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Two 1-D Coordination Polymers Containing Zinc(II) Hexaborates: $[Zn(en)\{B_6O_7(OH)_6\}]\cdot 2H_2O$ (en = 1,2-diaminoethane) and $[Zn(pn)\{B_6O_7(OH)_6\}]\cdot 1.5H_2O$ (pn = 1,2-diaminopropane)

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Abstract: The synthesis and characterization by single-crystal X-ray diffraction (XRD) studies of two new zinc(II) hexaborate(2−) complexes, $[Zn(en)\{B_6O_7(OH)_6\}]\cdot 2H_2O$ (en = 1,2-diaminoethane) (**1**) and $[Zn(pn)\{B_6O_7(OH)_6\}]\cdot 1.5H_2O$ (pn = 1,2-diaminopropane) (**2**), are reported. These complexes crystallize from aqueous solutions containing 10:1 ratios of $B(OH)_3$ and the appropriate Zn(II) amine complexes ($[Zn(en)_3][OH]_2$ or $[Zn(pn)_3][OH]_2$) through self-assembly processes. The hexaborate(2−) anions in **1** and **2** are coordinated to two Zn(II) centers and form one-dimensional (1-D) polymeric coordination chains. $R_2{}^2(8)$ and $R_2{}^2(6)$ inter-chain H-bond interactions play an important role in these self-assembly processes and are discussed.

Keywords: coordination polymer (1-D); H-bond; hexaborate(2−); oxidoborate; polyborate; self-assembly; X-ray structure; zinc(II) complex

1. Introduction

Anionic boron species are commonly referred to as borates. Hydroxyoxidopolyborates ("oxidoborates" or "borates") are a class of anionic boron derivatives that contain boron atoms bound only to hydroxyl oxygen atoms, or oxygen atoms that bridge boron centers. The boron centers may be three- or four-coordinate, and it is the latter (or occasionally deprotonated hydroxyl groups) that formally house the negative charges. Polyborates are readily synthesized from the addition of $B(OH)_3$ to a basic aqueous solution containing templating cations or by solvothermal methods [1]. Compounds are formed through self-assembly processes involving a dynamic combinatorial library (DCL) [2,3] of polyborate anions that are present in the aqueous reactant solution. The DCL of polyborate anions arise since dissolution of $B(OH)_3$ in aqueous solution at moderate pH results in numerous polyborate anions in fast-exchange equilibria [4,5]. The polyborate salts obtained from aqueous solution are usually comprised of discrete, insular anions, partnered by the templating cations. Crystalline products are formed, often in high yield, since they are self-engineered through energetically favorable solid-state interactions such as electrostatic charges, ligand–metal coordination bonds, steric effects, H-bonding interactions, and crystal packing forces [6,7]. Products often contain the pentaborate(1−) anion since this anion is well adapted to forming a wide variety of crystalline lattices that are held together by strong H-bond interactions [8–11]. Polyborates prepared via solvothermal methods are often more condensed with polymeric one-dimensional (1-D) anionic chains, two-dimensional (2-D) planes, or three-dimensional (3-D) nets [1,12]. In an attempt to encourage the formation of new polyborate anions, we recently adopted a strategy of using more highly charged (>+1) inert transition-metal complexes [13] as templating cations. In addition, cations that specifically could form many H-bond donor interactions with polyborate anions were chosen. This strategy was successful and we recently reported two such novel isolated polyborate anions: heptaborate(3−) [14] and octaborate(2−) [15].

