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Oxidoborates Templated by Cationic Nickel(II) Complexes and Self-Assembled from $B(OH)_3$

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Abstract: Several oxidoborates, self-assembled from $B(OH)_3$ and templated by cationic $Ni^{(II)}$ coordination compounds, were synthesized by crystallization from aqueous solution. These include the ionic compounds *trans*-$[Ni(NH_3)_4(H_2O)_2][B_4O_5(OH)_4]\cdot H_2O$ (**1**), s-$[Ni(dien)_2][B_5O_6(OH)_4]_2$ (dien = *N*-(2-aminoethyl)-1,2-ethanediamine (**2**), *trans*-$[Ni(dmen)_2(H_2O)_2]$ $[B_5O_6(OH)_4]_2\cdot 2H_2O$ (dmen = *N,N*-dimethyl-1,2-diaminoethane) (**3**), $[Ni(HEen)_2][B_5O_6(OH)_4]_2$ (HEen = *N*-(2-hydroxyethyl)-1,2-diaminoethane) (**4**), $[Ni(AEN)][B_5O_6(OH)_4]\cdot H_2O$ (AEN = 1-(3-azapropyl) -2,4-dimethyl-1,5,8-triazaocta-2,4-dienato(1-)) (**5**), *trans*-$[Ni(dach)_2(H_2O)_2][Ni(dach)_2]$ $[B_7O_9(OH)_5]_2\cdot 4H_2O$ (dach = 1,2-diaminocyclohexane) (**6**), and the neutral species *trans*- $[Ni(en)(H_2O)_2\{B_6O_7(OH)_6\}]\cdot H_2O$ (**7**) (en = 1,2-diaminoethane), and $[Ni(dmen)(H_2O)\{B_6O_7(OH)_6\}]\cdot 5H_2O$ (**8**). Compounds **1–8** were characterized by single-crystal XRD studies and by IR spectroscopy and **2**, **4–7** were also characterized by thermal (TGA/DSC) methods and powder XDR studies. The solid-state structures of all compounds show extensive stabilizing H-bond interactions, important for their formation, and also display a range of gross structural features: **1** has an insular tetraborate(2-) anion, **2–5** have insular pentaborate(1-) anions, **6** has an insular heptaborate(2-) anion ('O^{+}' isomer), whilst **7** and **8** have hexaborate(2-) anions directly coordinated to their $Ni^{(II)}$ centers, as bidentate or tridentate ligands, respectively. The $Ni^{(II)}$ centers are either octahedral (**1–4**, **7**, **8**) or square-planar (**5**), and compound **6** has both octahedral and square-planar metal geometries present within the structure as a double salt. Magnetic susceptibility measurements were undertaken on all compounds.

Keywords: borate anions; H-bonding; heptaborate(2-); hexaborate(2-); Nickel(II) complex; oxidoborate; pentaborate(1-); self-assembly; templated synthesis; tetraborate(2-); X-ray structures

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1. Introduction

Synthetic borates (oxidoborates is the IUPAC recommended name for this class of compounds [1]) show great structural diversity and their structures complement the variety of structural motifs observed in borate minerals [2–5]. Borate minerals have large scale economic importance [6–8] (e.g., as vitreous, agriculture, fire retardant products) and some of these minerals, and their synthetic counterparts, have also found more specialist uses [9–18] (e.g., as fluorescent, optical SHG and wide band-gap semi-conductor materials).

Structurally, borates salts consist of metallic or non-metallic cationic centers and hydroxyoxidoborate units, with variable degrees of condensation, as either insular anions or as anionic 1-D chains, 2-D layers or 3-D networks [2–5]. Oxidoborate materials can be synthesized from aqueous solution or from solid-state or solvothermal methods and the latter non-aqueous methods often lead to the formation of the more highly condensed oxidoborate structures [5]. In aqueous solution, oxidoborate speciation is pH and boron-concentration dependent [19,20], and a dynamic combinatorial library (DCL) [21] of oxidoborate anions co-exist in rapidly attained aqueous equilibria.

Many oxidoborate anions have been successfully crystallized from aqueous solution using $B(OH)_3$ and an appropriate templating cation, e.g., triborate(1-), tetraborate(2-),

pentaborate(1-), hexaborate(2-), heptaborate(2-) (two isomers), heptaborate(3-), octaborate(2-) (two isomers), nonaborate(3-), tetradecaborate(4-), and pentadecaborate(3-) anions [5]. These salts are selectively templated from the solution by the cations present in self-assembly processes [22–24]. However, pentaborate(1-) salts often crystallize out of such solutions and this is particularly so if the cation is relatively small and has a charge of +1 [5]. This process primarily occurs since the $[B_5O_6(OH)_4]^-$ anion is ideally shaped to form giant H-bonded lattices through anion–anion interactions with 'cavities' large enough to be occupied by the small cations [25–28].

We are interested in expanding the structural diversity of isolated and coordinated oxidoborate chemistry and have developed a strategy of incorporating relatively highly charged (>+1) and/or cations, with the potential of forming multiple H-bond interactions, into the aqueous DCL of borate anions so that they can template and crystal engineer novel structures [29,30]. Using labile cationic transition-metal complexes [31] introduces a further DCL of potential cations into reaction medium and leads to the possibility of oxidoborate anions entering the primary coordination shell of the metal, as *O*-donor ligands.

