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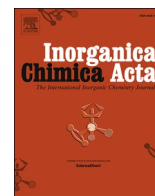
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Synthesis and characterization of a tertiary amine:boric acid (1:1) co-crystal and a neutral zwitterionic diamine pentaboron adduct

Mohammed A. Altahan^{a,1}, Michael A. Beckett^{a,*}, Simon J. Coles^b, Peter N. Horton^b, Charlotte L. Jones^a

^a School of Natural Sciences, Bangor University, Bangor, Gwynedd LL57 2UW, UK

^b Faculty of Engineering and Environmental Chemistry, Southampton University, Southampton SO17 1BJ, UK

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ABSTRACT

The syntheses of the 4,4'-trimethylenebis(*N*-methylpiperidine):boric acid (1:1) co-crystal, 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**), and a zwitterionic tetrahydroxidohexaoxidopentaboron adduct, [B₅O₆(OH)₄(κ*N*-NH₂CH₂CH₂NHET₂)·H₂O (**2**), (NH₂CH₂CH₂NEt₂ = deen) from appropriate combinatorial libraries primed with B(OH)₃, are reported together with their spectroscopic (NMR, IR) and single-crystal XRD characterization data. Solid-state H-bond interactions are the likely strong drivers for their formation, and these are described in detail. H-bond networks present in co-crystal **1** include C₂²(16), R₂²(8), and R₆⁶(36) whilst zwitterionic pentaboron derivative **2** has three R₂²(8) intermolecular H-bond interactions and the Et₂NH- group is involved in a S(7) intramolecular H-bond. Thermal (TGA/DSC) data are also reported for **1** which thermally decomposes to B₂O₃, in a multistage process: dehydration (60–70 °C) and oxidation and further dehydration (90–700 °C).

1. Introduction

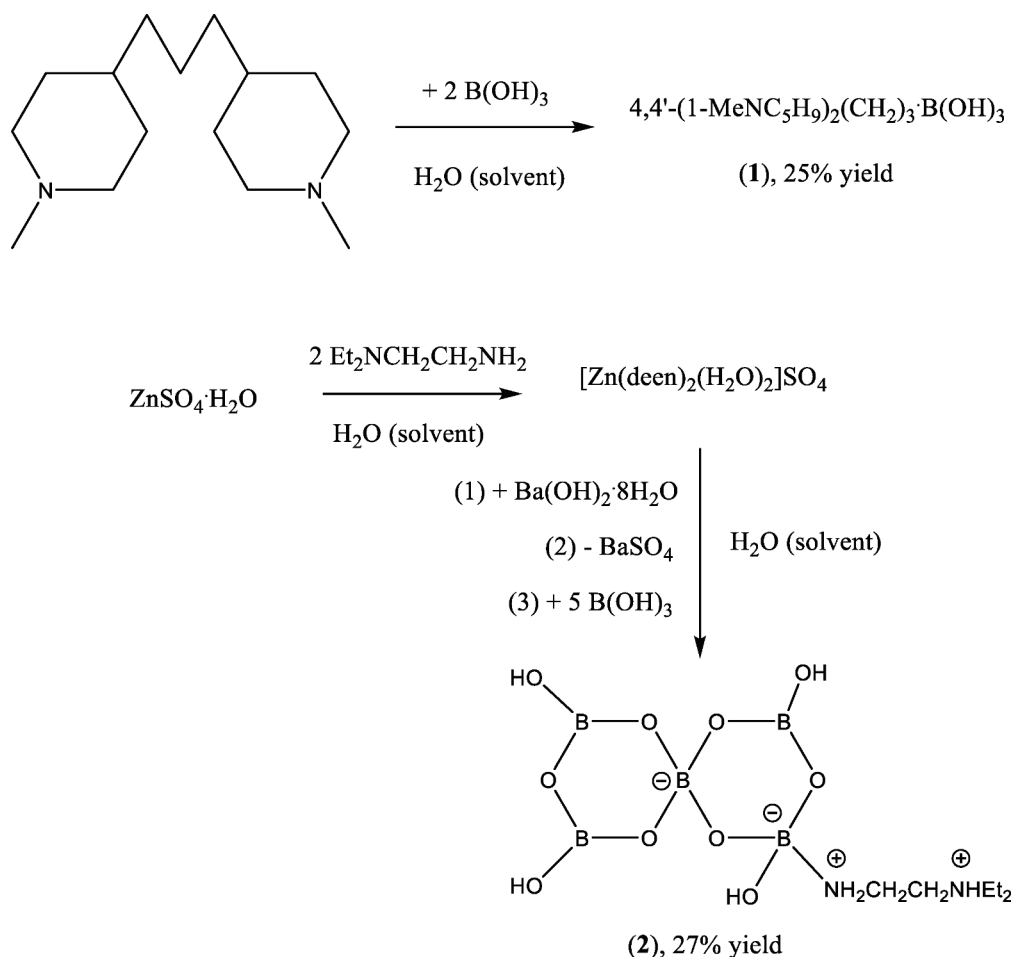
Hydroxidooxidoborates [1] are an important class of compounds that have found extensive industrial use [2–4] and also potentially have fine-chemical applications [5–6]. They are structurally diverse and are usually comprised of three- and/or four-coordinate boron centres bound to oxygen atoms that either bridge to other boron centres or terminate as hydroxido groups [7–11]. In some circumstances the oxygen atoms may terminate as O[−] [7–9], but more commonly the negative charge of the hydroxidooxidoborate is formally associated with the four-coordinate boron atoms, although QTAIM calculations indicate [12] that these centres carry a positive charge and the overall negative charge is associated with the electronegative oxygen atoms. We have developed a synthetic strategy of using non-metal (organic) or transition-metal complex cations to template and affect the self-assembly of hydroxidooxidoborate anions through crystallization of products from aqueous solutions originally primed with B(OH)₃ [10,11]. The various hydroxidooxidoborate species arise through well-known B(OH)₃/OH[−]/hydroxidooxidoborate anion equilibria [13,14] and products are templated by the cations present in solution [15,16]. H-bonding, cation steric effects, and cation charge, amongst other things, all play

