OXIDOPOLYBORATE ANIONS TEMPLATED BY TRANSITION-METAL COMPLEX CATIONS: SELF-ASSEMBLED SYNTHESES AND STRUCTURAL STUDIES (XRD) OF $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$, $[Ni(phen)_3][B_7O_9(OH)_5] \cdot 9.5H_2O$ and $[Zn(dac)_2(H_2O)_2][B_7O_9(OH)_5] \cdot H_2O$

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ABSTRACT

The new oxidopolyborate salts $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$ (**1**), $[Ni(phen)_3][B_7O_9(OH)_5] \cdot 9.5H_2O$ (**2**), and $[Zn(dac)_2(H_2O)_2][B_7O_9(OH)_5] \cdot H_2O$ (**3**), were crystallized, in moderate yields, from aqueous solutions containing $B(OH)_3$ and the hydroxide salt of the corresponding cationic metal complex (prepared *in situ*) in moderate yields. Complexes **1**-**3**, characterized by spectroscopic (NMR, IR) and thermal (TGA) methods and by single-crystal XRD studies, were obtained through cation-templated self-assembly reactions. Compound **1** contains insular tetraborate(2-) anions ($4\text{-}1{:}2\varDelta + 2T$) and **2** and **3** both contain insular heptaborate(2-) anions ('O$^+$' isomer, $6{:}(3\varDelta + 3T) + \varDelta$). The X-ray structures show that in all three compounds the polyborate anions are H-bonded together into extended networks, and there are multiple cation-anion H-bond interactions present in **1** and **3**. Compound **2** has cation-cation π-stacking interactions. These interactions are likely to be responsible for templating the observed structures. Thermal decomposition of **1**-**3** in air yielded amorphous anhydrous borates of composition $CoB_6O_{10.5}$, $NiB_7O_{11.5}$ and $ZnB_7O_{11.5}$, respectively.

Key Words: Heptaborate(2-); Oxidoborate; Tetraborate(2-); Transition-metal complex; XRD study.

1. INTRODUCTION

Oxidopolyborate (borate) anions are a well-known class of compounds with many synthetic materials adding to the several hundred known naturally occurring minerals [1-4]. Many of these compounds have been structurally characterised by XRD studies and their structures range from simple partially condensed insular isolated anions through to fully condensed anhydrous complex 3-D networks [5-10]. In all structures, with the exceptions of rare borate anions derived from boron suboxides, the boron centres are in either 4-coordinate (tetrahedral) or 3-coordinate (trigonal planar) environments and are bound solely to oxygen atoms with a negative charge associated with each 4-coordinate boron centre. Non boron-bridging oxygen atoms normally exist as hydroxyl groups in isolated structures whereas O$^-$ groups are not uncommon in the more condensed networks. Cations play an important role in stabilizing

such structures though solid-state interactions with the anions [1-10]. Borates are important industrially and are used in many vitreous, agricultural, biostatic, and fire retardant applications [11,12]. In aqueous solution $B(OH)_3$ exists as a complex mixture of interconverting polyborate anions [14,15] and as such constitute a Dynamic Combinatorial Library (DCL) [13]. Addition of cations to this DCL of polyborate anions facilitates self-assembly and crystallization of specific polyborate salts. Frequently, pentaborate(1-) salts are formed [16-19], and we have engaged in a research programme to investigate why this is so and have used this knowledge to encourage, by choice of preferred cations, the crystal engineering of non-pentaborate(1-) compounds [20,21]. This research has led us to believe that cation/anion H-bonding, cationic charge, and steric effects all play important roles in this self-assembly process [19,22]. In this manuscript we investigate the reactions of $[Co(NH_3)_6]^{3+}$ (a highly-charged and potentially multi-H-bond donor cation) and $[Ni(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) and $[Zn(dac)_2(H_2O)_2]^{2+}$ (dac = 1,2-diaminocyclohexane) (two sterically demanding 2+ cations) with the DCL of polyborate anions. The organic ligands 'phen' and 'dac' are drawn schematically in Figure 1. The compounds obtained from these solutions, a tetraborate(2-) salt and two heptaborate(2-) salts have been isolated and characterized by XRD studies and these results are reported herein. Schematic drawings of the structures of the insular tetraborate(2-) and the heptaborate(2-) anions, partnered by appropriate transition-metal complex cations, are also shown in Figure 1.
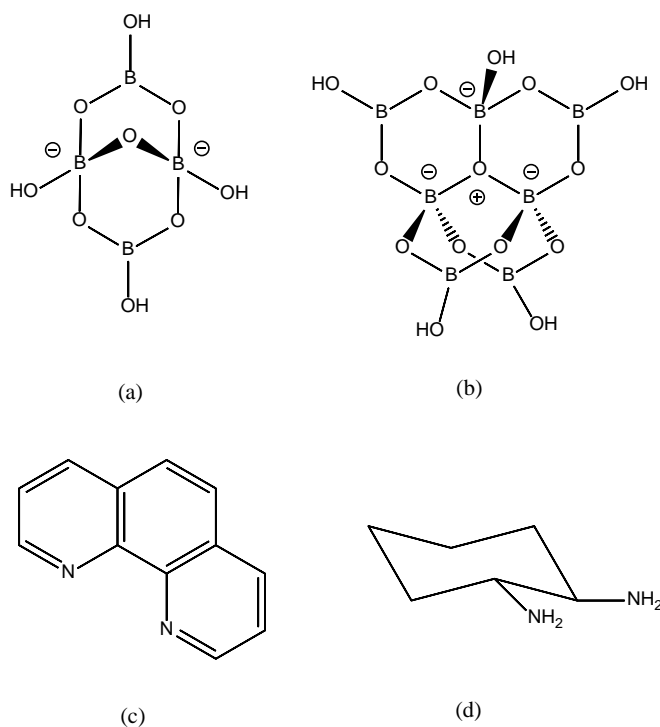

(a)   (b)

(c)   (d)

Figure 1. Schematic drawings of (a) the insular tetraborate(2-) anion, $[B_4O_5(OH)_4]^{2-}$, present in $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$ (**1**), (b) the insular heptaborate(2-) anion, $[B_7O_9(OH)_5]^{2-}$, present in $[Ni(phen)_3][B_7O_9(OH)_5] \cdot 9.5H_2O$ (**2**) and $[Zn(dac)_2(H_2O)_2][B_7O_9(OH)_5] \cdot H_2O$ (**3**), (c) phen, $C_{12}H_7N_2$, a ligand in **2**, and (d) dac, $C_6H_{12}N_2$ a ligand in **3**.