With this in the forefront of our mind, we have recently investigated the reactions of labile complexes of $Zn^{(II)}$ [32–35] and $Cu^{(II)}$ [36–40] and have prepared novel species containing coordinated $[B_2O_3(OH)_2]^{2-}$ [39], $[B_5O_6(OH)_4]^-$ [37], $[B_6O_7(OH)_6]^{2-}$ [34–38], $[B_{12}O_{18}(OH)_6]^{6-}$ [32,35] and $[B_{20}O_{32}(OH)_8]^{12-}$ [39] ligands. $Ni^{(II)}$ complexes and their reactions with $B(OH)_3$ have received little attention to date and reported oxidoborate species are restricted to an unusual hexadentate tris(aminoethoxy)hexaborate(2-) anion complex, $[Ni\{(H_2NCH_2CH_2O)_3B_6O_7(OH)_3\}]$ [41], and a series of salts containing the insular pentaborate(1-) [42–47] or heptaborate(2-) [33,48] anions.

$Ni^{(II)}$ complexes have a d^8 electronic configuration and should also be relatively labile [31]. In this manuscript we report on the use coordination complexes of $Ni^{(II)}$ containing *N*-donor ligands NH_3, en, dien, dmen, HEen, AEN, dach (see Figure 1 for ligand structures and abbreviations) to synthesize eight new oxidoborate compounds. Their single-crystal structures and their spectroscopic and physical properties are reported.

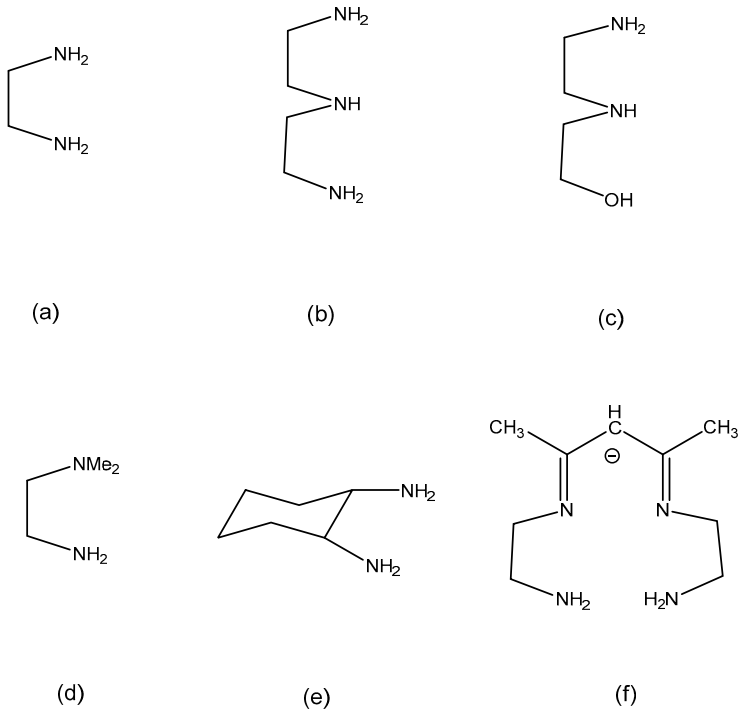
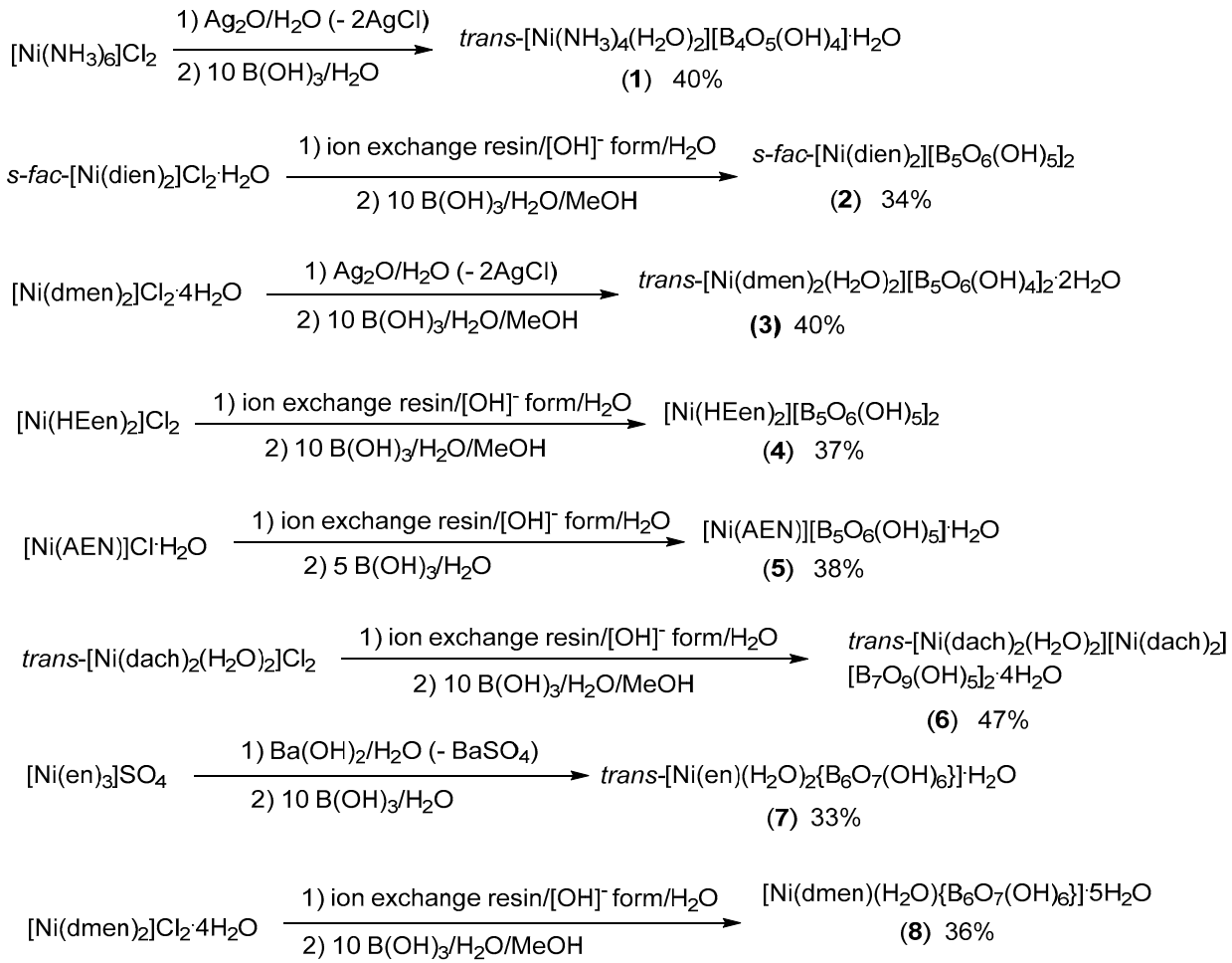