important roles in this templating process [17,18] and the scientific challenge is to get a greater understanding of how and why such interactions/reactions occur so that new materials can be intentionally targeted. The tetrahydroxidohexaoxidopentaborate(1-) anion appears to have exceptional stability [10,19] and can be templated by many cations but the above strategy has also led to the formation of unique and previously unobserved insular anions: e.g. [B₇O₉(OH)₆]^{3−} [20] and [B₈O₁₀(OH)₆]^{2−} [21] and to other novel structural hydroxidooxidoborate motifs [22,23]. Occasionally, unexpected products are observed and this manuscript reports on the synthesis and characterization of two such products: the co-crystallized 4,4'-trimethylenebis(*N*-methylpiperidine):boric acid (1:1) compound, 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**) and the zwitterionic tetrahydroxidohexaoxidopentaboron adduct B₅O₆(OH)₄(κ*N*-NH₂CH₂CH₂NHET₂)·H₂O (**2**) (NH₂CH₂CH₂NEt₂ = deen). This manuscript describes in detail their solid-state H-bond interactions that we believe play an important role in their formation.

* Corresponding author.

E-mail address: m.a.beckett@bangor.ac.uk (M.A. Beckett).

¹ Current address: Chemistry Department, College of Science, University of Thi-Qar, Nasiryah, Iraq.



Scheme 1. Reaction conditions for the formation of **1** and **2**.

2. Experimental

2.1. General

Reagents were commercially available. ^1H , ^{13}C and ^{11}B NMR spectra were obtained in D_2O solutions on a Bruker Avance 400 spectrometer and data are reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of BF_3OEt_2 (^{11}B) or TMS (^{13}C and ^1H). TGA/DSC analysis (in air) was performed on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles between 20 and 800 °C with a temperature ramp-rate of 10 °C min^{-1} . FTIR spectra were obtained on a Perkin-Elmer 100 FTIR spectrometer as KBr pellets. Single-crystal X-ray crystallographic analyses were performed at the EPSRC National Crystallography service at the University of Southampton. CHN analysis was obtained from OEA laboratories Ltd in Callington, Cornwall.

2.2. Synthesis of 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**)

4,4'-(1-MeNC₅H₉)₂(CH₂)₃ (4.8 g, 20.0 mmol) and B(OH)₃ (2.5 g, 40.0 mmol) were dissolved in 1:1 MeOH:H₂O (100 mL) with gentle warming. The solution was allowed to stand for 1 h before removal of the solvent under reduced pressure gave a dark cream solid which was oven dried at 50 °C for 24 h (7.3 g). The crude product was dissolved in and crystallized from H₂O to afford colourless needle-like crystals (1.5 g, 25%) suitable for X-ray diffraction studies. M.p: 72–74 (dec) °C. ^1H (δ /ppm): 1.26–1.35 (m, 10H), 1.47 (br 2H), 1.87 (d, 4H), 2.6 (m, br

10H), 3.22 (d, 4H), 4.79 (HOD, OH rapidly exchanging in D_2O). ^{13}C (/ppm): 22.66 (CH₂), 29.98 (4CH₂), 32.75 (δ 2CH), 35.20 (2CH₂), 43.54 (2CH₃), 54.68 (4CH₂); ^{11}B (δ /ppm): +4.7. IR (KBr, ν_{max} /cm⁻¹): 3345(br m), 3271(br,m), 2925(s), 2853(s), 2804(s), 2384(w), 1880(w), 1629 (w), 1457(s), 1429(s), 1412(s), 1379(m), 1281(s), 1217(br, m), 1143(s), 1113(w), 1099(w), 1072(m), 1042(w), 988(m), 976(m) 960(m), 869 (m), 832(m), 798(br,m), 766 (s), 706 (w), 680(s), 530(m), 506(m), 444 (m). Elemental analysis, *calc.* for C₁₅H₃₃N₂BO₃: C, 60.0%, H, 11.1%, N, 9.3%; *found*: C, 59.6%, H, 11.0%, N, 9.3%. TGA: Loss of 1H₂O (60–70 °C): 6.1% (6.0% calc), residual B₂O₃ (>600 °C) 11.7% (11.6% calc.). sc-XRD: C₁₅H₃₃BN₂O₃, $M_r = 300.24$, Triclinic, $P - 1$, $a = 6.29840$ (10) Å, $b = 10.7174(2)$ Å, $c = 13.9659(3)$ Å, $\alpha = 92.059(2)^\circ$, $\beta = 102.412(2)^\circ$, $\gamma = 100.376(2)^\circ$, $V = 902.90(3)$ Å³, $T = 100(2)$ K, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.075$ mm⁻¹ 15,600 reflections measured, 4119 unique ($R_{\text{int}} = 0.0212$) which were used in all calculations. The final wR_2 was 0.0975 (all data) and R_1 was 0.0370 ($I > 2\sigma(I)$).

2.3. Synthesis of B₅O₆(OH)₄(κ N-NH₂CH₂CH₂NHEt₂)·H₂O (**2**)

ZnSO₄·H₂O (1.4 g, 8 mmol) was dissolved in H₂O (10 mL) and deen (2.0 g, 17 mmol) was added dropwise with stirring over 10 mins. An aqueous solution (10 mL) of Ba(OH)₂·8H₂O (2.5 g, 8 mmol) was then added to the solution and left to stir for a further 5 mins. BaSO₄ was removed by filtration and B(OH)₃ (5.2 g, 85 mmol) was added to the filtrate and stirred for 30 min. The solution was filtered into several vials and left for 3 weeks to allow for slow evaporation of ca. 50% of the