2. EXPERIMENTAL

2.1. General

Chemicals were obtained from commercial sources. $[Co(NH_3)_6]Cl_3$ was prepared by a literature method [23]. Fourier transform Infrared spectra (FTIR) were obtained as KBr pellets over the range 450-4000 cm^{-1} on a Perkin-Elmer 100 FTIR spectrometer. NMR (^1H, ^{13}C, ^{11}B) were obtained on samples dissolved in D_2O on a Bruker Avance 400 spectrometer. NMR data are reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of TMS (^1H, ^{13}C) and $BF_3 \cdot OEt_2$ (^{11}B). TGA and DSC analysis was performed between 10-800 °C (in air) on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles, with a ramp temperature rate of 10 °C min^{-1}. Magnetic susceptibility measurements were obtained on a Johnson-Matthey balance at room temperature (10 °C). Single-crystal X-ray crystallographic analyses were undertaken at the EPSRC National Crystallography service (University of Southampton). CHN analyses data were obtained from OEA laboratories Ltd in Callington, Cornwall, UK.

2.2. Synthesis spectroscopic, analytical and crystallographic data for $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$ (1)

An aqueous solution (10 mL) of $[Co(NH_3)_6]Cl_3$ (0.71 g, 2.66 mmol) was added to an aqueous suspension (40 mL) of excess OH^--activated Dowex 550A (50 g) monosphere anion exchange resin. The resulting mixture was stirred at room temperature for 24 h. The Dowex 550A resin was separated by filtration with a Buchner funnel and washed with H_2O (4 × 5 mL). The filtrate and washings, containing $[Co(NH_3)_6](OH)_3$, were reduced to a volume of 15 mL using a rotary evaporator. $B(OH)_3$ (1.64 g, 26.6 mmol) was added to the solution and gently warmed with stirring for 2 h. The aqueous solvent was evaporated to 10 mL using a rotary evaporator and the product, $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$, crystallized from the solution as orange crystals. The product was separated by filtration and dried at 40 °C for 3 h. (0.60 g, 41%). M.p. = 258-260 °C (dec.). χ_m = -330×10^{-6} cm^3 mol^{-1}. $B_{12}Co_2H_{70}N_{12}O_{38}$. Anal. Calc.: H = 6.5%, N = 15.4%. Found: H = 6.5%, N = 15.4%. ^{11}B/ppm: 10.2. IR (KBr/cm^{-1}): 3480(s), 3272(s), 1630(m), 1435(s), 1365(s), 1337(s),1160(m), 1063(s), 999(s), 946(m), 818(s). TGA: 70-150 °C, loss of 11 interstitial H_2O: 17.8% (18.1% calc.); 150-350 °C, loss of 12 NH_3 and 6 H_2O 28.7% (28.5% calc.); residual $Co_2B_{12}O_{21}$ 53.5% (53.3% calc.). Crystal data: $B_{12}Co_2H_{70}N_{12}O_{38}$, M_r = 1094.26, monoclinic, $P2_1/c$, a = 21.8485(3) Å, b = 8.85340(10) Å, c = 21.6352(3) Å, $\alpha = \gamma$ = 90°, β = 101.3410(10)°, V = 4103.26(9) Å^3, T = 100(2) K, Z = 4, μ(MoK$_a$) = 0.937 mm^{-1}, 50,435 reflections measured, 9416 unique (R_{int} = 0.0245) which were used in all calculations. The final wR_2 was 0.0629 (all data) and R_1 was 0.0252 (I > 2σ(I)).

2.3. Synthesis spectroscopic, analytical and crystallographic data for [Ni(phen)₃][B₇O₉(OH)₅]·9.5H₂O (2)

An aqueous solution (5 mL) of 1,10-phen (5.4 g, 30 mmol) was added to an aqueous solution (10 mL) of NiSO₄·6H₂O (2.6 g, 10 mmol). The reaction mixture was stirred at room temperature for 1.5 h, and then an aqueous solution (15 mL) of Ba(OH)₂·8H₂O (3.1 g, 10 mmol) was added. The reaction mixture was stirred for a further 0.5 h and then filtered by gravity. An aqueous solution (15 mL) of B(OH)₃ (6.2 g, 100 mmol) was added to the filtrate and the solution was stirred at room temperature for a further 2 h. The volume of the solution was reduced to 20 mL (rotary evaporator) and the solution was distributed over a few small vials and left (10 d) to afford pink crystals of [Ni(phen)₃][B₇O₉(OH)₅]·9.5H₂O (4.3 g. 40%) which were isolated by filtration. M.p. > 300 °C (dec.). χ_m = 3220×10⁻⁶ cm³ mol⁻¹. C₃₆H₄₈B₇N₆NiO₂₃.₅. Anal. Calc.: C = 40.2%, H = 4.5%, N = 7.8%. Found: C = 39.8%, H = 4.8%, N = 7.6%. ¹¹B/ppm: 14.87. IR (KBr/cm⁻¹): 3393(s), 1648(m), 1519(m), 1426(s), 1338(s), 1164(s), 1147(s), 1071(s), 848(s), 803(s), 726(s). TGA: 100-220 °C, loss of interstitial 9.5 H₂O: 16.6% (16.0% calc.); 220-340 °C, condensation of polyborate which loss of 2.5 H₂O: 5.4% (4.2% calc.); 340-750 °C, oxidation of organic content 49.0% (50.0% calc.); residual NiB₇O₁₁.₅ 29.0% (29.7% calc.). Crystal data: C₃₆H₄₈B₇N₆NiO₂₃.₅, M_r = 1075.18, monoclinic, Ia (No. 9), a = 26.4855(3) Å, b = 15.86160(10) Å, c = 25.0865(3) Å, β = 115.2530(10)°, $\alpha = \gamma$ = 90°, V = 9531.72(18) Å³, T = 100(2) K, Z = 8, Z' = 2, μ(CuK$_\alpha$) = 1.385 mm⁻¹, 47968 reflections measured, 16407 unique (R_{int} = 0.0416) which were used in all calculations. The final wR_2 was 0.1758 (all data) and R_1 was 0.0609 (I > 2σ(I)).

2.4. Synthesis spectroscopic, analytical and crystallographic data for [Zn(dac)₂(H₂O)₂][B₇O₉(OH)₅]·H₂O (3)

An aqueous solution (20 mL) of cis-/trans-1,2-(NH₂)₂C₆H₁₀ (2.3 g, 20 mmol) was added to an aqueous solution (5 mL) of ZnSO₄·H₂O (1.8 g, 10 mmol). The reaction mixture was stirred for 0.1 h, and then an aqueous solution (15 mL) of Ba(OH)₂·8H₂O (3.1 g, 10 mmol) was added. The reaction mixture was stirred for a further 0.5 h and then filtered to remove BaSO₄. An aqueous solution (20 mL) of B(OH)₃ (6.2 g, 100 mmol) was added to the filtrate and the solution was stirred at room temperature for 2 h. The solution was then distributed over several vials and left for 14 days to yield to crystallize as colourless/light pink crystals of [Zn(dac)₂(H₂O)₂][B₇O₉(OH)₅]·H₂O (3.2 g, 49%). M.p. = 260-265 °C (dec.). χ_m = -290×10⁻⁶ cm³ mol⁻¹. C₁₂H₃₉B₇N₄O₁₇Zn. Anal. Calc.: C = 22.1%, H = 6.0%, N = 8.6%. found: C = 22.0%, H = 6.1%, N = 8.7%. ¹¹B/ppm: 16.83. IR (KBr/cm⁻¹): 3341(s), 3284(s), 2933(m), 2861(w), 1610(m), 1417(s), 1373(s), 1259(s), 1203(s), 1137(s), 1088(s), 1016(s), 956(m), 898(m), 850(s), 807(s). TGA: 100-200 °C, 1 interstitial and 2 coordinated H₂O 8.1% (8.3% calc.); 200-400 °C, condensation of polyborate with loss of further 2.5 H₂O: 7.9 % (6.9% calc.); 400-700 °C, oxidation of organic content 34.3% (34.9% calc.); residual ZnB₇O₁₁.₅ 49.7% (49.8% calc.). Crystal data:

$C_{12}H_{39}B_7N_4O_{17}Zn$, M_r = 652.51, monoclinic, C2/c (No. 15), a = 22.4387(3) Å, b = 10.96310(10) Å, c = 23.0303(3) Å, β = 108.3600(10)°, $\alpha = \gamma = 90°$, V = 5377.01(12) Å^3, T = 100(2) K, Z = 8, Z' = 1, μ(MoK$_\alpha$) = 0.997 mm^{-1}, 33978 reflections measured, 6166 unique (R_{int} = 0.0226) which were used in all calculations. The final wR_2 was 0.0987 (all data) and R_1 was 0.0351 (I > 2σ(I)).
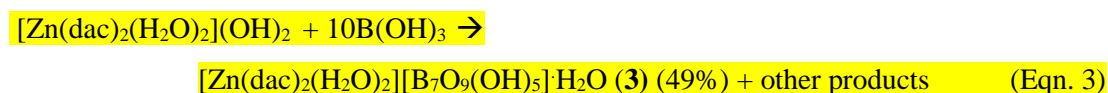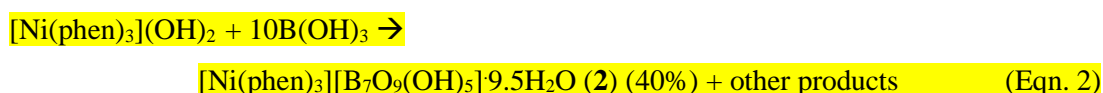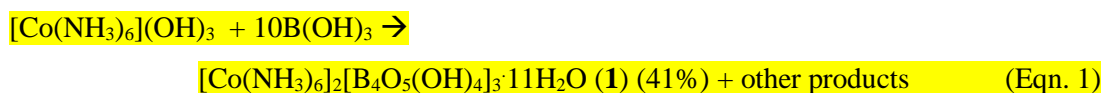
2.5. X-ray crystallography for 1, 2 and 3.

Suitable crystals of **1**, **2** and **3** was selected and mounted on MITIGEN holders in perfluoroether oil. 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 for **1**, or HF Varimax optics (100µm focus) was used for **3**. A Rigaku 007HF equipped with Varimax confocal mirrors and an AFC11 goniometer and HyPix 6000 detector diffractometer was used for **2**. Crystals were kept at T = 100(2) K during data collection. Cell determination and data collection for **1** were performed using *CrystalClear-SM Expert 3.1 b27* [24] whilst cell determination and data collection for **2** and **3** were performed using CrysAlisPro [25] that was also used for all data reduction, scaling and corrections. Using Olex2 [26] the structures were solved with the ShelXT [27] structure solution program by the Intrinsic Phasing solution method. The models were refined with SHELXL-2018/3 [28] using Least Squares minimisation.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The new compounds $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$ (**1**), $[Ni(phen)_3][B_7O_9(OH)_5] \cdot 9.5H_2O$ (**2**), and $[Zn(dac)_2(H_2O)_2][B_7O_9(OH)_5] \cdot H_2O$ (**3**) were obtained from the reaction of the appropriate transition-metal complex (with [OH]$^-$ counterions) and ten equivalents of B(OH)$_3$ as shown in Equations 1-3. The transition-metal complexes with [OH]$^-$ counterions were prepared *in situ* from the corresponding Cl$^-$ salt (for **1**) or SO$_4^{2-}$ salts (for **2** and **3**) using either ion exchange resin (for **1**) or metathesis reactions with Ba(OH)$_2$ (for **2** and **3**).

$[Co(NH_3)_6](OH)_3 + 10B(OH)_3 \rightarrow$

$\qquad [Co(NH_3)_6]_2[B_4O_5(OH)_4]_3 \cdot 11H_2O$ (**1**) (41%) + other products $\qquad$ (Eqn. 1)

$[Ni(phen)_3](OH)_2 + 10B(OH)_3 \rightarrow$

$\qquad [Ni(phen)_3][B_7O_9(OH)_5] \cdot 9.5H_2O$ (**2**) (40%) + other products $\qquad$ (Eqn. 2)

$[Zn(dac)_2(H_2O)_2](OH)_2 + 10B(OH)_3 \rightarrow$

$\qquad [Zn(dac)_2(H_2O)_2][B_7O_9(OH)_5] \cdot H_2O$ (**3**) (49%) + other products $\qquad$ (Eqn. 3)

Compounds **1-3** were prepared in moderate yields (40-49%) and characterized by magnetic susceptibilty measurements, spectroscopic (IR, NMR) and thermal (TGA/DSC) analysis (Section 3.2) and by single-crystal XRD studies (Section 3.3). Compounds **1-3** are formulated as ionic solids containing transition-metal complex cations, insular polyborate anions, and waters of crystallization. Elemental analysis of bulk samples were consistent with their formulations obtained by crystallography and thermal studies and single-crystal diffraction studies, indicating that the crystals chosen for XRD analyses were representative of bulk samples.

Compounds **1-3** crystallized from aqueous solution as ionic salts through cation templated self-assembly processes from the DCL of polyborate anions present in the basic solutions. Pentaborate(1-) salts are easily synthesised by this methodology particularly when the cations are organic and are not too sterically demanding [16-19]. Such non-metal cation salts usually exist as giant 3-dimensional pentaborate(1-) networks with cations situated within the cavities [7,17,29]; the networks are held together through strong $R_2^2(8)$ [19,30] anion-anion H-bonds between neighbouring pentaborate(1-) moieties. The driving force partly responsible for the formation of these pentaborate(1-) salts is the formation of the energetically favourable anion-anion H-bonded networks. The strategy of using sterically demanding, more highly charged ($> +1$), transition-metal complex cations to template non-pentaborate(1-) salts has been successful since a tetraborate(2-) and two heptaborate(2-) salts have been formed. The templating cations are too large to be accommodated within a simple pentaborate(1-) lattice [19,22] and therefore template other structures. The cations in **1** and **3** are not only large but also has the potential to form many energetically favourable H-bond cation-anion donor interactions. These additional interactions facilitate the formation of non-pentaborate(1-) salts. The solid-state structures of **1-3**, including their H-bond interactions are discussed in detail in Section 3.3.

