 2009

Received in revised form 14 September 2009

Accepted 18 September 2009

Available online 13 October 2009

Keywords:

Tetraphenylboroxinate anion

Monoborate cations

Zwitterionic borate cations

ABSTRACT

The salts, $[\text{Ph}_2\text{B}\{\text{OCH}_2\text{CH}_2\text{N}(\text{Me})(\text{CH}_2)_n\}_2][\text{Ph}_4\text{B}_3\text{O}_3]$ ($n = 4, 5$), were prepared in moderate yields in MeOH solution from reaction of $\text{Ph}_2\text{BOBPh}_2$ with $[\text{N}(\text{CH}_2)_n(\text{Me})(\text{CH}_2\text{CH}_2\text{OH})][\text{OH}]$ and $\text{PhB}(\text{OH})_2$ in a 1:2:4 ratio. The reactions also lead to $\text{Ph}_3\text{B}_3\text{O}_3$. Both salts were characterized by NMR (^1H , ^{13}C , ^{11}B) IR, and single-crystal XRD studies. The salts are comprised of cationic monoborates (zwitterionic, 2N^+ and 1B^-) and tetraphenylboroxinate anions.

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1. Introduction

In recent years there have been an increasing number of reports relating to structural aspects of non-metal cation (NMC) containing salts of hydroxyborate and organoborate anions [1–9]. The NMCs are often ‘non-innocent’, templating observed structures through their ability to H-bond, and provide interesting insights into their structure directing effects with regards lattice architectures *e.g.* pentaborate salts, $[\text{NMC}][\text{B}_5\text{O}_6(\text{OH})_4]$ [1]. Of additional interest is that occasionally NMCs generate salts of novel and previously unobserved borate anions. *e.g.* $[\text{H}_3\text{N}(\text{CH}_2)_7\text{NH}_3][\text{B}_7\text{O}_9(\text{OH})_5]\cdot\text{H}_2\text{O}$ [2], $[\text{C}_3\text{H}_5\text{N}_2]_3[\text{B}_9\text{O}_{12}(\text{OH})_6]$ [3], and $[\text{C}_4\text{H}_{15}\text{N}_3]_2[\text{B}_{14}\text{O}_{20}(\text{OH})_6]$ [4]. Salts of organoborate anions are relatively rare and until recently have been restricted to the following: $[\text{Rh}(\text{PMe}_3)_4][\text{Ar}_4\text{B}_5\text{O}_6]$ ($\text{Ar} = \text{C}_6\text{H}_4\text{-Ome-4}$, and $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) [5], $[1,8\text{-C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}][(\text{MeO})_4\text{B}_5\text{O}_6]$ [6] and $[\text{X}][\text{Ph}_4\text{B}_3\text{O}_3]$ ($\text{X} = \text{NMe}_4$ [7] and $\{\text{Bu}_3\text{PAu}\}_4\text{P}$ [8]). We are currently undergoing a research programme investigating the structure directing effects of NMCs (which have the potential to H-bond) and have recently reported the synthesis and structures of the organoborate derivatives, $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}][\text{Ph}_4\text{B}_3\text{O}_3]$ and $[\text{Et}_3\text{NH}][\text{Ph}_3\text{B}_3\text{O}_3(\text{OH})]$ [9]. The former, with a 2-hydroxyethyl substituent on N, exhibits ion-pair H-bonding in the solid-state, and the latter is a novel hybrid hydroxy/organoborate which is a H-bonded dimer in the solid-state. This manuscript reports an

extension of this work into the direction of 1-(2-hydroxyethyl)-1-Me-pyrrolidinium and 1-(2-hydroxyethyl)-1-Me-piperidinium salts of $[\text{Ph}_4\text{B}_3\text{O}_3]^-$. Interestingly, although the expected $[\text{Ph}_4\text{B}_3\text{O}_3]^-$ salts were obtained, the cations were more complex than anticipated and consisted of cationic monoborates obtained through condensation of the hydroxyethyl function of the cation precursor with the diphenylborinic acid anhydride. Their syntheses and solid-state structures are discussed in this report.