Our work with templating Zn(II) complexes led us to prepare $[(H_3NCH_2CH_2)Zn\{B_{12}O_{18}(OH)_6\}Zn(en)(NH_2CH_2CH_2NH_3)]\cdot 8H_2O$ containing an isolated dodececaborate(6−) anion coordinated to two Zn(II) atoms in monodentate and tridentate modes [16]. Zn(II) amine complexes are labile, with rapid ligand dissociation and substitution reactions [13]; therefore, they form their own DCL of potentially templating cations. Polyborate/Zn((II) chemistry is quite well represented in the literature as either salts of isolated polyborates [17,18] or as polyborates coordinated to Zn(II) sites [17–24]. Additionally, coordinated polyborates may be "isolated" [17,19] or "condensed" [20–24]. The complex $Zn[B_3O_4(OH)_3]$, which contains infinite polyborate chains coordinated to a tetrahedral Zn(II) center [25], is an industrially important polymer additive and preservative in wood composites.

In this manuscript, we describe the synthesis and X-ray diffraction (XRD) structures of two new zinc(II) hexaborate(2−) complexes, $[Zn(en)\{B_6O_7(OH)_6\}]\cdot 2H_2O$ (**1**) and $[Zn(pn)\{B_6O_7(OH)_6\}]\cdot 1.5H_2O$ (**2**) (pn = $NH_2CH_2CHMeNH_2$), which are templated from $B(OH)_3$ and the Zn(II) amine complexes $[Zn(en)_3][OH]_2$ and $[Zn(pn)_3][OH]_2$, respectively. A schematic diagram of the hexaborate(2−) anion found in **1** and **2** is shown in Figure 1. The hexaborate(2−) anions in these complexes are coordinated to two Zn(II) centers and form 1-D polymeric coordination chains. Novel inter-chain H-bond interactions are described and discussed in this manuscript.

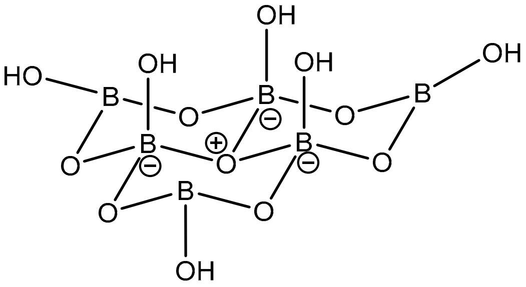


Figure 1. Schematic drawing of the hexaborate(2−) anion, $[B_6O_7(OH)_6]^{2-}$. The three four-coordinate boron centers have formal charges of −1 and the three-coordinate O center has a formal charge of +1, resulting in a di-anion. The three hydroxyl oxygen atoms on the four-coordinate boron atoms are ideally positioned to function as a tridentate ligand. The other three hydroxyl oxygen atoms are peripheral and point radially out from the O^+ center.

2. Materials and Methods

2.1. General

All chemicals were obtained commercially. Fourier-transform infrared (FTIR) spectra were obtained (KBr pellets) on a Perkin-Elmer 100 FTIR spectrometer (Perkin Elmer, Seer Green, UK). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis (in air) were undertaken on an SDT Q600 V4.1 Build 59 instrument (New Castle, DE, USA) using Al_2O_3 crucibles, between 10 and 800 °C (ramp temperature rate of 10 $°C\cdot min^{-1}$). NMR spectra were recorded on a Bruker Avance 400 spectrometer (Bruker, Coventry, UK) in D_2O and data are reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of tetramethylsilane (TMS) (^1H, ^{13}C) and $BF_3\cdot OEt_2$ (^{11}B). Carbon/hydrogen/nitrogen (CHN) analyses were obtained from OEA laboratories Ltd. in Callington, Cornwall, UK.