3.2. Magnetic, spectroscopic and thermal studies

Magnetic susceptibility measurements on **1-3** were determined at room temperature by using a Evans (Johnson-Matthey) balance [31]. These measurements confirmed the expected magnetic properties of the salts with compounds **1** (d^6, Co^{3+}) and **3** (d^{10}, Zn^{2+}) diamagnetic and compound **2** (d^8, Ni^{2+}) paramagnetic. The observed μ_{eff} of 2.77 BM for **2** corresponds well with the calculated spin-only $\mu_{s.o.}$ value for 2 unpaired electrons, (2.82 BM) and is consistent with μ_{eff} values for other octahedral Ni^{2+} complexes [32]. Attempts were made to obtain NMR data on **1-3** but these compounds were all insoluble in organic solvents and only dissolved (with decomposition) in D_2O. The decomposition occurs in aqueous solution as the DCL's of the original starting species are reformed. ^{11}B NMR spectra of these decomposition solutions were obtained for **1-3** and these all show just 1 peak consistent with fast $B(OH)_3/[B(OH)_4]^-$ exchange [14]. The ^{11}B signal originating from the decomposition **1** was upfield

of those observed for those originating from the decomposition of in **2** and **3**. The observed [11]B chemical shifts for **1** and **2** were in agreement with shifts calculated from the boron/charge ratio [14,19] whereas **3** was slightly more downfield than expected. The ^{1}H spectra of **1** was not reported since it only contains exchangeable H atoms on NH_3 ligands and ^{1}H and ^{13}C spectra of **2** were not obtained due to the paramagnetic nature of the metal complex. [1]H and ^{13}C spectra of **3** were obtained (see Supplementary Information) but are not reported since they were not characteristic of the salt and indicated that the Zn(II) complex was also labile and that an equilibrium mixture was present.

IR spectra of polyborate species may be assigned with reference to Li *et al*. [33], The strong bands in the B-O region of the tetraborate(2-) salt, **1**, are therefore assigned as $\nu_{as}(B_{(3)}\text{-O})$ (1435, 1365 and 1337cm^{-1}), $\nu_{as}(B_{(4)}\text{-O})$ (1063, 999 cm^{-1}), $\nu_{s}(B_{(3)}\text{-O})$ (946 cm^{-1}) and $\nu_{s}(B_{(4)}\text{-O})$ (818 cm^{-1}). IR spectra of the heptaborate(2-) ion contained in **2** and **3** are not specifically included in work of Li *et al*. [33] but similar general assignments are possible. Bands at 905 and 860 cm^{-1} have been observed in both the non-metal cation salts $[cyclo\text{-}C_6H_{11}NH_3]_2[B_7O_9(OH)_5].3H_2O\cdot B(OH)_3$ and $[cyclo\text{-}C_7H_{13}NH_3]_2[B_7O_9(OH)_5].2H_2O\cdot 2B(OH)_3$ and were previously proposed as diagnostic for this anion [34]. Since then further synthetic and IR studies on $[C_{10}H_{22}N_2][B_7O_6(OH)_5]\cdot 2H_2O$ [22] and $[Cu(dac)_2(H_2O)_2][Cu(dac)_2][B_7O_9(OH)_5]_2\cdot 4H_2O$ [35] have only confirmed the lower energy band, indicating that the 905 cm^{-1} band in the original study probably had $B(OH)_3$/organic-based origins. In agreement with this, compounds **2** and **3** show strong bands in the $\nu_{s}(B_{(4)}\text{-O})$ region at 848 and 850 cm^{-1}, respectively.

TGA plots were obtained for compounds **1-3** (in air) over the temperature range 20-800 °C (see Supplementary Information). Compounds **1-3** thermally decompose in air to afford anhydrous metal borates of composition $CoB_6O_{10.5}$, $NiB_7O_{11.5}$ and $ZnB_7O_{11.5}$, respectively. These specific metal/boron ratios are in accord with their original stoichiometries in **1-3**. Such behaviour has been noted before for polyborate salts containing transition-metal complexes [20,21,35-40]. Interestingly, the decomposition process is concluded by ~400 °C for **1** but temperatures in excess of 700 °C are required for both **2** and **3**. This may be explained since for **1** steps involving the loss of interstitial H_2O, loss of coordinated NH_3 and loss of H_2O through polyborate condensation are observed. Compounds **2** and **3** also lose interstitial H_2O and undergo loss of H_2O through polyborate condensation at lower temperatures, but differ from **1** in that they also possess organic ligands and these are lost through oxidative processes which occur at higher temperatures.

3.3. Crystallographic studies

Compound **1** is formulated as $[Co(NH_3)_6]_2[B_4O_5(OH)_4]_3\cdot 11H_2O$ and crystallographically contains three $[Co(NH_3)_6]^{3+}$ cations, with two of them bisected by an internal plane of symmetry and therefore equating