solvent. A few drops of EtOH were added to each vial to encourage crystallization of the product. After a few days colourless crystals of **2** had formed and these were collected by filtration, combined, and placed in an oven for 30 mins to dry (1.6 g, 27%). These crystals were suitable for single-crystal XRD studies. M.p.: >300 °C. NMR (D₂O): ¹H (δ/ppm): 1.2 (t, 6H), 3.0 (q, 4H), 3.03 (br m, 4H), 4.79 (9H, HOD, NH, OH rapidly exchanging in D₂O); ¹³C (δ/ppm): 8.8 (CH₃), 47.1 (CH₂CH₃), 51.6 (CH₂NEt₂), 35.6 (CH₂NH₂); ¹¹B (δ/ppm): +16.2. IR (KBr, ν_{max}/cm⁻¹): 3556(s), 3481(br), 3370(O), 3275(br), 3103(m), 1619(m), 1498(w), 1472(w), 1449(m), 1406(s), 1371(s), 1318(s), 1215(m), 1083(s), 1042(s), 1009(m), 937(m), 899(s), 708(w). Elemental analysis, Calc. for C₆H₂₂N₂B₅O₁₁: C, 20.4%, H, 6.6%, N, 7.9%; Found: C, 20.0%, H, 6.7%, N, 7.5%. sc-XRD: C₆H₂₃B₅N₂O₁₁, M_r = 353.31, triclinic, P-1 (No. 2), a = 8.9225(3) Å, b = 9.3115(3) Å, c = 9.9764(4) Å, α = 85.001(3)°, β = 75.559(3)°, γ = 78.425(3)°, V = 785.74(5) Å³, T = 100(2) K, Z = 2, Z' = 1, μ(CuKα) = 1.133 mm⁻¹, 10,752 reflections measured, 2842 unique (R_{int} = 0.0230) which were used in all calculations. The final wR₂ was 0.0834 (all data) and R₁ was 0.0304 (I > 2σ(I)).

2.4. X-ray crystallography

A suitable crystal of **1** was mounted on 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 HF Varimax optics (100 μm focus). A suitable crystal of **2** was mounted on a MITIGEN holder in perfluoroether oil on a Rigaku 007HF equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000 detector. The crystals were kept at T = 100 (2) K during data collection. Data collection for **1** was obtained using CrystalClear-SM Expert 3.1 b27 [24]. Data collection for **2** and cell determination, data reduction, cell refinement and absorption correction for **1** and **2** were obtained using CrysAlisPro [25]. Using Olex2 [26] the structures were solved with the ShelXT [27] structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2018/3 of ShelXL [28] using Least Squares minimisation.

3. Results and discussion

3.1. Synthesis and characterisation

The synthetic strategy for the preparation of the new compounds involves crystallization at room temperature from aqueous or ethanolic aqueous solutions by self-assembly from appropriate dynamic combinatorial libraries [13–15,16]. Solutions primed with B(OH)₃ and non-metal cations generally afford hydroxidooxidoborate salts [10] and those primed with B(OH)₃ and transition metal complex cations generally afford either hydroxidooxidoborate salts or hydroxidooxidoborate complexes [10,11]. The reagents/solvents for the formation of **1** and **2** are given in Scheme 1.

Tetrahydroxyhexaoxidopentaborate(1-) salts are most commonly prepared from unipositive amine based cations in aqueous solution irrespective of the amine:B(OH)₃ ratio, although yields are generally quantitative with a 1:5 ratio [10]. Amine cations that can be dipositive have been known to afford tetrahydroxidotrioxidotriborate(1-) anions especially at lower amine:B ratios [10,29]. Cognisant of this we attempted the synthesis of a hydroxidooxidoborate salt from 4,4'-trimethylenebis(N-methylpiperidine) at a nitrogen:boron ratio of 1:1 and **1** crystallized from the aqueous solution in low yield. The crystals obtained were suitable for a X-ray diffraction study and a single crystal X-ray analysis revealed that **1** was not a hydroxidooxidoborate salt but an unexpected co-crystallized material of the starting compounds in a 1:1

stoichiometry. This observed product may arise through preferential crystallization of a neutral product from the polar aqueous solvent. Co-crystallized materials containing B(OH)₃ are not uncommon and B(OH)₃ often fills 'voids' as H-bonded spacers between anions in hydroxidooxidoborate salts with sterically demanding cations [30–33]. Boric acid also forms co-crystallized materials with lactams [34], aromatic amines [35,36] and Ph₃PO [37]; to our knowledge **1** is the first example of B(OH)₃ co-crystallized with a tertiary amine. One can only speculate as to why this product was obtained in preference to a hydroxidooxidoborate salt, but solubility, and solid-state intermolecular interactions (e.g. packing and H-bonding) and reactant stoichiometry are logical drivers. Solid-state interactions are discussed in detail in section 3.2.

We have shown that cationic complexes containing Zn^(II) and amine/ammine ligands such as [Zn(dac)₂(H₂O)₂]²⁺ (dac = 1,2-diaminocyclohexane), [Zn(dien)₂]²⁺ (dien = NH(CH₂CH₂NH₂)₂), [Zn(NH₃)₆]²⁺, and [Zn(en)₃]²⁺ (en = 1,2-diaminoethane) can template the formation of hydroxidooxidoborate salts e.g. [Zn(dac)₂(H₂O)₂][B₇O₉(OH)₅]·H₂O [38], or the formation of complexes containing hydroxidooxidoborate ligands e.g. [NH₄]₂[Zn{B₆O₇(OH)₆}₂(H₂O)₂·2H₂O [39], [Zn(dien){B₆O₇(OH)₆}]·0.5H₂O [39] and [Zn(en){B₆O₇(OH)₆}]·2H₂O [40]. We employed the same reaction methodology as used in the cited examples with deen as the amine ligand for the synthesis/crystallization of **2** and despite being confident that the labile complex salt, [Zn(deen)₂(H₂O)₂](OH)₂ had been prepared *in situ* compound **2** surprisingly did not contain Zn. This was confirmed by a single-crystal X-ray diffraction study since the crystals obtained for **2** were suitable for such a study. This study revealed that **2** was B₅O₆(OH)₄(κN-NH₂CH₂CH₂NHET₂)·H₂O, a further example of an otherwise rare zwitterionic tetrahydroxidohexaoxidopentaborate(1-) adduct. Other known examples are limited to B₅O₆(OH)₄{NH₂(CH₂)_nNH₃} (n = 5, 6) and [H₃N(CH₂)₈NH₃][B₅O₆(OH)₄(NH₂(CH₂)₈NH₂)-B₅O₆(OH)₄]}·2B(OH)₃·2H₂O [33,41]. It is likely that since **2** was obtained in low yield there were Zn-borate species present in the reaction solution but these failed to crystallize under the prevailing conditions. The observed product may therefore arise through preferential crystallization of a neutral product from the polar medium. Again, solid-state intermolecular interactions (e.g. packing and H-bonding) are logical drivers for the formation of crystalline **2** and solid-state interactions are discussed in detail in section 3.3.