2. Results and discussion

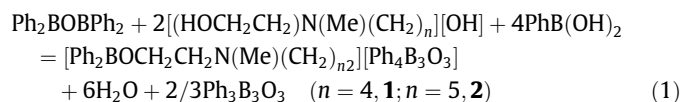
2.1. Synthesis

Rettig and co-workers [7] have published a synthesis of $[\text{NMe}_4][\text{Ph}_4\text{B}_3\text{O}_3]$ using $[\text{NMe}_4][\text{OH}]$ and we successfully adapted this procedure for the synthesis of $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}][\text{Ph}_4\text{B}_3\text{O}_3]$ [9]. In order to attempt the preparation by this route of new 2-hydroxyethyl substituted non-metal cation salts of $[\text{Ph}_4\text{B}_3\text{O}_3]^-$ it was first necessary to prepare solutions of the desired non-metal cation hydroxides. The iodide salts [1-(2-hydroxyethyl)-1-Me-pyrrolidinium] iodide, $[(\text{HOCH}_2\text{CH}_2)\text{N}(\text{Me})(\text{CH}_2)_4]\text{I}$, and [1-(2-hydroxyethyl)-1-Me-piperidinium] iodide, $[(\text{HOCH}_2\text{CH}_2)\text{N}(\text{Me})(\text{CH}_2)_5]\text{I}$, were prepared by literature methods from the free bases using MeI, and their purity confirmed by NMR and/or mp data [10,11]. The iodide salts were converted to methanolic solutions of their corresponding hydroxide salts $[(\text{HOCH}_2\text{CH}_2)\text{N}(\text{Me})$

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(CH₂)₄][OH] and [(HOCH₂CH₂)N(Me)(CH₂)₅][OH] quantitatively using an hydroxide activated anion exchange resin (Dowex 550A). Aliquots of these basic methanolic solutions (containing known quantities of non-metal cation hydroxides) were then used as solvents for the reaction with solid Ph₂BOBPh₂ and PhB(OH)₂ in the molar ratios of 2:1:4. The reaction mixtures were stirred for a short time at room temperature before the solvent was removed to yield crude white solids. NMR analysis (integration of ¹H signals) and MS analysis of both of these crude products indicated that they were both mixtures of two compounds: Ph₃B₃O₃ (identified by MS and NMR) was present in both samples together with the salts [Ph₂B{OCH₂CH₂N(Me)(CH₂)₄}]₂[Ph₄B₃O₃] (**1**) or [Ph₂B{OCH₂CH₂N(Me)(CH₂)₅}]₂[Ph₄B₃O₃] (**2**). NMR analysis indicated that the stoichiometry of the reaction was likely to be that shown in Eq. (1). This reaction equation differs from that previously observed by Rettig and co-worker (and us) in analogous reactions. Recrystallization of the crude samples from CH₃COCH₃ yield pure crystalline samples **1** and **2** (with crystals suitable for X-ray diffraction studies) and the co-product, Ph₃B₃O₃, remaining in solution.



Compounds **1** and **2** both contained the expected anion, [Ph₄B₃O₃]⁻, but were partnered by the unexpected, but closely related and unusually substituted diphenylborinate cations, [Ph₂B{OCH₂CH₂}N(Me)(CH₂)₄]₂⁺ and [Ph₂B{OCH₂CH₂}N(Me)(CH₂)₅]₂⁺, respectively. The cations with overall +1 charge, are zwitterionic and arise from condensation of two triorgano(2-hydroxy-ethyl)ammonium(+1) cations with a diphenylborinate(1-) anion, [Ph₂B(OH)₂]⁻, produced *in situ* from Ph₂BOBPh₂. Related neutral and cationic zwitterionic monoborate species derived from diol functionalized tetraalkylammonium cations have recently been reported [12]. As noted above, zwitterionic cations were not obtained in the related choline system [9] with the energetics of the two reactions being finely balanced despite very similar bond-making and breaking processes. There is a net increase by 2B–O and 2O–H covalent bonds in both systems, but the anticipated drop in lattice energies in this system (compared to Rettigs), and ring strain associated with formation of Ph₃B₃O₃ [13,14] must therefore be offset by (zwitterionic) electrostatic interactions and a less strained OBO angle within the cation.