2.2. Synthesis, Spectroscopic, Analytical, and Crystallographic Data for Complex **1**

A slight excess of ethylenediamine (en) (2.33 mL, 70% aq., 24.45 mmol) was added to a solution of $ZnSO_4 \cdot H_2O$ (1.46 g, 8.15 mmol) in H_2O (10 mL). $Ba(OH)_2 \cdot 8H_2O$ (2.57 g, 8.15 mmol) in H_2O (35 mL) was added to this solution which was rapidly stirred at room temperature for 10 min. The white precipitate of $BaSO_4$ was removed by filtration, and $B(OH)_3$ (5.04 g, 81.5 mmol) was added to the filtrate. After stirring for 30 min, the volume of the solution was reduced to 5 mL by gentle evaporation on a warm water bath. The concentrated solution was left for 10 days in NMR tubes for crystallization, and yielded colourless crystals of $[Zn(en)\{B_6O_7(OH)_6\}] \cdot 2H_2O$ (**1**) (1.2 g, 33%). Melting point (m.p.) $\geq$300 °C. Analytical calculations: C = 5.4%, H = 4.1%, N = 6.3%. Found: C = 5.2%, H = 4.0%, N = 6.6%. NMR, ^1H (400 MHz)/ppm: 2.86 (s, 4H), 4.79 (s, NH_2, H_2O, OH); ^{13}C (100 MHz)/ppm: 39.36. ^{11}B (128 MHz)/ppm: 16.1. IR (KBr/cm^{-1}): 3441(s), 2926(m), 1645(m), 1442(s), 1356(s), 1254(m), 1117(s), 1075(m), 1036(m), 952(m), 863(m), 800(m). TGA: 100–180 °C, loss of two interstitial H_2O 7.2% (8.2% calculated); 180–320 °C, condensation of polyborate with loss of three further H_2O 21.7% (20.5% calculated); 320–470 °C, oxidation of ethylenediamine ligand 33.9% (34.1% calculated); residual ZnB_6O_{10} 66.1% (65.9% calculated). Magnetic susceptibility: $\chi_m = -390 \times 10^{-6}$ $cm^3 \cdot mol^{-1}$. Crystallographic data: $C_2H_{18}B_6N_2O_{15}Zn$, M_r = 440.41, triclinic, P-1 (No. 2), a = 7.3635(2) Å, b = 8.1262(2) Å, c = 13.1817(2) Å, α = 96.991(2)°, β = 94.610(2)°, γ = 104.375(2)°, V = 753.35(3) $Å^3$, T = 100(2) K, Z = 2, Z' = 1, $\mu(MoK_\alpha)$ = 1.715; 33,638 reflections measured, 3453 unique (R_{int} = 0.0237) which were used in all calculations. The final wR_2 was 0.0536 (all data) and R_1 was 0.0191 (I > 2(I)).

2.3. Synthesis, Spectroscopic, Analytical, and Crystallographic Data for Complex **2**

A solution of 1,2-propanediamine (pn) (2.56 mL, 30 mmol) in H_2O (3 mL) was added to a solution of $ZnSO_4 \cdot H_2O$ monohydrate (1.79 g, 10 mmol) in H_2O (10 mL). The reaction mixture was stirred at room temperature for 60 min, and then a solution of $Ba(OH)_2 \cdot 8H_2O$ (3.15 g, 10 mmol) in H_2O (20 mL) was added. The reaction mixture was stirred for a further 30 minutes and then filtered to remove the white precipitate of $BaSO_4$. To the filtrate was added $B(OH)_3$ (6.18 g, 100 mmol), and the mixture was then stirred at room temperature for a further three hours. The volume of the resulting solution was reduced to 20 mL using a rotary evaporator. The solution was distributed over a few small vials and left for 10 days and yielded colourless crystals of $[Zn(pn)\{B_6O_7(OH)_6\}] \cdot 1.5H_2O$ (**2**) (1.7 g, 38%); m.p. >300 °C (decomposes.). Analytical calculations: C = 8.1%, H = 4.3%, N = 6.3%. Found: C = 7.9%, H = 4.5%, N = 6.2%. NMR, ^1H (400 MHz)/ppm: 1.1 (d, 3H), 2.3 (t, 1H, CH), 2.8 (m, 1H), 3.0 (m, 1H), 4.8 (s, NH_2, OH, H_2O); ^{13}C (100 MHz)/ppm: 19.16 (CH_3), 44.98 (CH_2), and 46.65 (CH). ^{11}B (128 MHz)/ppm: 16.6. IR (KBr/cm^{-1}): 3351(s), 3295(s), 1600(m), 1417(s), 1363(s), 1268(m), 1191(m), 1104(s), 1044(s), 1022(s), 956(m), 902(m), 849(m), 808(s), 703(m). TGA: 100–190 °C, loss of 1.5 interstitial H_2O 7.9% (6.1% calculated); 190–280 °C, condensation of polyborate with loss of three further H_2O 17% (18.2% calculated); 250–650 °C, oxidation of organic content 36.1% (34.8% calculated); residual ZnB_6O_{10} 63.9% (65.2% calculated). Magnetic susceptibility: $\chi_m = -260 \times 10^{-6}$ cm^3 mol^{-1}. Crystallographic data: $C_3H_{19}B_6N_2O_{14.5}Zn$, M_r = 445.43, triclinic, P-1 (No. 2), a = 7.5169(3) Å, b = 8.1310(3) Å, c = 13.1409(4) Å, α = 96.203(3)°, β = 94.121(3)°, γ = 103.277(3)°, V = 773.23(5) $Å^3$, T = 100(2) K, Z = 2, Z' = 1, $\mu(MoK_\alpha)$ = 1.670; 19,362 reflections measured, 3522 unique (R_{int} = 0.0308) which were used in all calculations. The final wR_2 was 0.0648 (all data) and R_1 was 0.0256 (I > 2(I)).