Solution NMR (¹H, ¹¹B, and ¹³C) spectra of samples of **1** and **2** were obtained in D₂O. However, these were largely uninformative and did not reflect the anticipated spectra for **1** and **2**. Rather, the spectra obtained reflected the various combinatorial components of **1** and **2** arising through the rapidly attained equilibria reactions associated with hydroxidooxidoborates in aqueous solution [14]. Thus, ¹³C spectra arising from **1** and **2** have 6 and 4 signals at the expected chemical shifts for 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ and deen, respectively. The ¹¹B spectrum of **1** is not that expected for B(OH)₃ (+18 ppm) but is shifted considerably upfield to + 4.7 ppm due to B(OH)₃/[B(OH)₄]⁻ equilibria arising through aqueous protonation of the 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ with release of [OH]⁻ [13,14]. The ¹¹B spectrum of **2** has an one equilibrium signal at + 16.2 ppm, close to that generally observed, and predicted [14,19], for dilute hydroxidooxidopentaborate(1-) salts again resulting from the B(OH)₃/[B(OH)₄]⁻ equilibria in a less basic solution. Although **2** is formally an adduct of a hydroxidooxidopentaborate(1-), with an additional 4-coordinate boron centre, dissociation of the ligand in solution would result in the salt [Et₂NHCH₂CH₂NH₂][B₅O₆(OH)₄] which would then undergo the expected hydroxidooxidoborate equilibria reactions.

The IR spectrum of **1** showed a broad peak at 3271 cm⁻¹ and strong broad bands at 1429, 1143 and 869 cm⁻¹ that can be assigned to (O—H), ν_{as}(B—O), ν_{as}(B—O) and ν_s(B—O) of B(OH)₃, respectively [42], and

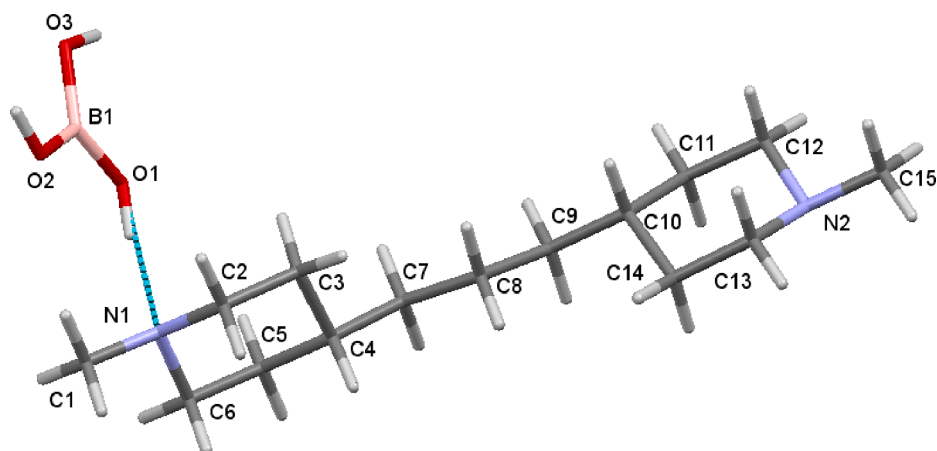


Fig. 1. Drawing of the structure of **1** showing non-hydrogen atomic numbering.

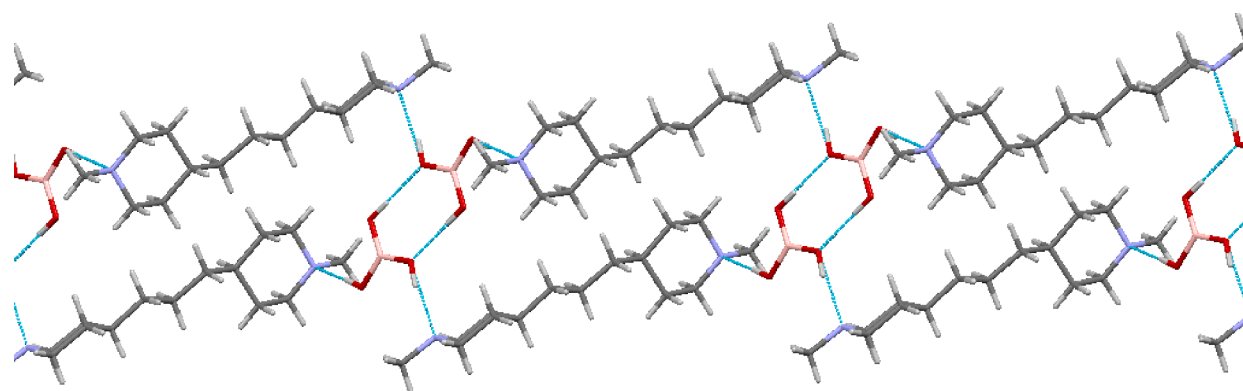


Fig. 2. H-bonding interactions in **1** illustrating $C_2^i(16)$ chains crosslinked by $B_2^i(8)$ borate interactions and resulting in the formation of larger centrosymmetric $R_6^i(36)$ interchain rings.

the other signals can be attributed to the organic moiety. Likewise, the IR of spectrum of **2** has signals that can be attributed to the $Et_2NHCH_2CH_2NH_2$ fragment and other strong signals at 1371, 1042, 937 and 899 cm^{-1} which may be assigned to the tetrahydroxidohexaoxidopentaborate(1-) unit as $\nu_{as}(B_{trig}-O)$, $\nu_{as}(B_{tet}-O)$, $\nu_s(B_{trig}-O)$ and $\nu_s(B_{tet}-O)$ stretches [42]. A band at 937 cm^{-1} is observed in the zwitterionic

compound **2** and this is likely to be related to the diagnostic band observed at ca. 925 cm^{-1} for tetrahydroxidohexaoxidopentaborate(1-) salts [10,19,29–32].