Compounds **1** and **2** were characterized by IR and NMR spectroscopy (¹H, ¹³C, ¹¹B), and also gave satisfactory elemental analysis. The signals associated with the anions in **1** and **2** were consistent with an earlier assignment assigned [7] with phenyl protons of the PhB groups resonating at a lower frequencies relative to that of analogous protons on the Ph₂B moieties. The cations showed the expected signals and in the case of **1** the CH₂ protons adjacent to N in the pyrrolidine ring were at different chemical shifts and coupled to one another. For **2**, a similar situation arose but this had to be inferred from integration intensities since the signals for the CH₂ protons adjacent to N in the piperidine ring were overlapped with signals for the OCH₂CH₂N group. The aromatic region of the ¹³C-{¹H} spectra of **1** and **2** were well resolved, with all expected signals observed except for those for the *ipso* carbons. ¹¹B-{¹H} NMR in both cases showed signals corresponding to 3 co-ordinate (+27) and 4 co-ordinate centres (+4). Compound **1** showed two barely resolved peaks for the low frequency 4 co-ordinate centres and it is likely that the higher frequency peak of the two is associated with [Ph₄B₃O₃]⁻. We were unable to resolve the 4-coordinate signals for compound **2** but his is not unsurprising since ¹¹B chemical shifts are sensitive to local environment and in both cases the B centres are bound to 2O and 2C atoms, and the signals are probably accidentally co-incident [15]. Additionally, compounds **1** and **2** were also characterized by single-crystal X-ray

diffraction methods and their solid-state structures are discussed below.

2.2. X-ray structures of **1** and **2**

Single crystal structural data for **1** and **2** confirm that zwitterionic monoborate cations and anionic tetraphenylboroxinate anions are present in both **1** and **2** and drawings of their structures are shown in Figs. 1 and 2 respectively, with selective bond-lengths and bond angles presented in legend to the figures. Both compounds were crystallized from acetone and compound **1** was obtained as an acetone semi-solvate and **2** was obtained as an acetone mono-solvate.

The cations in **1** and **2** each have a 4-coordinate B centre and two 4-coordinate N centres. Although chemically equivalent, the 2 quaternary N centres in each cation are crystallographically inequivalent. The pyrrolidine rings in **1** (one containing N61 is disordered) adopt skewed envelope structures, with the N atom in the flap, and the Me group endo. One of the piperidine rings in **2** (containing N41) is in the chair conformation with the smaller substituent (Me) equatorial, the other piperidine ring (containing N31) is in also in the chair conformation but with the Me substituent axial. Angles about N atoms are close to the expected tetrahedral values with those in **1** ranging from 102.13(19)–113.68(17)° and those in **2** ranging from 107.07(13)–113.77(14)°; the smallest angle at N62 in **1** accommodates the 2 ring carbons (C85, C82) of the pyrrolidine ring. Geometries at the B centres in **1** and **2** are very similar: both are 4 co-ordinate and tetrahedral and bound to two phenyl groups and two O atoms of two 2-ethoxytriorganonammonium cations. The B–O bond-lengths average at 1.490(3) (**1**) and 1.495(2) (**2**), and the B–C bonds lengths average at 1.635(3) (**1**) and 1.632(3) (**2**). The bond angles at B range from 107.18(18)–110.93(18)° (**1**) and 106.13(14)–111.62(14)° (**2**) with the two smallest angles in both structures being between OBC vectors; the average angle at B is close to the expected tetrahedral angle. Corresponding data for closely related 4 co-ordinate B centres