2.4. X-Ray Crystallography

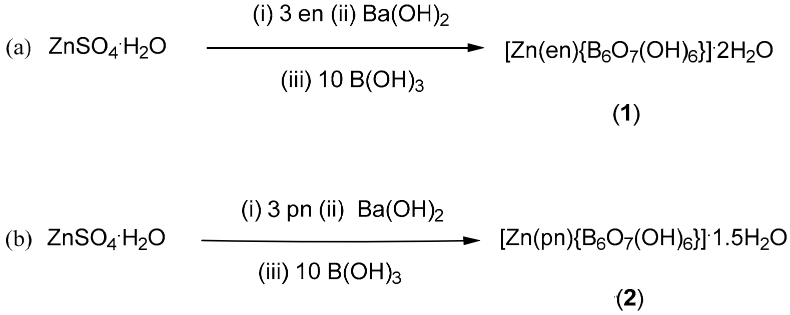
Single-crystal X-ray crystallography was undertaken at the Engineering and Physical Sciences Research Council (EPSRC) National Crystallography Service at the University of Southampton (Southampton, UK). Suitable crystals of **1** and **2** were selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with either HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector (**1**) or VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector (**2**). The crystals were kept at T = 100(2)

K during data collection. Using Olex2 [26], the structures were solved with ShelXT [27] and refined with ShelXL [28] (version 2014/7 for **1** and version 2018/3 for **2**) using least-squares minimization. Cambridge Crystallographic Data Centre (CCDC) 1879895 (**1**) and 1879894 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Synthesis and Characterization

The two new Zn(II) hexaborate(2−) complexes **1** and **2** were prepared as crystalline solids. These solids crystallized after a few days from solutions that originally contained $B(OH)_3$ and either $[Zn(en)_3][OH]_2$ or $[Zn(pn)_3][OH]_2$, respectively. The amine complexes were prepared in situ from the corresponding zinc(II) sulfate salts by addition of $Ba(OH)_2$ prior to reaction with boric acid (Scheme 1).



Scheme 1. Synthesis of Zn(II) hexaborate(2−) complexes **1** and **2**; (**a**) en = 1,2-diaminoethane, (**b**) pn = 1,2-diaminopropane.