to one, three independent $[B_4O_5(OH)_4]^{2-}$ anions and eleven interstitial waters of crystallization. A thermal ellipsoid drawing of these components is shown in Figure 2.
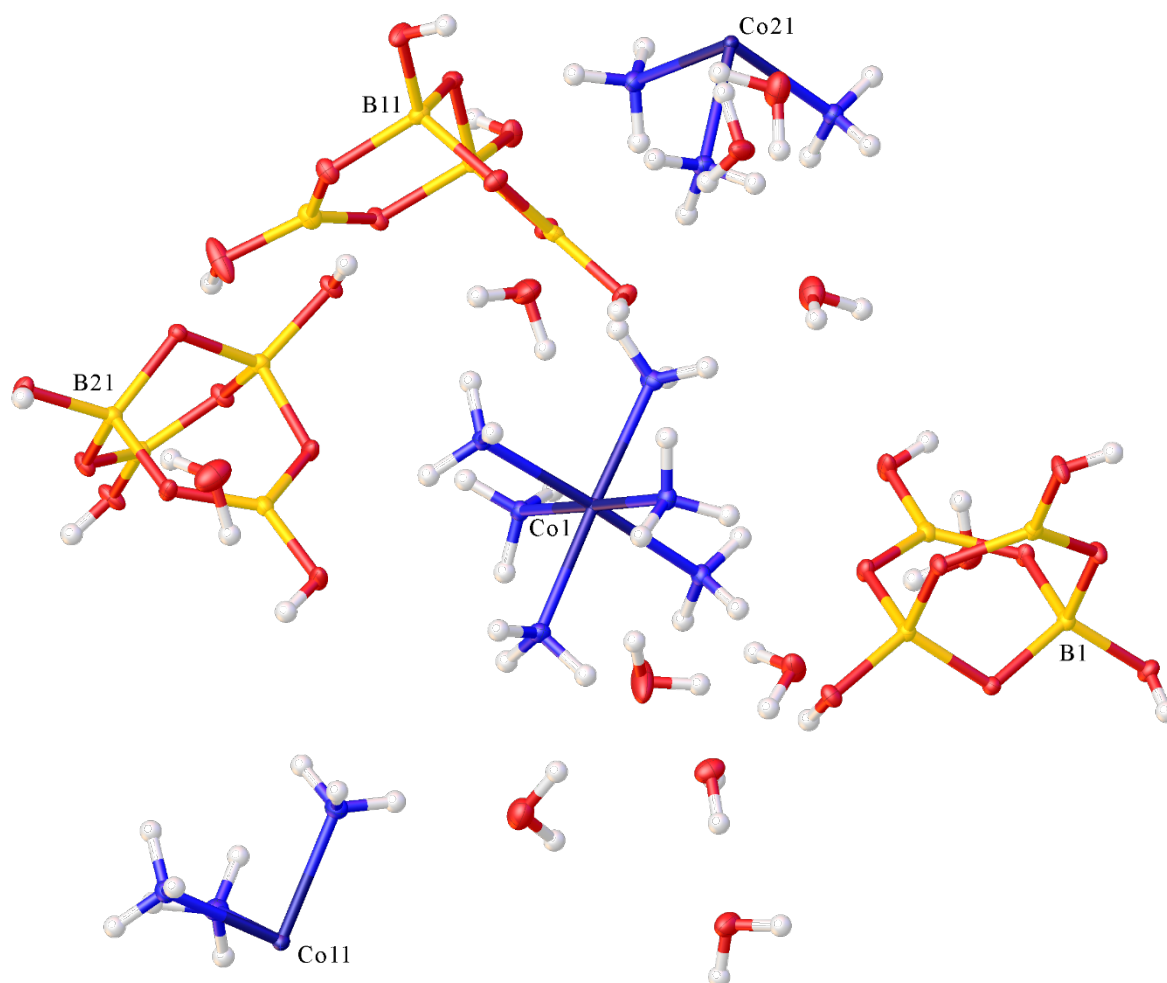

Figure 2. Crystal diagram showing the asymmetric unit of **1** with basic atomic numbering scheme.

The $[Co(NH_3)_6]^{3+}$ cations are octahedral with Co-N bond lengths ranging from 1.9557(12)–1.9761(12) Å and are typical of those observed in other reported $[Co(NH_3)_6]^{3+}$ salts [41]. The tetraborate(2-) anion is well-known with the structural descriptor [42] of 4-1:2Δ +2T. It occurs in borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ [43] and a number of other crystallographically determined structures with bond lengths and bond-angles in agreement with data published for transition-metal complex tetraborates [44-46] and non-metal cation tetraborates [47-49]. The tetraborate(2-) anions H-bond together to a giant supramolecular anionic network. These H-bond interactions are of two types: numerous pairwise $R_2^2(8)$ interactions and many simple D interactions incorporated into complex polymeric chains (Etter

nomenclature [30]). Pairwise $R_2^2(8)$ interactions are known to be particularly energetically favourable and dominate the energetics of more commonplace pentaborate(1-) structures [19]. Diagrams of these anion-anion interactions can be seen in the Supplementary Information (Figures S1-S4), and full details of all the H-bond interactions are available in the Supplementary Information. The potential of $[Co(NH_3)_6]^{3+}$ cations as a multi-H-bond donors is noted in the introduction. It is evident that cation-anion interactions also make significant contribution to stabilizing the supramolecular H-bonded tetraborate(2-) network since the crystallographic cations in compound **1** use *all* amino hydrogen atoms in donor interactions to either tetraborate(2-) anions or interstitial H_2O molecule. A drawing the secondary coordination sphere around Co1 is shown in Figure 3 where it can be seen to form donor interactions with six tetraborate(2-) anions (and six H_2O molecules, not shown). The combination of these cation-anion H-bond interactions, together with the strong pairwise $R_2^2(8)$ anion-anion H-bond interactions, are implicated in the preference of this system to self-assemble into a tetraborate(2-) salt rather than pentaborate(1-) salt. However, other factors such as charge on the cation (> 1), steric effects, stoichiometry, and packing must also play important roles.
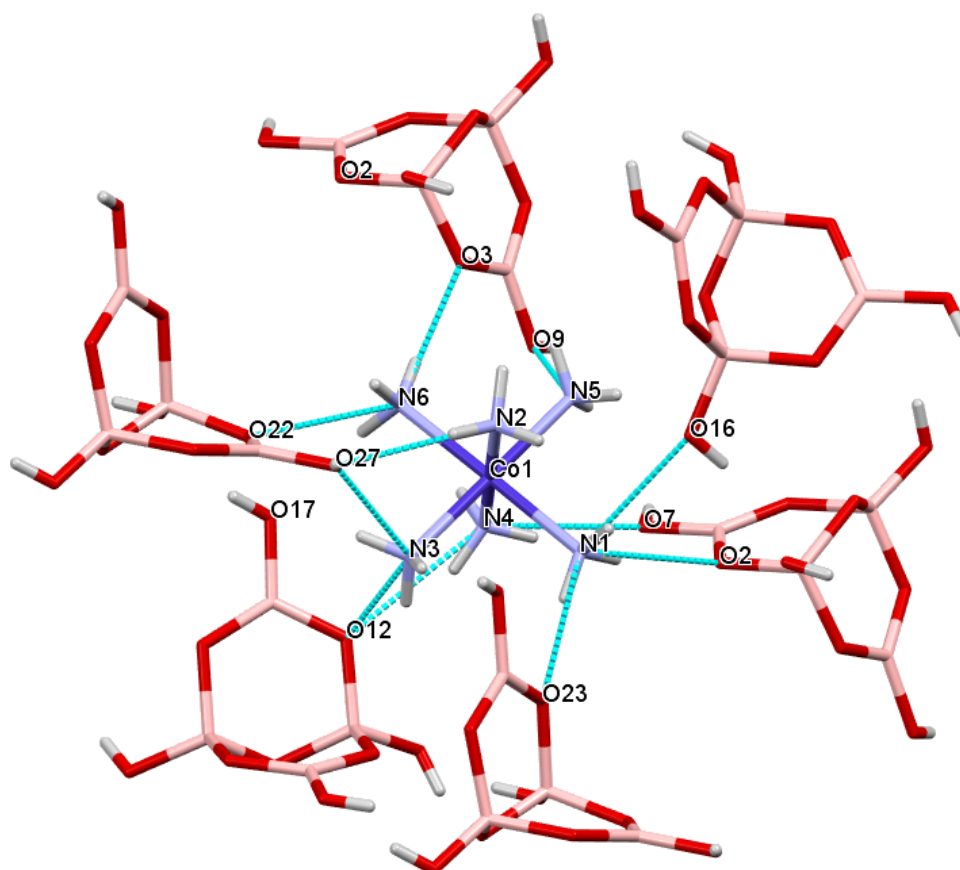

Figure 3. The H-bond interactions of the $[Co(NH_3)_6]^{3+}$ cation in **1** containing Co1 with six tetraborate(2-) anions. Additional interactions with H_2O molecules exist but are not shown.