Compound **1** was a crystalline low melting solid that decomposed at its melting point. This thermal decomposition was investigated by TGA/DSC. Compound **1** is thermally decomposed to a glassy B_2O_3 residue (calc. 11.6%, found 11.7%) in a multistep process: the first lower temperature step occurred at $60\text{--}70\text{ }^\circ\text{C}$. This first step is endothermic and appears to be consistent with loss of one H_2O by dehydration and crosslinking of $B(OH)_3$ to HBO_2 [4,43]. Subsequent steps, with both exothermic and endothermic DSC peaks, are likely to be associated with the oxidation of the amine and further loss of $1/2H_2O$. Such behaviour has been observed before in many non-metal cation hydroxidooxidoborates [10,19,28–33] although the initial dehydration/crosslinking step generally occurs at a higher temperature (ca. $> 200\text{ }^\circ\text{C}$) than that observed for **1**. However, $B(OH)_3$ is known to start to dehydrate at $60\text{--}90\text{ }^\circ\text{C}$ [4,43] and the lower temperature dehydration of **1** is not inconsistent with this.

3.2. X-ray structure of 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**)

The solid-state structure of **1** is free from disorder and comprises one molecule of $B(OH)_3$ and one molecule of 4,4'-trimethylenebis(*N*-methylpiperidine) in the asymmetric unit. A diagram of **1** showing non-hydrogen atomic numbering is given in Fig. 1.

The B-O bond-lengths in **1** range from 1.3612 (14)–1.3723 (13) Å (av. 1.3671 (14) Å) and are not significantly different from those observed in other co-crystallised $B(OH)_3$ structures [30–37], or $B(OH)_3$ [44] itself. Likewise, OBO bond angles range from $119.79(10)\text{--}120.27(9)^\circ$ (av.

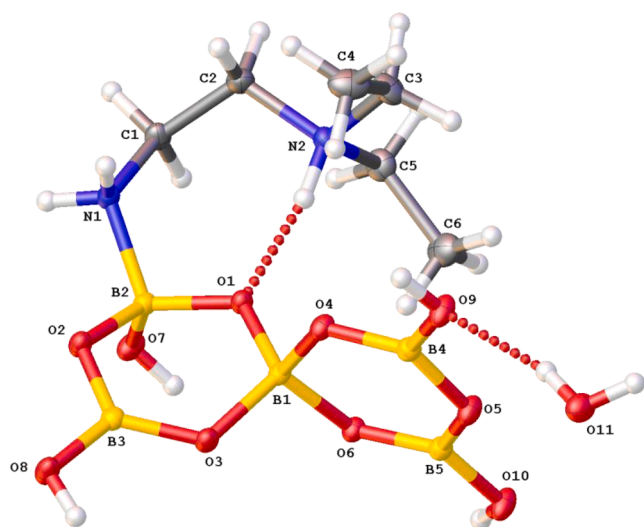


Fig. 3. A drawing of **2** showing non-hydrogen atomic numbering, the $S(7)$ intramolecular H-bond and the intermolecular $O11-H11\cdots O9$ H-bond.

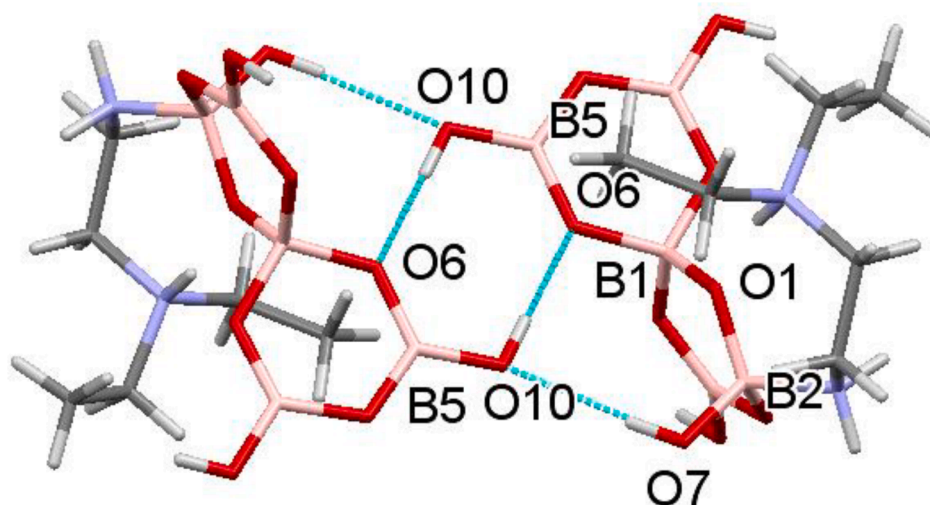


Fig. 4. A view of the structure of **2** showing the reciprocal $R_2^2(8)$ interactions involving $O10H10 \cdots O6$ and the unusual $R_2^2(8)$ interaction involving $O7H7 \cdots O10$ and $O10H10 \cdots O6$.

120.00(10) $^\circ$) and their sum at 360.00(10) $^\circ$ confirms the expected trigonal planar boron centre. The two *N*-methyl piperidines of the organic component of the co-crystal are crystallographically non-equivalent and both adopt chair conformations, with methyl groups equatorial, and have typical C—C and C—N bond-lengths. The C—N—C angles at N1 and N2 range from 110.19(8)–110.77(8) $^\circ$ (av. 110.51(8) $^\circ$) and 109.71(8)–110.76(7) $^\circ$ (av. 110.39(8) $^\circ$), respectively. The sum of the angles at N1 (331.52(8) $^\circ$) and N2 (331.18(8) $^\circ$) confirms that these centres are trigonal pyramidal, as are expected for tertiary amines.

We believe H-bonding plays an important role in building the lattice of **1** with each $B(OH)_3$ forming two donor bonds ($O1-H1 \cdots N1$ and $O2-H2 \cdots N2'$) as a bridge between two 4,4'-trimethylenebis(*N*-methylpiperidine) molecules. This results in the formation of infinite alternating diamine/ $B(OH)_3$ $C_2^2(16)$ chains [45]. Furthermore, the third hydroxy group on B1 is associated with a dimeric reciprocal $R_2^2(8)$ interaction with a neighbouring $B(OH)_3$ ($O3-H3 \cdots O1'-B1'-O3'-H1' \cdots O1-B1-$). Since there is only one crystallographically unique $B(OH)_3$ in **1** this neighbouring $B(OH)_3$ also bridges two 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ molecules and forms a $C_2^2(16)$ chain. Overall, this results in cross-linking of the two chains with the formation of larger $R_6^6(36)$ rings (Fig. 2). As the two nitrogen atoms of the 4,4'-(1-MeNC₅H₉)₂(CH₂)₃ units are crystallographically non-equivalent (N1 and N2), as are the two piperidine rings, and the resulting larger $R_6^6(36)$ rings are centrosymmetric with their chains running in opposite directions.