Figure 1. Drawings of the organic ligand structures found in compounds **1**–**8** with abbreviations as follows: (**a**) en, 1,2-diaminoethane), (**b**) dien, *N*-(2-aminoethyl)-1,2-ethanediamine, (**c**) HEen, *N*-(2-hydroxyethyl)-1,2-diaminoethane, (**d**) dmen, *N*,*N*-dimethyl-1,2-diaminoethane, (**e**) dach, 1,2-diaminocyclohexane, (**f**) AEN, 1-(3-azapropyl)-2,4-dimethyl-1,5,8-triazaocta-2,4-dienato(1-).

2. Results and Discussion

2.1. Synthesis and General Discussion

The $Ni^{(II)}$ complex oxidoborates **1–8** were prepared in acceptable yields as a crystalline solids from the reaction of a $Ni^{(II)}$ complex cation hydroxide salt with boric acid in a ratio of either 1:5 or 1:10 (Scheme 1). The $Ni^{(II)}$ complex cation hydroxides were obtained in situ from the corresponding salts containing either chloride or sulfate anions. Anion exchange (from Cl^-) was used for **2**, **4, 5, 6**, and **8** and stoichiometric reactions with Ag_2O (from Cl^-) was used for **1** and **3** and a stoichiometric reaction with $Ba(OH)_2{\cdot}8H_2O$ (from SO_4^{2-}) was used for **7**.



Scheme 1. Reagents and stoichiometry of reactants involved in self-assembly of $Ni^{(II)}$ oxidoborates from cationic $Ni^{(II)}$ complexes with $B(OH)_3$ in aqueous or methanolic aqueous solution.

The new compounds were identified by XRD single-crystal studies (Section 2.2), IR spectroscopic analysis and accompanied by thermal decomposition analysis (TGA and DSC) and powder XRD studies for **2**, **4–7** (Section 2.3). Six of these eight compounds contain insular oxidoborate anions and two compounds contain coordinated hexaborate(2-) anions; the oxidoborate anions found in these new compounds are drawn out in Figure 2. The coordination geometry around the $Ni^{(II)}$ centers are either octahedral (**1–4**, **7**, **8**) or square-planar (**5**) and compound **6** has both octahedral and square-planar metal geometries present within the structure as a double salt. The new $Ni^{(II)}$ oxidoborate complexes are coloured with those with square-planar centres (**5** and **6**) are orange/red with the others having blueish hues. All compounds were stable in the solid state were insoluble in organic solvents and decomposed by aqueous solution (see ^{11}B NMR, Section 2.3). Since the products arise through self-assembly processes that we believe are associated with H-

bonded structure directing effects induced by the cations present [21–24], these interactions are discussed in detail in Section 2.2.2.

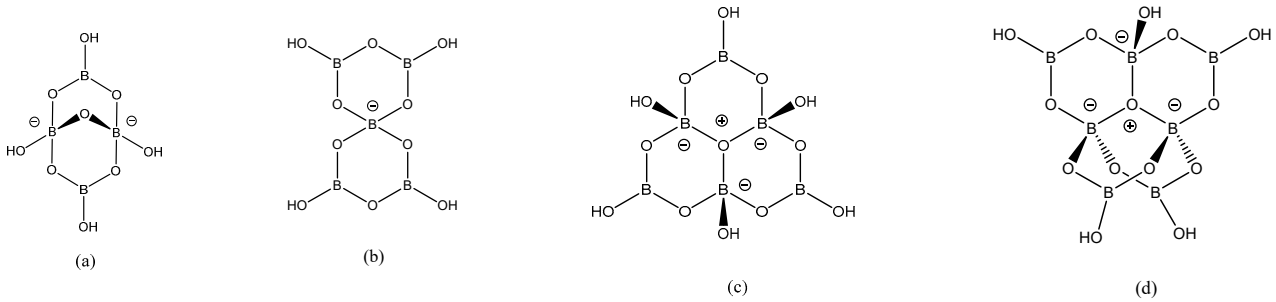


Figure 2. Drawings of the oxidoborate structures found in (**a**) **1**, (**b**) **2–5**, (**c**) **7**, **8** and (**d**) **6**.