Compound **2** is formulated as [Ni(phen)$_3$][B$_7$O$_9$(OH)$_5$]·9.5H$_2$O with the crystallographic asymmetric unit of the crystallographic cell comprised of two independent [Ni(phen)$_3$]$^{2+}$ cations, two independent [B$_7$O$_9$(OH)$_5$]$^{2-}$ anions and 19 waters of crystallization; there is disorder in some of these H$_2$O molecules. A thermal ellipsoid drawing of the structure of **2** is shown in Figure 4. The cations in **2** are both essentially distorted octahedral with Ni-N bonds lengths not significantly and range from 2.082(5)-2.098(5) Å (Ni1) and 2.086(5)-2.108(6) Å (Ni2). The narrow bite of the phen ligand imposes three N-Ni-N angles per cation significantly smaller [av. 79.7(2)º] than the 90º angles expected for an octahedral arrangement and also influences the magnitude of the *trans* angles. The cations in **2** are chiral with the Δ configuration adopted for the cation containing Ni1 whereas the cation containing Ni2 has the Λ configuration [50]. The average Ni-N bond lengths (2.095(8) Å) and N-Ni-N angles [169.3(2)º, 90.1(2)º] are in accord with literature values for other reported [Ni(phen)$_3$]$^{2+}$ cations [51].

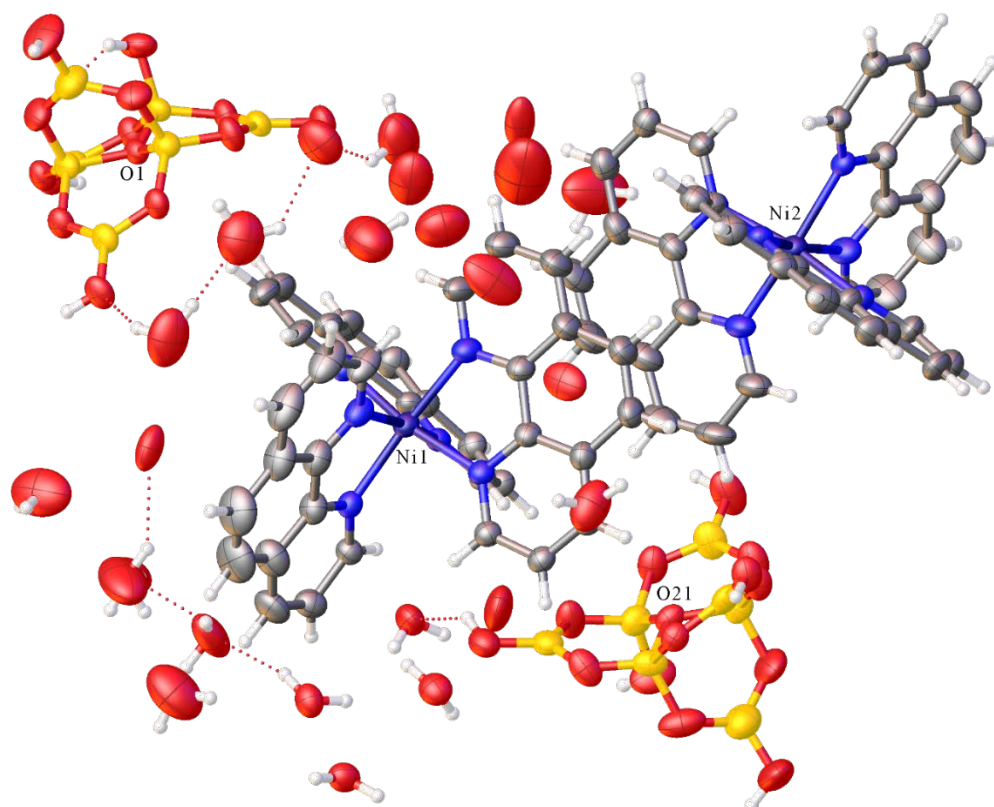**Figure 4.** Structure of **2** showing (selected) atomic numbering scheme.

Compound **3** is formulated as [Zn(dac)$_2$(H$_2$O)$_2$][B$_7$O$_9$(OH)$_5$]·H$_2$O and has the asymmetric unit of the crystallographic unit cell comprised of a [B$_7$O$_9$(OH)$_5$]$^{2-}$ anion partnered with two independent 'half-cations' of [Zn(dac)$_2$(H$_2$O)$_2$]$^{2+}$ and a water of crystallization (Figure 5); the cations are disordered into two components. Each independent cation has a distorted octahedral geometry with two H$_2$O ligands

trans and the two dac ligands arranged centrosymetrically around the zinc(II) centre. The cyclohexyl rings of the dac ligands in **3** are in chair conformations with their amino groups equatorial. The stereochemistry of one dac ligand of each cation is is *R,R* whilst the other dac ligand has *S,S* stereochemistry. Zn-O and Zn-N bond lengths are not significantly different to data from known distorted octahedral aqua or amine zinc(II) complexes [52].
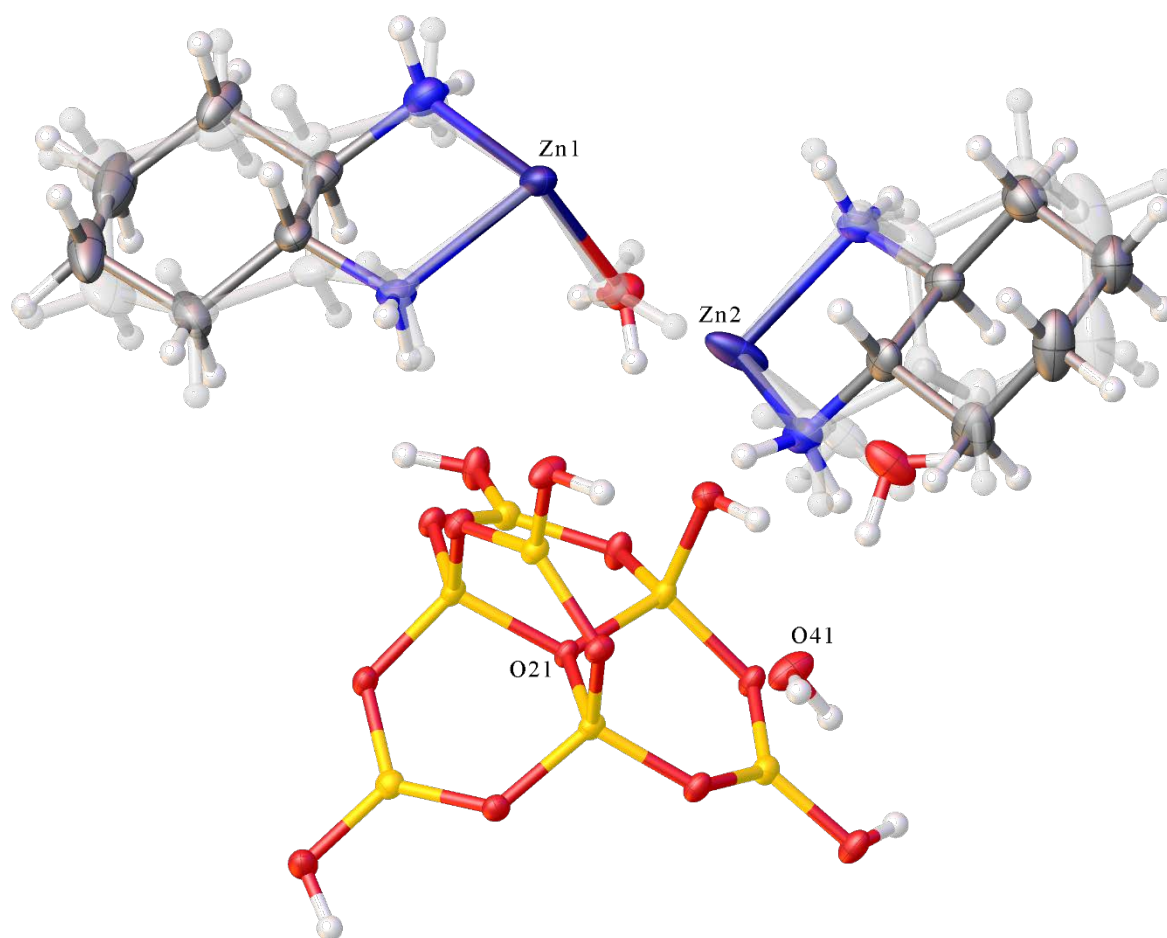