3.3. X-ray structure of $B_5O_6(OH)_4(\kappa N-NH_2CH_2CH_2NHEt_2) \cdot H_2O$ (**2**)

The solid-state structure of **2** is comprised of neutral zwitterionic hydroxidooxidopentaborate(2-) derivative, $B_5O_6(OH)_4(\kappa N-NH_2CH_2CH_2NHEt_2)$, co-crystallized with one water of crystallization. The structure is disorder free. The hydroxidooxidoborate containing moiety in **2** is structurally derived from a substituted pentahydroxidohexaoxidopentaborate(2-) anion with a FBB of $5:2T + 3A$, [7,9] with one of the two hydroxido groups on the tetrahedral ring boron in $[B_5O_6(OH)_5]^{2-}$ replaced by a monoprotonated diammine ligand. Thus, $[H_2NCH_2CH_2NHEt_2]^+$, is coordinated to B2 via the lone pair on the unprotonated N1 atom (see Fig. 3 for non-hydrogen atomic numbering). Hydroxidooxidopentaborate (2-) derivatives with this FBB occur in several minerals e.g. ezcurrite, $Na_{2n}[\{B_5O_7(OH)_3\}_n] \cdot 2nH_2O$ [46] and a few synthetic nonmetal hydroxidooxidopentaborates e.g. $[H_3N(CH_2)_3NH_3]_n[\{B_5O_8(OH)\}_n]$ [47]; these species are both comprised of

more highly condensed hydroxidooxidoborate networks rather than insular moieties. Insular hydroxidooxidopentaborate(2-) derivatives with this FBB are uncommon and are currently limited to the three zwitterionic derivatives noted earlier [33,41].

The B-O bond-lengths associated with the trigonal and tetrahedral boron atoms in **2** range from 1.3544(16)–1.3892(16) Å and 1.4418(16)–1.4872(15) Å, respectively and are typical of hydroxidooxidoborate structures [19,22,29–33]. The O-B-O angles are also in the ranges expected for oxidoborate species in general [19,22,29–33] and more specifically, the zwitterionic derivatives [41]. The B-O bond-lengths to tetrahedral B2 (bound to N1) in **2** range from 1.4418(16)–1.4706(16) Å (av. 1.4564(16) Å) are slightly, but significantly, shorter than the B-O bond-lengths around the tetrahedral (spiro) B1 (1.4465(15)–1.4872(15) Å, av. 1.4705(16) Å). The B2-N1 bond length in **2** is 1.6078(16) Å and this is significantly shorter than in the other reported complexes where the boron acceptor atom is otherwise only bound to oxygen [48]. Angles about B2 range from 104.04(9)–114.89(10) $^\circ$ and indicate a tetrahedrally hybridized boron centre but the *N*-B-O angles are smaller (104.04(9)–108.92(10) $^\circ$) than the O-B-O angles (111.65(10)–114.89(10) $^\circ$) corresponding to tetrahedral character value (THC_{DA}, [48,49]) of 75.6%. This value is in the middle the broad range reported for other *N* → BO_3 sets (58.6–90.0) [49–53] and extends the narrower range (82.1–85.6) for the other three reported zwitterionic hydroxidooxidopentaborate derivatives [41]; the latter values were recalculated from the published bond angles [41].

There are potentially 3NH and 6OH H-bond donor sites within **2** and all are used in H-bonding interactions. Three of the hydroxidooxidopentaborate OH group partake in reciprocal $R_2^2(8)$ interactions: ($O6-B5-O10-H10 \cdots O6'-B5'-O10'-H10' \cdots$, $O3-B3-O8-H8 \cdots O3'-B3'-O8'-H8' \cdots$, and $O4-B4-O9-H9 \cdots O4'-B4'-O9'-H9' \cdots$). Such interactions are strong (ca. 21 kJ. mol⁻¹ / H-bond) and are a well-known influence in the stability of hydroxidooxidopentaborate structures [19]. The hydroxido group containing O7 is involved in an unusual $R_2^2(8)$ ring interaction ($O7-H7 \cdots O10'-H10' \cdots O6-B1-O1-B2$); this includes the same O10', which is now the acceptor site, involved in the reciprocal donor interaction to $O6-H6$ (Fig. 4). The Et_2NH- group is involved in an unusual S(7) intramolecular H-bond to O1 ($B2-N1-C1-C2-N2-H2 \cdots O1-$) (Fig. 3) and the $-NH_2B$ group H-bonds to two hydroxidooxidopentaborates at symmetry related O2 and O11 sites. The H_2O molecule (containing O11) bridges two hydroxidooxidopentaborate moieties at O9 and a symmetry related O7' acceptor sites (Fig. 3).

4. Conclusions

Two unusual organic-borate containing species, 4,4'-(1-MeNC₅H₉)₂(CH₂)₃B(OH)₃ (**1**) and B₅O₆(OH)₄(KN-NH₂CH₂CH₂NHEt₂)·H₂O (**2**) were obtained as crystalline solids from combinatorial library solutions containing B(OH)₃ and the organic fragments by self-selection processes. Compound **1** is a co-crystallized product and **2** is an internally condensed zwitterionic monoprotonated diamine/tetrahydroxidohexaoxidopentaborate derivative (FBB = 5:2T + 2Δ). The plethora of H-bond interactions found in both solid-state structures are described in detail using Etter terminology and since these H-bond interactions are strongly stabilizing we conclude that they are a very important factor in directing the self-selection crystallization processes.