*2.2. Crystallographic Studies on **1–8** and Their Solid-State H-Bonding Interactions*

2.2.1. General Considerations for **1–6** and the Structures of **7** and **8**

Selected crystallographic data for **1–8** can be found in Experimental Methods (Section 3) and full crystallographic details are available as Supplementary Materials. Compounds **1–6** are all anionic compounds containing discrete insular cationic $Ni^{(II)}$ coordination complexes with *N*-donor or *O*-donor ligands, partnered with anionic oxidopolyborate anions. The cations in **2–6** are as found in their precursor complexes whilst **1** contains the partially aquated *trans*-$[Ni(NH_3)_4(H_2O)_2]^{2+}$ cation. The cationic charges are neutralized by the insular oxiodopolyborate anions $[B_4O_5(OH)_4]^{2-}$, $[B_5O_6(OH)_4]^{-}$, or $[B_7O_9(OH)_5]^{2-}$ for **1**, **2–5** and **6**, respectively. Compounds **1**, **3**, **5** and **6** also contain one, two, one and four interstitial H_2O molecules per formula unit, respectively. The dien ligand in **2**, and the HEen ligand in **4** are both disordered over two positions. Compounds **7** and **8** are uncharged coordination compounds with $[B_6O_7(OH)_6]^{2-}$ coordinated as *O*-donor ligands to octahedral $Ni^{(II)}$ centres either as a bidentate or a tridentate ligand in **7** or **8**, respectively. Compounds **7** and **8** have one and five interstitial H_2O molecules, respectively, and are also partially aquated. There is some disorder of the interstitial H_2O molecules in both **7** and **8** and some additional disorder in the en ligand and the dmen ligands of **7** and **8**. Compound **6** is unusual and is best formulated as a double salt. It contains both octahedral *trans*-$[Ni(dach)_2(H_2O)_2]^{2+}$ and square-planar $[Ni(dach)_2]^{2+}$ cations partnered by two crystallographically equivalent $[B_7O_9(OH)_5]^{2-}$ anions and four interstitial H_2O molecules. The dach ligands are also disordered in **6** but have chair conformations with their amino groups equatorial and with one dach ligand in each cation having *R*,*R* stereochemistry and the other *S*,*S*. Interestingly, two of these interstitial H_2O molecules (O22) in **6** are in 'axial' positions in the square-planar complex at 3.1517(13) Å (T = 0.61 [49]). In the octahedral complex, these two H_2O ligands (O21) are at 2.1422(15) Å (T = 0.98). A structurally related (but d^9) $Cu^{(II)}$ compound, prepared by an identical method [37], contains a square-planar (also with very long axial H_2O 'bonds', T = 0.70) and a Jahn–Teller distorted axially elongated octahedral complexes (T = 0.80). Structurally, the insular $[B_7O_9(OH)_5]^{2-}$ dianion is previously known to adopt either a 'chain' or 'O^+' isomeric forms [28,50–52] and the 'O^+' isomer is present in **6**. The new $Ni^{(II)}$ oxidoborates complex salts **1–6** all contain cations and anions that are known in other salts and the gross structures of the component ions, bond distances and internuclear angles for the component ions in **1–6** are as expected and need no further comment [5,53–55]. The uncharged complexes **7** and **8** are structurally novel although similar compounds have been observed in $Co^{(II)}$, $Cu^{(II)}$ and $Zn^{(II)}$ oxidoborate chemistry [34–38,56–58]. Compounds **7** and **8** contain isolated species [35,37,38] rather than polymer 1-D coordination chains [34,36,38] and these two structures will be discussed in more detail below.

A drawing of the structure of *trans*-$[Ni(en)(H_2O)_2\{B_6O_7(OH)_6\}]\cdot H_2O$ (**7**), with selected crystallographic numbering, can be found in Figure 3. Compound **7** is a distorted neutral octahedral $Ni^{(II)}$ complex with *trans* H_2O ligands (containing O21 and O22), a

disordered 1,2-diaminoethane ligand and a bidentate $[B_6O_7(OH)_6]^{2-}$ ligand that is coordinated through two hydroxy groups (containing O8 and O9). A single disordered water of crystallization containing O31 (s.o.f. 0.47(2)) or O31B (s.o.f. 0.53(2)) is also shown. The O21-Ni1-O22 angle is 171.67(12)° and the average Ni-(OH_2) distance is 2.089(3) Å. This average distance is slightly longer than the average oxidoborate O8/O9-Ni1 distance of 2.065(3) Å. The chelating en ligand significantly distorts the $Ni^{(II)}$ centre where the Ni1-N1 and Ni1-N2 distances are 2.086(4) and 2.085(4) Å, respectively. The N1-Ni1-N2 angle is 82.80(16)° and the oxidoborate/en ligand O8-Ni1-N2 and O9-Ni1-N1 angles are both significantly <180°, whilst the O8-Ni1-O9 angle is 90.48(14)°. These Ni-N and Ni-(OH_2) bond lengths are within the expected ranges for $Ni^{(II)}$ complexes [53–55] but this is the first example of a Ni-O bondlength arising from an oxidoborate ligand and it is not significantly different from other N-O bondlengths. The B-O bondlengths and OBO and BOB angles of the hexaborate(2-) ligand are in accord with previously reported data for this ligand including three very long B-O bondlengths (1.498(6)–1.538(6)°; av. 1.517(6)°) to the three-coordinate O atom (O1) [28,29,48,51,52]. There is an intramolecular H-bond from an oxidoborate hydroxy group (containing O10) and the coordinated aqua ligand (containing O21), O10H10 ··· O21, with a O10 ··· O21 distance of 2.704(5) Å and a O10-H10-O21 angle of 144.9° (Figure 3). This H-bond is part of two $R_1^1(8)$ rings [59] and both rings involve the $Ni^{(II)}$ centre and two Ni-O coordinate bonds. There is a similar H-bond interaction in the only other known example of a bidentate hexaborate(2-) complex, $(NH_4)_2[Zn(H_2O)_2(B_6O_7(OH)_6\}_2]$, but here, interestingly, the H-bond originates from the aqua ligand and the uncoordinated hydroxy site of the oxidoborate is the acceptor [35].