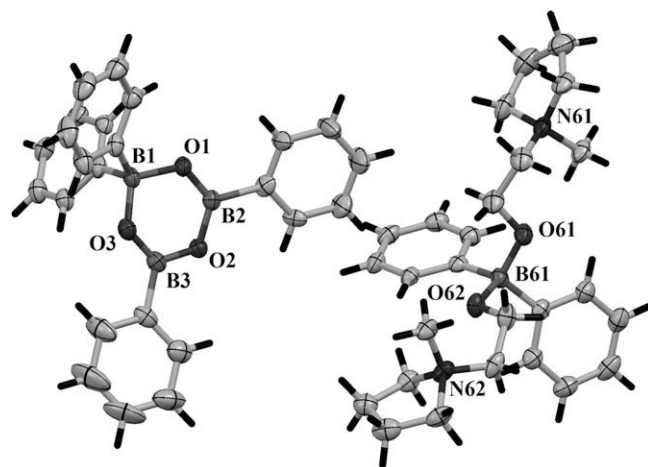


Fig. 1. Drawing of the structure of [Ph₂B{OCH₂CH₂N(Me)(CH₂)₄}]₂[Ph₄B₃O₃]_{1/2}·CH₃COCH₃ [(1)·1/2acetone], showing the atomic numbering scheme (acetone omitted). Selected bond-lengths (Å) and angles (°) with esd's in parenthesis are: B1–O1, 1.506(3); B1–O3, 1.496(3); B2–O1, 1.329(3); B2–O2, 1.396(3); B3–O2, 1.402(3); B3–O3, 1.334(3); B1–C1, 1.616(3); B1–C7, 1.630(3); B2–C13, 1.613(4); B3–C19, 1.583(3); B61–O61, 1.483(3); B61–O62, 1.497(3); B61–C61, 1.630(3); B61–C67, 1.639(3); B1–O1–B2, 120.64(18); B2–O2–B3, 117.95(18); B1–O3–B3, 121.02(17); O1–B1–O3, 109.59(17); O1–B2–O2, 122.3(2); O2–B3–O3, 121.4(2); O1–B1–C1, 109.06(19); O1–B1–C7, 107.82(17); O3–B1–C1, 110.31(18); O3–B1–C7, 108.21(19); C1–B1–C7, 111.82(18); O1–B2–C13, 118.6(3); O2–B2–C13, 118.9(3); O2–B3–C19, 118.7(2); O3–B3–C19, 119.8(2); O61–B61–O62, 110.85(19); O61–B61–C61, 107.18(18); O61–B61–C67, 110.58(18); O62–B61–C61, 110.93(18); O62–B61–C67, 107.23(18); C61–B61–C67, 110.11(18).

Table 1
Crystallographic data for **1** and **2**.

Crystal	1	2
Empirical Formula	C _{51.5} H ₆₃ B ₄ N ₂ O _{5.5}	C ₅₅ H ₇₀ B ₄ N ₂ O ₆
Formula weight (g mol ⁻¹)	841.28	898.37
Crystal system, space group	Triclinic, P1̄	Triclinic, P1
a (Å)	9.3206(2)	9.2267(1)
b (Å)	15.6241(4)	16.3630(4)
c (Å)	17.0680(4)	17.2981(4)
α (°)	79.941(1)	99.089(1)
β (°)	78.413(2)	100.737(1)
γ (°)	80.178(2)	90.697(1)
V (Å ³)	2375.66(10)	2531.34(9)
Z, calc density (Mg m ⁻³)	2, 1.176	2, 1.179
Absorption coefficient (mm ⁻¹)	0.074	0.074
F(0 0 0)	900	964
Crystal	Colourless cut	Colourless cut
	slab	block
Crystal dimensions (mm ³)	0.28 × 0.14 × 0.08	0.28 × 0.24 × 0.22
θ Range (°)	2.95–27.48	2.91–27.48
No. of reflections collected	36 627	54 995
R _{int}	0.0475	0.0699
No. of data/restraints/parameters	10 772/436/672	11 575/14/647
Final R indices [F ² > 2σ(F ²): R ₁ , wR ₂	0.0762, 0.1522	0.0561, 0.1238
R indices (all data): R ₁ , wR ₂	0.1126, 0.1747	0.1022, 0.1457
Largest difference peak and hole (e Å ⁻³)	0.344, -0.376	0.310, -0.217

1: 1/2CH₃COCH₃, C_{51.5}H₆₃B₄N₂O_{5.5}: C, 73.5; H, 7.6; N, 3.3. Found: C, 71.8; H, 7.5; N, 3.0%.