Products **1** and **2** were obtained through self-assembly processes in moderate yields (33% and 38%, respectively) and were characterized by single-crystal diffraction analysis (see below), as well as thermal (TGA/DSC) and spectroscopic (IR, NMR) studies. Elemental analyses data were consistent with their single-crystal formulations as neutral coordination compounds with either two or 1.5 additional waters of crystallization. TGA data on the bulk materials supported these formulations, and both compounds resulted in glassy residues with masses consistent with the formation of the anhydrous borate, ZnB_6O_{10}. Thermal decomposition data for **1** and **2** were also in agreement with multistep processes involving initial loss of interstitial H_2O, then condensation of hexaborate(2−) ligands with loss of more H_2O, and finally oxidation of the organic ligands. Similar decomposition processes were observed for other polyborate compounds containing transition-metal complexes [29–31]. Compounds **1** and **2** were soluble in H_2O, but dissolution led to their decomposition with ^{1}H and ^{13}C spectra consistent with diamine ligands, and ^{11}B spectra of **1** and **2** both showing only one peak of approximately −16 ppm. This single peak results from rapid $B(OH)_3/[B(OH)_4]^-$ equilibria [4,5], but these chemical shifts are slightly more downfield than expected for a hexaborate(2−) anion (~14 ppm) for a B/charge ratio of three [10]. IR spectra, obtained as KBr pellets, showed numerous strong B–O stretches in the range 1500–800 cm^{-1} and, as tabulated by Li et al. [32], have medium/strong bands at ~810 cm^{-1} and ~958 cm^{-1} diagnostic of the hexaborate(2−) anion.

3.2. X-Ray Crystallography of Compounds *1* and *2*

Compounds **1** and **2** are structurally very similar, but subtle differences in their structural parameters are apparent under detailed analysis. In summary, compounds **1** and **2** both contain the hexaborate(2−) anion (Figure 1) coordinated in a tridentate facial manner to a distorted octahedral Zn(II) center by hydroxyl oxygen atoms ($\kappa^3 O,O',O''$). Both compounds also contain a bidentate (*cis*) 1,2-diaminoalkane ($\kappa^2 N,N'$) ligand. The sixth donor atom is from a peripheral hydroxyl oxygen

($\kappa^1 O^{*\prime\prime\prime}$) from an “adjacent” hexaborate(2−) unit. Thus, 1-D polymer chains are set up with each hexaborate(2−) ligand bridging two zinc(II) centers in alternating tridentate and mondentate modes.

A displacement ellipsoid [26] drawing of **1** is shown in Figure 2. The hexaborate(2−) ligand is tridentate to a distorted octahedral Zn(II) metal center with Zn1–O11, Zn1–O12, and Zn1–O13 distances of 2.3874(9) Å, 2.0790(9) Å, and 2.0196(9) Å, respectively. The Zn-donor atom distances associated with the 1,2-diaminoethane ligand are Zn1–N1, 2.1345(11)Å and Zn1–N2, 2.0753(11) Å. A coordinate *O* donor bond involving an “adjacent” hexaborate(2−) unit, Zn1–O10* 2.2320(9) Å, completes the octahedral coordination geometry around the Zn(II) atom. This latter interaction is not shown in Figure 2. O10* is *trans* to O11 (O10–Zn1–O11 = 170.18(3)). A view of the coordination polymer chain in **1** is shown in Figure 3. The B–O distances and angles within the hexaborate(2−) anion of **1** are not significantly different from those observed in related B–O systems with three- and four-coordinate boron centers in general [33–35] and, more specifically, to other reported hexaborate(2−) complexes such as $[Cu(Me_2NCH_2CH_2NMe_2)\{B_6O_7(OH)_6\}]\cdot 6H_2O$ [36], $[Me_2NHCH_2CH_2NHMe_2][Zn\{B_6O_7(OH)_6\}_2]\cdot 2H_2O$ [37], and $[C_4N_2H_{12}][Co\{B_6O_7(OH)_6\}_2]\cdot 6H_2O$ [38].