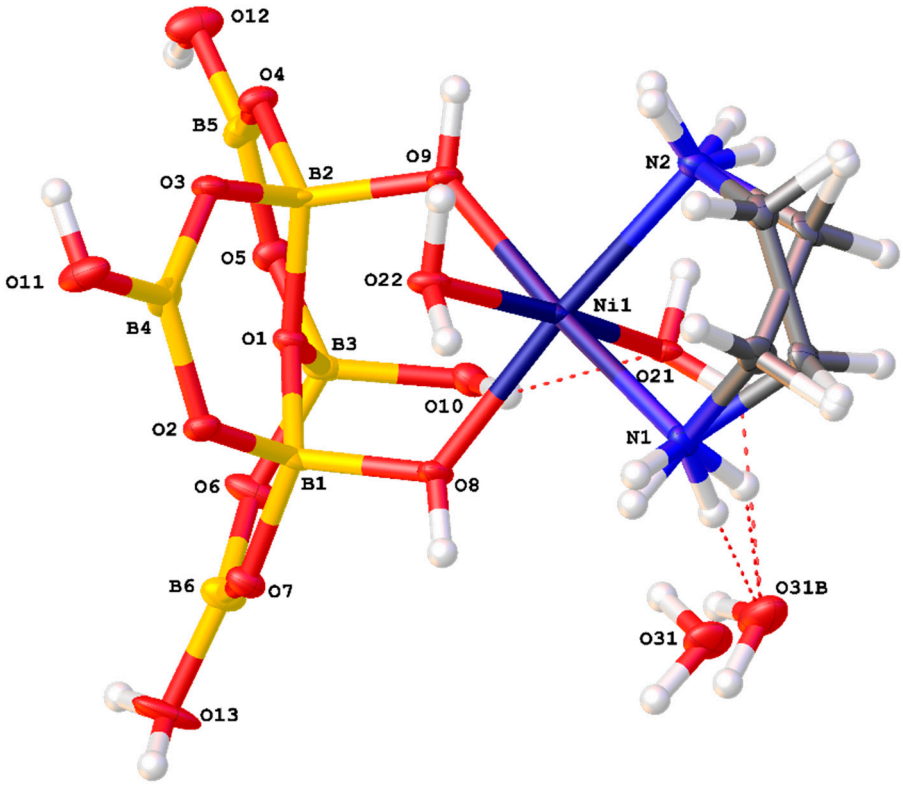


Figure 3. Drawing of structure *trans*-$[Ni(en)(H_2O)_2\{B_6O_7(OH)_6\}]\cdot H_2O$ (**7**), showing selected crystallographic numbering.

A drawing of the structure of $[Ni(dmen)(H_2O)\{B_6O_7(OH)_6\}]\cdot 5H_2O$ (**8**), with selected crystallographic numbering, is shown in Figure 4. Compound **8** is a distorted neutral octahedral $Ni^{(II)}$ complex with disordered aqua ligand (containing O21) and dmen ligands (0.496(5) s.o.f shown) and a tridentate $[B_6O_7(OH)_6]^{2-}$ ligand coordinated through three hydroxy groups (containing O11, O12 and O13). The five waters of crystallization contain

O31-O35. The Ni1-O21 distance for the aqua ligand (2.131(11) Å) is significantly longer than the Ni-O distances associated with the three hydroxy groups of the tridentate oxidoborate ligand (2.0415(17)–2.0978(17) Å; *av*. 2.078(2) Å) but this difference was not significant for **7**. The N1-Ni1-N2 angle associated with the chelating dmen ligand is 84.5(12)° and angles between the three *O*-donor atoms of the *fac*-hexaborate ligand range from 84.26(7)–90.66(6)°; *av*. 86.94(8)°. The aqua ligand with O21 is *trans* to oxidoborate O11 with an angle of 173.2(3)°, and the other *trans* angles are significantly <180.0°. The Ni1-N distances of 2.031(11) Å (N1) and 2.13(2) Å (N2) are significantly different but there is more steric demand at N2 as it is substituted by the two methyl groups. Overall, the bondlengths and angles associated with the $Ni^{(II)}$ centre and those within the hexaborate(2-) ligand in **8** are in accord with comparable data for **7**.