3.4. Synthesis of [Ph₂B{OCH₂CH₂N(Me)(CH₂)₅}₂][Ph₄B₃O₃]·CH₃COCH₃ (2·CH₃COCH₃)

A mixture of Ph₂BOBPh₂ (0.20 g; 0.58 mmol), PhB(OH)₂ (0.28 g; 2.30 mmol) and [(HOCH₂CH₂)N(Me)(CH₂)₅][OH] (1.20 mmol) dissolved in MeOH (15.7 ml) were stirred under a N₂ atmosphere (30 min). Removal of solvent yielded a fluffy white solid (0.51 g). Recrystallization from acetone gave colourless crystals of **2**·CH₃COCH₃ (0.27 g; 52%). M.p. 89–94 °C. NMR: (500 MHz, CD₃COCD₃) δ_H: 8.18 (dd, J 5.4, 2.5 4H, o-PhB), 7.76 (d, J 7.6, 4H, o-Ph₂B), 7.42 (d, J 7.3, 4H, o-Ph₂B), 7.34 (m, 6H, m,p-PhB), 7.05 (t, J 7.4, 4H, m-Ph₂B), 7.03 (t, J 7.6, 4H, m-Ph₂B), 6.95 (t, J 6.9, 2H, p-Ph₂B), 6.86 (t, J 6.9, 2H, p-Ph₂B), 3.80 (m, 4H, CH₂O), 3.78 (m, 4H, NCH), 3.47 (m, 4H, CH₂N), 3.45 (m, 4H, NCH), 2.85 (s, 6H, CH₃N), 1.93 (m, 8H, 2CH₂), 1.68 (m, 4H, CH₂). (125 MHz, CD₃COCD₃) δ_C: 20.84, 21.80, 56.89, 62.69, 124.03, 124.64, 126.62, 126.88, 127.77, 129.95, 132.63, 133.78, 135.50. (160 MHz, CD₃COCD₃) δ_B: 3.4, 27.0. IR (KBr disc) (ν_{max}/cm⁻¹): 3372, 3062, 3021, 2947, 1971, 1911, 1843, 1598, 1462, 1414, 1348, 1233, 1141, 1112, 756, 740, 707. Elemental Anal. Calc. for **2**·CH₃COCH₃, C₅₅H₇₀B₄N₂O₆: C, 73.5; H, 7.9; N, 3.1. Found: C, 72.8; H, 7.3; N, 3.3%.

3.5. Single-crystal X-ray structure determinations of [Ph₂B{OCH₂CH₂N(Me)(CH₂)₄}₂][Ph₄B₃O₃]·1/2CH₃COCH₃ (**1**·1/2CH₃COCH₃) and [Ph₂B{OCH₂CH₂N(Me)(CH₂)₅}₂][Ph₄B₃O₃]·CH₃COCH₃ (**2**·CH₃COCH₃)

Suitable crystals of **1**·1/2CH₃COCH₃ and **2**·CH₃COCH₃ were grown from acetone solution, selected and measured on a Bruker

Nonius KappaCCD Area Detector at the window of a Bruker Nonius FR591 rotating anode (λ_{Mo Kα} = 0.71073 Å) driven by COLLECT [19] and processed by DENZO [20] software at 120 K. The structures were determined in SHELXS-97 and refined using SHELXL-97 [21]. Crystal data and refinement results for both samples are collated in Table 1.

Appendix A. Supplementary data

CCDC 749066 and 749067 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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