CRedit authorship contribution statement

Mohamed A. Altahan: Investigation, Writing - review & editing. **Michael A. Beckett:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing. **Simon J Coles:** Funding acquisition, Resources. **Peter N. Horton:** Investigation, Data curation, Writing - review & editing. **Charlotte Jones:** Investigation, Writing - review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- M.A. Beckett, B. Brellocks, I.T. Chizhevsky, T. Damhus, K.-H. Hellwich, J.D. Kennedy, R. Laitinen, W.H. Powell, D. Rabinovich, C. Vinas, A. Yerim, Nomenclature for boranes and related species (IUPAC Recommendations 2019), *Pure Appl. Chem.* **92** (2020) 355–381.
- D.M. Schubert, Borates in industrial use, *Struct. Bond.* **105** (2003) 1–40.
- D.M. Schubert, Hydrated zinc borates and their industrial use, *Molecules* **24** (2019) 2419.
- D.M. Schubert, Boron oxide, boric acid, and borates, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Ed., J. Wiley Sons, NY, 2011, pp. 1–68.
- Y. Wang, S. Pan, Recent developments of metal borate halides: crystal chemistry and application in second-order NLO materials, *Coord. Chem. Rev.* **323** (2016) 15–35.
- P. Becker, Borate materials in nonlinear optics, *Adv. Materials* **10** (1998) 979–992.
- G. Heller, A survey of structural types of borates and polyborates, *Top. in Curr. Chem.* **131** (1986) 39–98.
- J.D. Grice, P.C. Burns, F.C. Hawthorne, Borate minerals II. A hierarchy of structures based upon the borate fundamental building block, *Canad. Min.* **37** (1999) 731–762.
- C.L. Christ, J.R. Clark, A crystal-chemical classification of borate structures with emphasis on hydrated borates, *Phys. Chem. Minerals* **2** (1–2) (1977) 59–87.
- M.A. Beckett, Recent advances in crystalline hydrated borates with non-metal or transition-metal complex cations, *Coord. Chem. Rev.* **323** (2016) 2–14.
- S.-S. Xin, M.-H. Zhou, M.A. Beckett, C.-Y. Pan, Recent advances in crystalline oxidoborate complexes of d-block or p-block metals: structural aspects, syntheses and physical properties, *Molecules* **26** (2021) 3815.
- M.A. Beckett, R.A. Davies, C.D. Thomas, Computational studies on gas phase polyborate anions, *Comp. and Thechem.* **1044** (2014) 74–79.
- J.L. Anderson, E.M. Eyring, M.P. Whittaker, Temperature jump rate studies of polyborate formation in aqueous boric acid, *J. Phys. Chem.* **68** (1964) 1128–1132.
- G. Salentine, High-field 11B NMR of alkali borate. Aqueous polyborate equilibria, *Inorg. Chem.* **22** (1983) 3920–3924.
- P.T. Corbett, J. Leclaire, L. Vial, K.R. West, J.-L. Wietor, J.K.M. Sanders, S. Otto, Dynamic combinatorial chemistry, *Chem. Rev.* **106** (9) (2006) 3652–3711.
- J. Solà, M. Lafuente, J. Atcher, I. Alfonso, Constitutional self-selection from dynamic combinatorial libraries in aqueous solution through supramolecular interactions, *Chem. Commun.* **50** (35) (2014) 4564–4566.
- J.D. Dunitz, A. Gavezotti, Supramolecular synthons: validation and ranking of intermolecular interaction energies, *Cryst. Growth Des.* **12** (2012) 5873–5877.
- G.R. Desiraju, Supramolecular synthons in crystal engineering – a new organic synthesis, *Angew. Chem. Int. Ed. Engl.* **34** (21) (1995) 2311–2327.
- M.A. Beckett, S.J. Coles, R.A. Davies, P.N. Horton, C.L. Jones, Pentaborate(1-) salts templated by substituted pyrrolidinium cations: synthesis, structural characterization, and modelling of solid-state H-bond interactions by DFT calculations, *Dalton Trans.* **44** (2015) 7032–7040.
- M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, A new polyborate anion [B₇O₉(OH)₆]³⁻: self-assembly, XRD and thermal properties of *s-fac*-[Co(en)₃][B₇O₉(OH)₆]·9H₂O, *Inorg. Chem. Commun.* **59** (2015) 95–98.
- M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, A new decaoxidooctaborate(2-) anion, [B₈O₁₀(OH)₆]²⁻: synthesis and characterization of [Co(en)]₂[B₈O₁₀(OH)₆]·5H₂O (en = 1,2-diaminoethane), *Inorg. Chem.* **54** (2015) 412–414.
- M.A. Beckett, P.N. Horton, S.J. Coles, D.W. Martin, Synthesis and structural characterization of an unprecedented nonmetal cation polyborate salt containing two different 'isolated' polyborate anions: [H₂en]₂[B₄O₅(OH)₄][B₇O₉(OH)₅]·3H₂O (en = H₂NCH₂CH₂NH₂), *Inorg. Chem.* **50** (2011) 12215–12218.
- M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, Synthesis and characterization by a single-crystal XRD study of [H₃O]₄[Cu₇(NH₃)₂(H₂O)₄(B₂₄O₃₉(OH)₁₂)]·13H₂O: an unusual bis(hydroxytrioxodidoborate) tri-metallic chain supported by a [Cu₄O]₂(B₂₀O₃₂(OH)₈)⁶⁻ cluster, *J. Cluster Sci.* **219** (2018) 1337–1343.
- CrystalClear-SM Expert 3.1 b27*, Rigaku, (2013).
- CrysAlisPro Software System*, Rigaku Oxford Diffraction, (2021).
- O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, Olex2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* **42** (2009) 339–341.
- G.M. Sheldrick, ShelXT-intergrated space-group and crystal structure determination, *Acta Cryst. A* **71** (2015) 3–8.
- G.M. Sheldrick, Crystal structure refinement with ShelXL, *Acta Cryst. C* **27** (2015) 3–8.
- M.A. Beckett, P.N. Horton, M.B. Hursthouse, D.A. Knox, J.L. Timmis, Triborate and pentaborate salts of non-metal cations derived from *N*-substituted piperazines; Synthesis, structural (XRD) and thermal properties, *RSC Adv.* **3** (2013) 15185–15191.
- C.C. Freyhardt, M. Wiebcke, J. Felsche, N(²³²Pr₄)[B₅O₆(OH)₄][B(OH)₃]₂ and N(²³⁸Bu)₄[B₅O₆(OH)₄][B(OH)₃]₂: clathrates with a diamondoid arrangement of the hydrogen bonded pentaborate anions, *J. Incl. Phen. Mol. Recog. in Chem.* **18** (1994) 161–175.
- M.A. Beckett, P.N. Horton, M.B. Hursthouse, J.L. Timmis, K.S. Varma, Templated heptaborate and pentaborate salts of cyclo-alkylammonium cations: structural and thermal properties, *Dalton Trans.* **41** (2012) 4396–4403.
- M.A. Beckett, S.J. Coles, P.N. Horton, C.L. Jones, Polyborate anions partnered with large nonmetal cations: triborate(1-), pentaborate(1-) and heptaborate(2-) salts, *Eur. J. Inorg. Chem.* **2017** (38–39) (2017) 4510–4518.
- M.Z. Visi, C.B. Knobler, J.J. Owen, M.I. Khan, D.M. Schubert, Structures of self-assembled nonmetal borates derived from -diaminoalkanes, *Cryst. Growth Des.* **6** (2006) 538–545.
- A. Perrin, M.J. Goodwin, O.M. Musa, D.S. Yuffit, J.W. Steed, Boric acid as co-crystals in Guar Gum, *Cryst. Eng. Comm.* **19** (2017) 7125–7131.
- A. Mirjafari, L. Pham, P.J. Smith, R.E. Sykora, J.H. Davis Jr., A co-crystal of 1,10-phenanthroline with boric acid: a novel aza-aromatic complex, *Acta Cryst E* **69** (2013) o1067–o1068.
- L.E. Cheruzel, M.S. Mashuta, R.M. Buchanan, A supramolecular assembly of side-by-side polyimidazole tripod coils stabilized by π-π stacking and unique boric acid templated hydrogen bonding interactions, *Chem. Commun.* (17) (2005) 2223.
- A.N. Khekhlov, Synthesis and crystal structure of the 1:1 adduct of boric acid and triphenylphosphine oxide, *Zhurnal Neorganicheskoy Khimii* **50** (2005) 1298–1302.
- M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, Oxidopolyborate anions templated by transition metal complex cations; Self-assembled synthesis and structural (XRD) of [Co(NH₃)₆]₂[B₄O₅(OH)₄]·11H₂O, [Ni(phen)₂][B₇O₉(OH)₅]·9.5H₂O and [Zn(dac)₂(H₂O)₂][B₇O₉(OH)₅]·H₂O, *J. Mol. Struct.* **1200** (2020), 127071.
- M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, Hexaborate(2-) and dodecaborate(12-) anions as ligands to zinc(II) centres: self-assembly and single crystal XRD characterization of [Zn{K³O-B₆O₇(OH)₆}(K²N-dien)]·0.5H₂O (dien = NH(CH₂CH₂NH₂)₂), (NH₄)₂[Zn{K²O-B₆O₇(OH)₆}(H₂O)₂]·2H₂O and (1,3-pn)₃[(K¹N-NH₃(CH₂)₃NH₂)₂Zn{K³O-B₁₂O₁₈(OH)₆}]₂·14H₂O, *Inorganics* **7** (2019) 44.
- M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, Two 1-D coordination polymers containing Zinc(II) hexaborates: [Zn(en)]₂[B₆O₇(OH)₆]·2H₂O (en = 1,2-diaminoethane) and [Zn(pn)]₂[B₆O₇(OH)₆]·1.5H₂O (pn = (+/-)-1,2-diaminopropane), *Crystals* **8** (2018) 470.
- D.M. Schubert, C.B. Knobler, M.Z. Visi, Diamine pentaborates with B-N bonds – zwitterionic and tethered polyborates, *Main Group Chem.* **11** (2012) 69–88.
- L.i. Jun, X. Shuping, G. Shiyang, FT-IR and Raman spectroscopic study of hydrated borates, *Spectrochim. Acta* **51** (4) (1995) 519–532.
- C. Huber, S.S. Jahromy, F. Birkelbach, J. Weber, C. Jordan, M. Schreiner, M. Harasek, F. Winter, The multistep decomposition of boric acid, *Energy Sci. Eng.* **8** (5) (2020) 1650–1666.