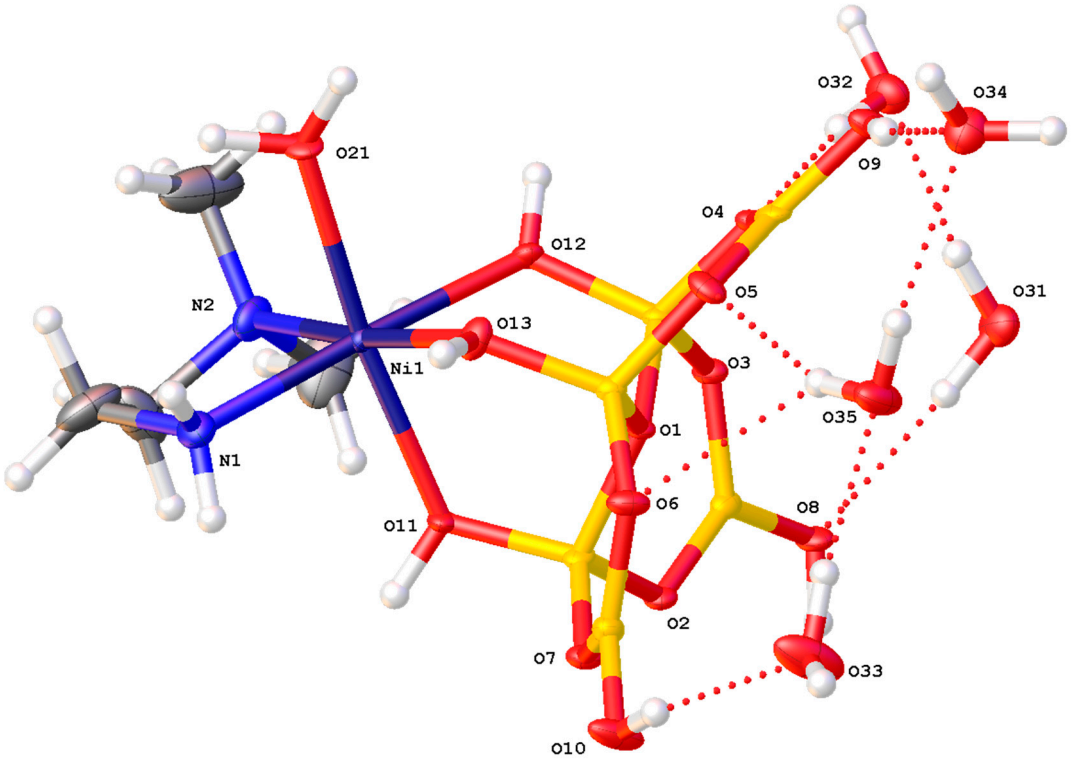


Figure 4. Drawing of structure of $[Ni(dmen)(H_2O)\{B_6O_7(OH)_6\}]\cdot 5H_2O$ (**8**), showing (selected) crystallographic numbering.

2.2.2. Solid-State H-Bonding Interactions in **1**–**8**

Compounds **1**–**8** are self-assembled and crystallized from the various oxidoborate and the $Ni^{(II)}$ amine complexes that are each in equilibrium in the reacting aqueous solution [19,20,31]. There is a strong preference for the oxidoborate anion to enter the primary coordination shell in related $Cu^{(II)}$ and $Zn^{(II)}$ chemistry with the formation of energetically favourable *O*-donor coordinate bonds [32,34–40,58]. Interestingly, $Ni^{(II)}$ salts are described as labile, although in practice they are often considerably less labile than corresponding $Cu^{(II)}$ and $Zn^{(II)}$ complexes [31]. In accord with this, the $Ni^{(II)}$ cations used in this study generally remain more or less intact in salts **1**–**6** after prolonged crystallization from aqueous solution, with formation of oxidoborate *O*-donor bonds only observed in compounds **7** and **8**. H-bond interactions also appear to be of paramount importance in driving this crystallization process and these interactions are described in detail for each compound in the following paragraphs.

A drawing of the components of the formula unit of **1**, showing important atomic numbering, is shown in Figure 5. The cations, anions and interstitial H_2O molecules have numerous H-bond donor and/or acceptor sites and all potential H-bond donor sites are used in the solid-state structure. The dotted red lines in Figure 5 illustrate H-

bond interactions which link cation to anion (O11H11 ··· O6), cation to interstitial H_2O (N11H11 ··· O21), and anion to interstitial H_2O (O6H6 ··· O21) forming a $R_2^2(8)$ ring incorporating the $Ni^{(II)}$ centre. These interactions as well as anion–anion interactions template the formation of the tetraborate salt. Full details of all H-bond interactions are available in the Supplementary Materials. Siveav and co-workers [46] have analysed H-bond interactions in tetraborate(2-) systems using the terminology of Zolatarev et al. [60] but we prefer the complimentary and more widely known Etter symbolism [59] in this manuscript. $R_2^2(8)$ interactions are very important at stabilizing hydroxyoxidopolyborate anions and three of the four boron based hydroxy centres are involved in such interactions: observed in $R_2^2(8)$ interactions are very important at stabilizing hydroxyoxidopolyborate anions and three of the four boron based hydroxy centres are involved in such interactions with O8-H8 ··· O5′ and O9′-H9′ ··· O3 paired in a $R_2^2(8)$ ring and O7-H7 ··· O1′ and O7′-H7′ ··· O1 forming a reciprocal pair in another $R_2^2(8)$ ring. The fourth boron based hydroxy group O6H6 is a donor to a H_2O molecule, O21 (Figure 5) forming an unusual $R_3^3(8)$ ring {Ni1-O11A-H11A ··· O6-H6 ··· O21 ··· H11E-N11} and is also part of a larger $R_4^4(12)$ ring {O6-H6 ··· O21-H21A ··· O3′-B1′-O6′-H6′ ··· O21′-H21A′ ··· O3-B1-} (Figure 6). Since the cation is involved in templating the structure its H-bond interactions are very important and these include O11-H11A ··· O6, O11-H11B . . . O8, O12-H12A ··· O4, O12-H12B ··· O2, N14-H14A ··· O8, N12-H12D ··· O7 and N12-H12C ··· O7 which originate from the aqua or ammine ligands. Further patterns are difficult to visualize although $R_2^2(8)$ {Ni1-N12-H12C ··· ·O7-B2-O2 ··· H12B-O12-} and a $C_2^2(10)$ {Ni1-O11-H11A ··· O6-B1-O3-B3-O8 ··· H14A′-N14′-} are discernable.