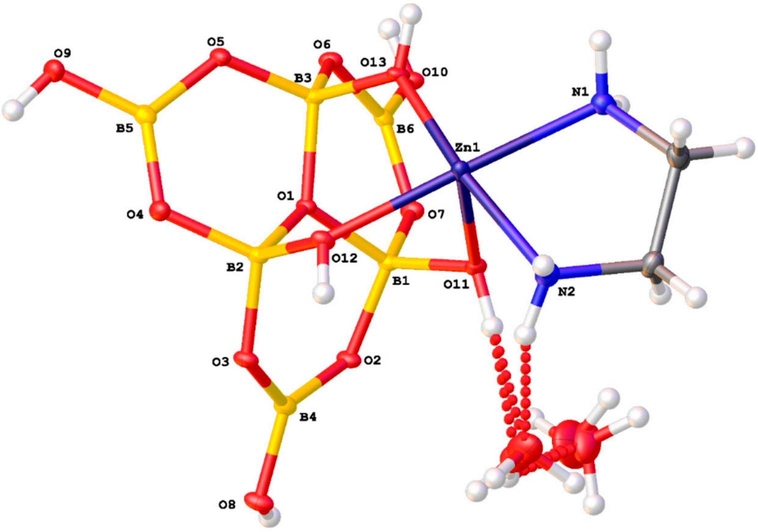


Figure 2. Crystal structure of the repeating unit $[Zn(en)\{B_6O_7(OH)_6\}]\cdot 2H_2O$ (**1**), with ellipsoids at 50%.

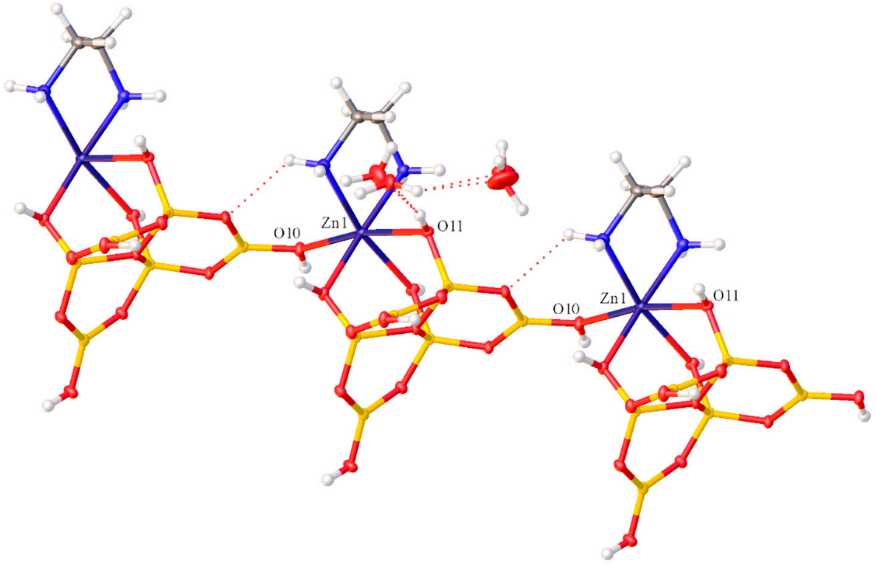


Figure 3. A segment of the infinite coordination polymer chain observed in $[Zn(en)\{B_6O_7(OH)_6\}\cdot 2H_2O$ (**1**), highlighting the O10–Zn1–O11 linkage.