- [44] M. Gajhede, S. Larsen, S. Rettrup, Electron density of orthoboric acid determined by X-ray diffraction at 105 K and ab initio calculations, *Acta Cryst. B* 42 (6) (1986) 545–552.
- [45] M.C. Etter, Encoding and decoding hydrogen-bond patterns of organic chemistry, *Acc. Chem. Res.* 23 (1990) 120–126.
- [46] E. Cannillo, A. Dal Negro, L. Ungaretti, The crystal structure of ezcurrite, *Amer. Minerolog.* 58 (1973) 110–115.
- [47] G.M. Wang, C.-Y. Pan, S.-T. Zheng, G.-Y. Yang, Poly[propane-1,3-diammonium hydroxydeca-2-oxo-pentaborate], *Acta Cryst E* 63 (2007) o1104–o1105.
- [48] H. Hopfl, The tetrahedral character of the boron atom newly defined – a useful tool to evaluate a N-B bond, *J. Organomet. Chem.* 581 (1999) 129–149.
- [49] S. Toyota, M. Oki, Structure of intramolecular boron-amine complexes and proposed tetrahedral character for correlation between molecular structure and barrier to dissociation of the N-B bonds, *Bull. Chem. Soc. Jap.* 65 (1992) 1832–1840.
- [50] R. Mattes, D. Fenske, K.-F. Tebbe, The crystal and molecular structure of triptych-boroxazolidine, *Chem. Ber.* 105 (1972) 2089–2094.
- [51] Z. Taira, K. Osaki, The molecular structure of tri-n-propylamineborate, *Inorg. Nucl. Chem. Lett.* 9 (1973) 207–208.
- [52] E. Muller, H.B. Burgi, Complexes of 2,2',2''-nitrotriphenol. Part 1. A study of bimolecular nucleophilic substitution at the boron atom, *Helv. Chim. Acta.* 70 (1987) 499–510.
- [53] E. Muller, H.B. Burgi, 47. Boron-nitrotriacetate, $N(CH_2COO)_3B$: Synthesis and Crystal-Structure Determinations at 293K and 110K, *Helv. Chim. Acta.* 67 (1984) 399–405.