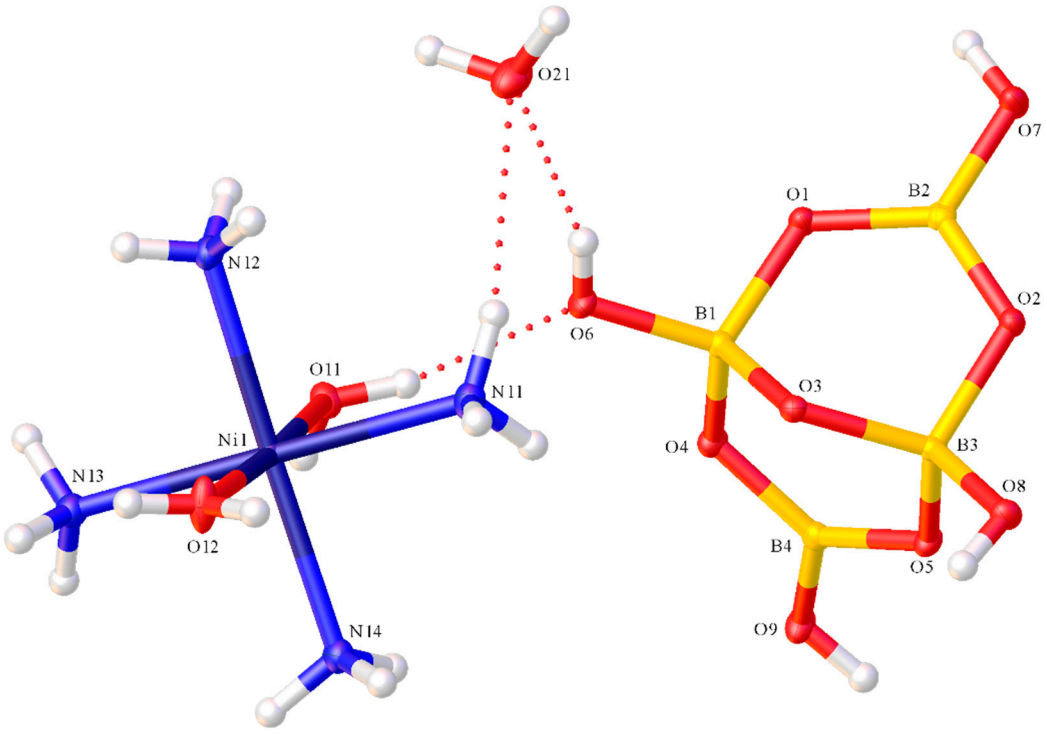


Figure 5. Drawing of structure of *trans*-$[Ni(NH_3)_4(H_2O)_2][B_4O_5(OH)_4]\cdot H_2O$ $[Ni(dmen)(H_2O)\{B_6O_7(OH)_6\}]\cdot 5H_2O$ (**1**), showing (selected) crystallographic numbering and the $R_3^3(8)$ ring system: {Ni1-O11A-H11A ··· O6-H6 ··· O21 ··· H11E-N11}.

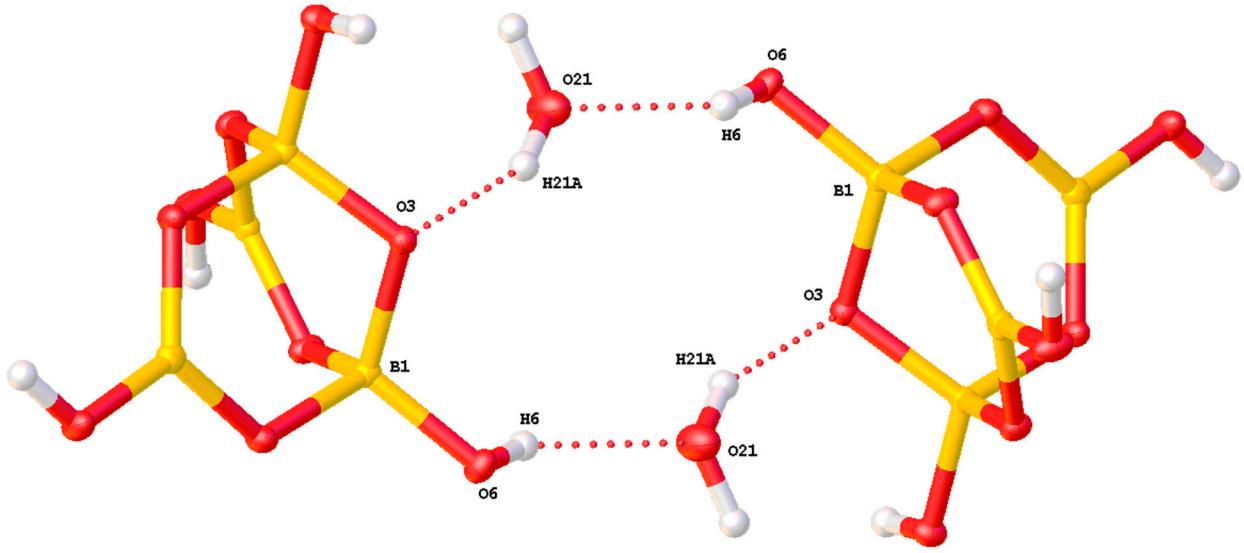


Figure 6. Drawing of the $R_4^4(12)$ ring, {O6-H6 ··· O21-H21A ··· O3′-B1′-O6′-H6′ ··· O21′-H21A′ ··· O3-B1-}, in *trans*-$[Ni(NH_3)_4(H_2O)_2][B_4O_5(OH)_4]\cdot H_2O$ (**1**).