Figure 5. Structure of **3** showing $[B_7O_9(OH)_5]^{2-}$ anion partnered with two independent 'half-cations' of $[Zn(dac)_2(H_2O)_2]^{2+}$ and a water of crystallization. (The lesser components of disordered dac is shown in light grey.

Compounds **2** and **3** both contain structurally similar insular $[B_7O_9(OH)_5]^{2-}$ anions and these are conveniently discussed together. There are two known insular heptaborate(2-) anions and these have been referred to in the literature as the 'chain' isomer or the 'O⁺' isomer [7]. Compounds **2** and **3** are

both further examples of this 'O$^+$' isomer (Figure 1b) and this isomer has the structural descriptor [42] of 6:(3Δ + 3T) + Δ. Salts containing this 'O$^+$' isomer are rare and examples are limited to four organic-cation salts [22,34,53] and two transition-metal complex cation salts [35,54]. The 'O$^+$' isomer of the heptaborate(2-), has the characteristic structural motif of a pyramidal 3-coordinate O atom (bearing a formal positive charge) bound to three 4-coordinate B centres (each bearing formal negative charges). In **2** these oxygen atoms are O1 and O21 for the two independent anions and in **3** it is O21. The O1 and O21 to B bond lengths (in **2**) vary from 1.499(8)-1.532(6) Å and those for O21 (in **3**) range from 1.5086(19)-1.5152(19) Å. These distances are significantly longer than the other B-O distances in the anion which are in the usual ranges for B$_{trig}$-O and B$_{tet}$-O bonds [16-22,34,35,53,54]. As expected, these O$^+$ atoms are pyramidal with O-B-O angles sums of 347.9(4)^o and 349.0(5)^o (in **2**) and 349.59(11)^o (in **3**). Other B-O-B, O-B$_{trig}$-O and O-B$_{tet}$-O angles are within the usual ranges observed in polyborate and related boroxole species [16-22,34,35,53-57].

Since cation-anion H bond donor interactions can strongly influence the observed templated polyborate structures (*e.g.* as in **1**) it is important to examine the potential cation H-bond donor sites in **2** and **3**. There are no potential H-bond cation donor sites in **2**. The supramolecular architecture of **2** is discussed in detail in the next paragraph. Compound **3** is structurally very similar to [Cu(dac)$_2$(H$_2$O)$_2$][Cu(dac)$_2$][B$_7$O$_9$(OH)$_5$]$_2$·4H$_2$O [35] and has 8 dac amino ligand hydrogens atoms and 4 coordinated-water hydrogens per cation as potential H-bond donors. A diagram of the secondary coordination sphere around Zn1 of **3** is shown in Figure 6. There are two heptaborate(2-) anions within the secondary coordination shell around Zn1 and O29 is the heptaborate acceptor site from N1H1C. The coordinated H$_2$O ligand (O1) forms a H-bond to the same heptaborate (O34) forming a R$_2^2$(8) ring, which includes Zn1 within the ring system. The two (symmetery related) O1 atoms also receive donor H-bonds from two aqua ligands (O11) on neighbouring cations, which contain Zn2. The secondary coordination sphere around Zn2 also involves 3 out of the 4 dac amino H-atoms H-bonding to 4 heptaborate(2-) anions. The hetaborate(2-) anions also H-bond to one another *via* strong R$_2^2$(8) interactions similar to those found in **1** and in many pentaborate(1-) structures [16-19]. Details of all these H-bonding interactions and a diagram of the secondary coordination sphere around Zn2 are available in the Supplementary Information (Figure S5). Again, the combination of these cation-anion H-bond interactions, together with the strong pairwise R$_2^2$(8) anion-anion H-bond interactions, are implicated in the preference of this system to self-assemble into a rarely observed heptaborate(2-) salt.
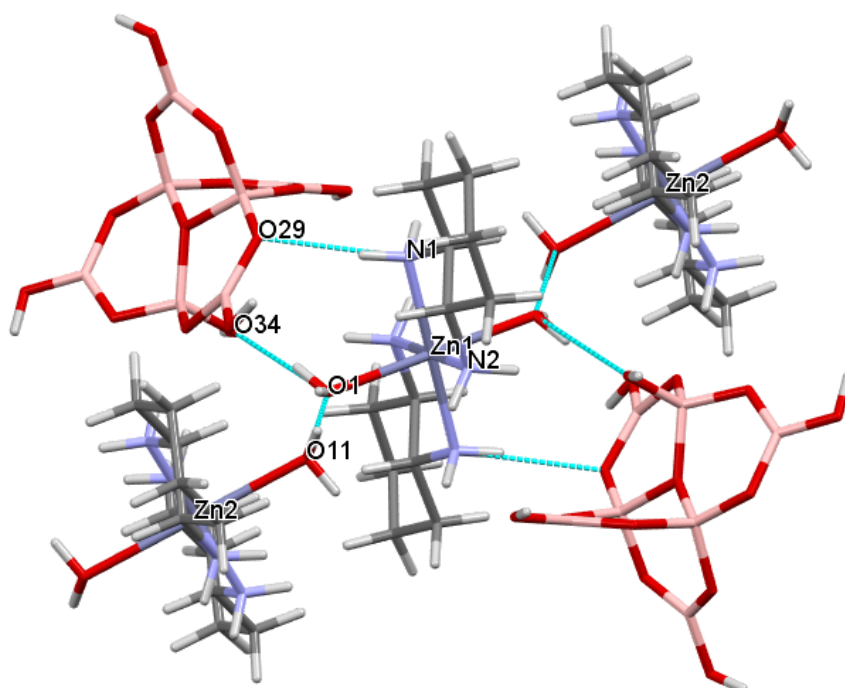
Figure 6. Secondary coordination shell around the Zn1 centre in **3**.