There are 10 potential H-bond donors in the neutral monomeric unit "Zn(en){$B_6O_7(OH)_6$}" of **1** and 14 potential donor sites, when including interstitial H_2O, which lead to a complex set of H-bond arrangements. Reciprocal $R_2^2(8)$ (Etter nomenclature [39]) pairs emanate from hydrogens on O8, O10, and O13. The hydrogen atom on O11 is an H-bond donor to a water molecule (O21), whilst hydrogens on O9, O11, and O12 all partake in unusual $R_2^2(6)$ ring interactions. These interactions both include Zn1 and either amino-hydrogens on N1 or N2. The $R_2^2(6)$ involving N1H1A is a cyclic donor arrangement involving a neighboring hexaborate(2−) hydroxyl, O9*H9*, as the second donor. The $R_2^2(6)$ interaction involving N2H2B is a pincer H-bond interaction originating from O12H12 and N2H2B to a neighboring hexaborate(2−) acceptor at O8*. These two interactions are shown in Figure 4. Full details of these and other H-bond interactions are in the Supplementary Materials. The reciprocal $R_2^2(8)$ interaction was calculated to be strong [10] and the $R_2^2(6)$ are likely to have comparable H-bond strength. These $R_2^2(8)$ and $R_2^2(6)$ interactions are all inter-chain and they stabilize the solid-state structure through linking together hexaborate(2−) ligands of adjacent 1-D coordination polymer chains. There are no intra-chain H-bond interactions. These inter-chain H-bond interactions, in association with formation of Zn–O coordinate bonds, have a strong influence in stabilizing the templated self-assembled structure of **1**.

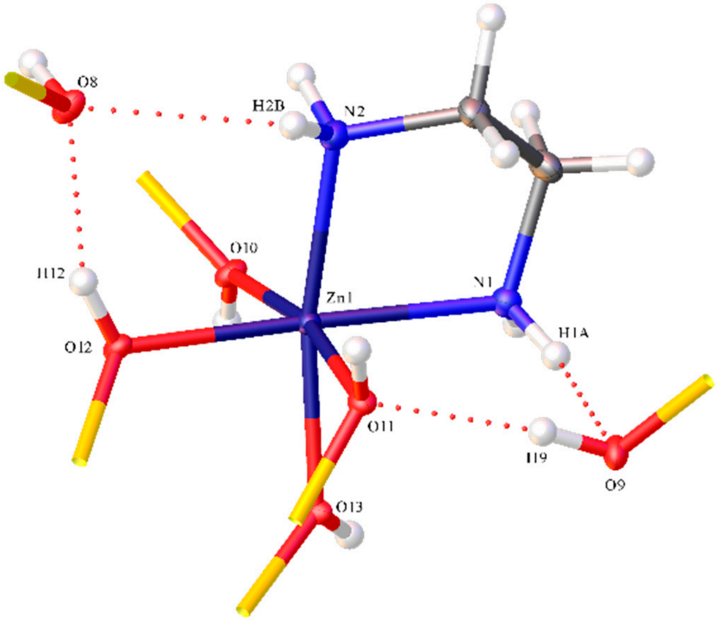


Figure 4. View of **1** showing focusing on the metal coordination center and the two unusual $R_2^2(6)$ rings in **1**. O9*H9* from a neighboring hexaborate(2−) unit is an H-bond donor to O11. O8* (from a different neighboring hexaborate(2−) unit) is an H-bond acceptor from both N2H2B and O12H12 which "chelate" O8*. The full neighboring hexaborates are not shown for clarity.

A displacement ellipsoid [26] drawing of **2** is shown in Figure 5. As noted in the caption to Figure 5, there is disorder in the structure of compound **2**. In particular, there are two Zn(II) positions (Zn1, Zn1A; site occupation factor (s.o.f.) 0.8:0.2) that matches up with the pn ligand disorder. The overall geometry around both Zn(II) centers is, similarly to **1**, (distorted) octahedral.