has no potential H-bond donor sites the cation must be influencing the observed polyborate architecture by other means. To a first approximation it is a relatively large, approximately spherical, cation (diameter of ~11.5 Å) presenting hydrophobic CH bonds to the polyborate anions. This cation size is too large to fit comfortably within a possible pentaborate(1-) anion structure [22]. In addition to this steric issue, each cation in **2** interacts with 3 neighbouring cations in face-to-face π-stacking arrangements [58] forming layers of cations in a supramolecular 2-D hexagonal honeycomb 6,3-net topology (Figure 7). The π-stacking interactions are 3.5-3.8 Å (Supplementary Information Figure S6) and these distances are typical for such interactions [58]. The heptaborate(2-) anions are linked together into chains by strong reciprocal $R_2^2(8)$ interactions and the chains are cross-linked into 2-D planes by the interstitial H_2O molecules (Figure 8). Detailed H-bond interactions and a packing diagram of the structure is available in Supplementary Information (Figure S7). The combination of steric effects, cation-cation π-stacking interactions and anion-anion H-bond interactions all contribute to the energetics responsible for templating this unusual heptaborate(2-) structure.
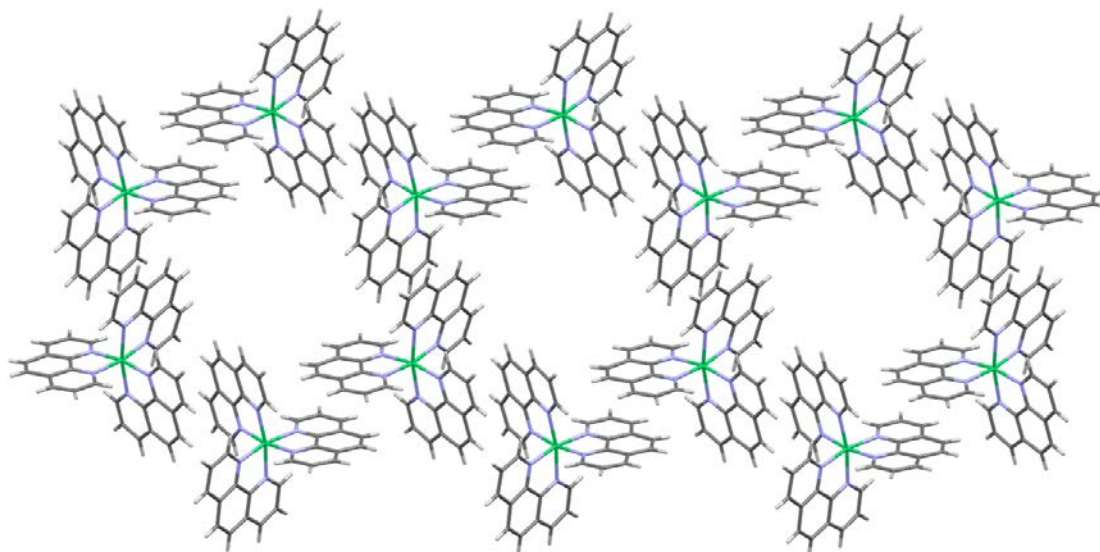
Figure 7. Honeycomb arrangement of the [Ni(phen)₃]²⁺ cations in **2**.
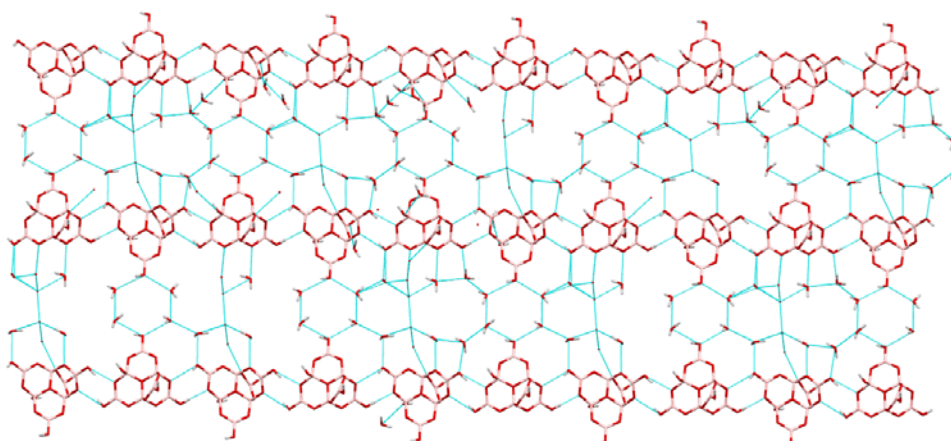
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Figure 8. A plane in **2** comprised of chains of heptaborate(2-) anions linked by $R_2^2(8)$ H-bonding interations and cross-linked by H-bonded H_2O molecules.

4. CONCLUSION

Three new polyborate salts (**1-3**), containing the insular tetraborate(2-) and heptaborate(2-) anions, have been prepared by adopting a synthetic strategy with the aim of avoiding the synthesis of pentaborate(1-) salts. The strategy involved the use of a highly-charged and potentially multi-H-bond donor cation,

$[Co(NH_3)_6]^{3+}$, and two sterically demanding 2+ cations ($[Ni(phen)_3]^{2+}$ and $[Zn(dac)_2(H_2O)_2]^{2+}$) to template their synthesis from a DCL of polyborate anions which coexist in alkaline aqueous solution. XRD diffraction studies confirm that multiple cation-anion H-bond interactions are present in **1** and **3**. Compounds **1-3** all show extensive anion-anion $R_2^2(8)$ H-bond interactions. These H-bond interactions are important in stabilizing their observed solid-state structures. Compounds **2** and **3** contain more sterically demanding cations and it is believed this also influences the templating energetics. Furthermore, **2** is unable to form H-bond interactions with the heptaborate(2-) anions but the structure is stabilized by cation-cation π-stacking interactions. This study further confirms that cation/anion H-bonding, cationic charge, and steric effects all play important roles in these self-assembly processes.

Acknowledgments

Supplementary materials

Crystallographic data (including detailed H-bond data, and additional Figures) TGA plots, IR and NMR spectroscopic data, have been deposited as supplementary information. CCDC1939463, CCDC1939464, and CCDC1939465 also contain the 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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