The hexaborate(2−) ligand is tridentate to the Zn(II) metal center with Zn1–O11, Zn1–O12, and Zn1–O13 distances of 2.071(2), 2.017(2), and 2.648(1) Å, respectively. The corresponding distances involving Zn1A are 2.063(8), 2.033(8) and 2.309(7) Å. Representative Zn-donor atom distances associated with the 1,2-diaminopropane ligand are Zn1–N1, 2.081(2)Å and Zn1–N2, 2.131(2) Å. Full bond distances and bond angles are available in the Supplementary Materials. A Zn1–O9* (and Zn1A–O9*) interaction from an "adjacent" hexaborate(2−) at 2.1762(17) Å (and 2.521(1)) Å) completes the coordination geometry around the Zn(II) atom. These axial interactions are present but not shown in Figure 5. The B–O distances and angles at B and O within the hexaborate(2−) anion of **2** are not significantly different from those of **1** or other reported structures [36–38]. The structure of **2** displays numerous structure-directing H-bond interactions, in a similar manner to those observable in **1**. In particular, $R_2^2(8)$ interactions involving hydrogens on O9, O10, and O12 link together the polymeric chains, the amino-H atoms engage in in the both types of $R_2^2(6)$ rings, and the hydrogen on O13 H-bonds to an acceptor water molecule (O21). Full details of these H-bond interactions are available in the Supplementary Materials.

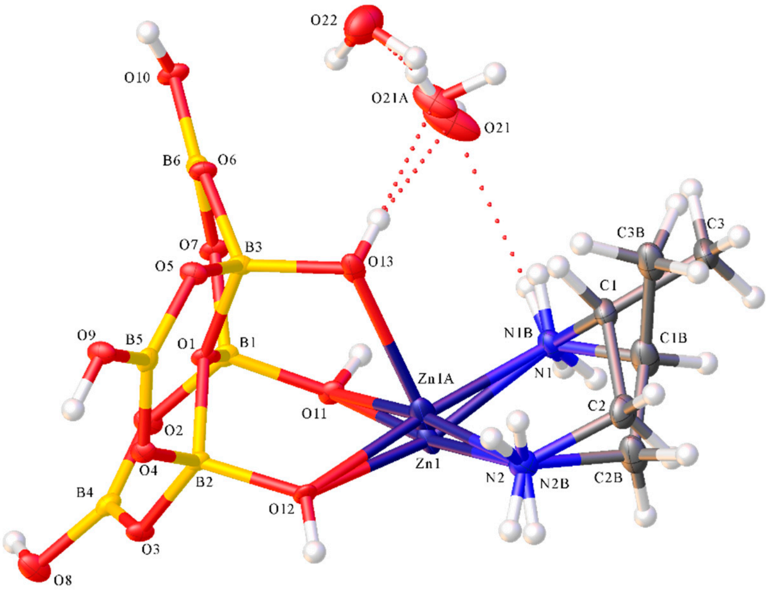


Figure 5. Crystal structure of the repeating unit $[Zn(pn)\{B_6O_7(OH)_6]\cdot 1.5H_2O$ (**2**), with ellipsoids at 50%. The Zn(II) center and 1,2-diamonopropane ligand are disordered over two sites with site occupation factor (s.o.f.) of 0.8:0.2 each. Axial interaction from O9* (neighboring hexaborate) not shown.

4. Conclusions

The 1-D coordination chain polymers **1** and **2** arise through self-assembled processes and crystallize from aqueous solution containing dynamic combinatorial libraries of borate and zinc(II) amine complexes. Their structures display numerous well-known reciprocal $R_2^2(8)$ and novel $R_2^2(6)$ inter-chain H-bond interactions which link together hexaborate(2−) moieties in adjacent coordination polymer chains. The novel $R_2^2(6)$ interactions are unusual in that they both involve Zn(II) centers within their six-membered rings and amino-hydrogens of their coordinated diamine ligands as H-bond donors. One $R_2^2(6)$ ring has a cyclic H-bond arrangement, whereas the other has a pincer H-bond arrangement. These H-bond interactions, together with formation of Zn–O coordinate bonds, stabilize the solid-state structures of **1** and **2** and help facilitate these self-assembly processes.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/8/12/470/s1: TGA and single-crystal XRD data.

Author Contributions: M.A.B. conceived the experiments; M.A.A. synthesized and characterized the complexes and grew single crystals; P.N.N. and S.J.C. solved the crystal structures; M.A.B. wrote the paper with contributions from all co-authors.

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Conflicts of Interest: The authors declare no conflicts of interest.

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