Compounds **2**–**5** are all pentaborate(1-) salts and anion–anion H-bond interactions are well known to strongly influence their formation [5,25–28] since each pentaborate(1-) anion has four donor H-bond sites that are sterically arranged to form 3D H-bonded anionic giant structures, in which the cations occupy vacant 'open-sites' in the anionic lattice. The anion–anion interactions are conveniently described using a combination of 'acceptor-sites nomenclature', as defined by Schubert [26], and Etter terminology [59]. Compounds **2**–**4** have very similar anion–anion interactions and the four acceptor sites can be described as α,α,α,β with the α-site interactions reciprocal $R_2^2(8)$ and the β-interactions reciprocal $R_2^2(12)$; both types of interactions are common in pentaborate(1-) structures [5,27]. The anion interactions in **5** are different with three pentaborate(1-) acceptor sites (α,α,γ), all reciprocal $R_2^2(8)$, and an interstitial H_2O acceptor site. The cations in **2**–**5** are situated within the anionic lattices and have the potential to be H-bond donors (and acceptors) which can further stabilize the anionic lattices and help to template their self-assembly. Examples of such interactions, which involve novel ring systems that incorporate the $Ni^{(II)}$ centres, ligands interstitial molecules and pentaborate(1-) anions, are $R_4^4(14)$ {Ni1-N3B-H3B ··· O10-O1OH ··· O9-O9H ··· O4-B1-O1-B2-O7 ··· H2B-N2B-} (**2**) (includes three pentaborate(1-) anions), $R_2^2(8)$ {Ni1-O11-H11B ··· O7-B2-O2 ··· H12A-N12-} (**3**) (one pentaborate(1-) anion), $R_2^2(8)$ {Ni1-N11-H11D ··· O11-B2-O7 ··· H11-O11-} (**4**) (one pentaborate(1-) anion) and $R_2^2(8)$ {Ni1-N11-H11D ··· O1-B2-O7 ··· H11-O11-} (**4**) (one pentaborate(1-) anion), and $R_4^4(16)$ {Ni1-N1-H1C ··· O5-B4-O4-B1-O3 ··· H1A-O11 ··· H7-O7-B2-O1 ··· H4A-N4-} (**5**) (two pentaborate(1-) anions and one interstitial H_2O with O11). The $R_2^2(8)$ interaction for **3** is illustrated in Figure 7. Full details of all these interactions (and associated atomic numbering systems) are available in the Supplementary Materials.

Compound **6** is a heptaborate(2-) salt with numerous opportunities for interionic H-bonding interactions with the each anion possessing 14 potential acceptor sites and five donor sites and the two cations potentially having 20 donor sites and four acceptor sites; there are also four interstitial H_2O molecules. Potentially templating cation–anion interactions include the $R_2^2(8)$ {Ni1-N12-H12A ··· O10-B4-O3 ··· H11A-N11-}, the $R_3^3(8)$ {Ni2-N12-H12D ··· O23-H23B ··· O11 ··· H11D-N11-}, and the $R_2^2(10)$ {Ni1-O21-H21B ··· O14-B1-O1-B2-O6 ··· H2B-N2-}. The familiar $R_2^2(8)$ anion–anion interaction is present in {O12-H12 ··· O9′-B7′-O13′-H13′ ··· O7-B6-} and the reciprocal {O11-H11 ··· O5′-B5′-O11′-H11′ ··· O5-B5-} and there is also a $R_2^2(12)$ interaction, {O10-H10 ··· O8′-B2′-O2′-B4′-O10′-H10′ ··· O8-B2-O2-B4-}. The fifth heptaborate hydroxy group (containing O14) does not form a donor bond but O14 has a $R_2^2(10)$ acceptor interaction with a cation, as described above.

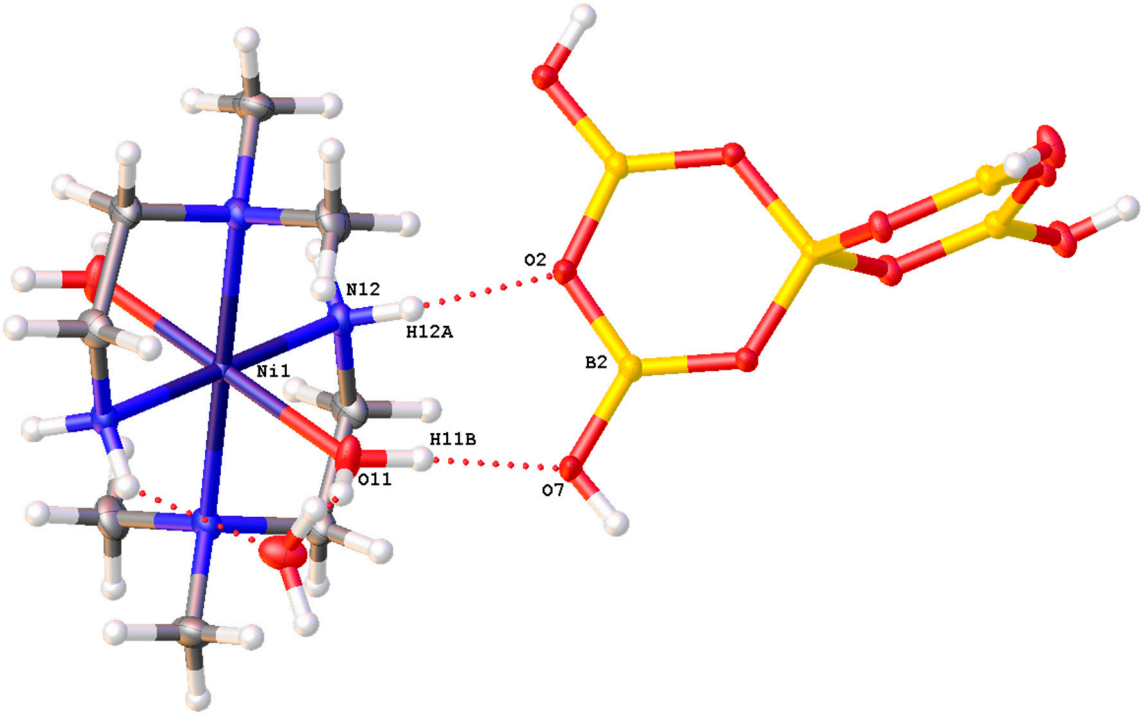


Figure 7. Drawing of the $R_2^2(8)$ {Ni1-O11-H11B ··· O7-B2-O2 ··· H12A-N12-} interaction involving the $Ni^{(II)}$ in *trans*-$[Ni(dmen)_2(H_2O)_2]$ $[B_5O_6(OH)_4]_2{\cdot}2H_2O$ (**3**).

Intermolecular H-bonding, in addition to the intramolecular interaction found in **7** (Section 2.2.1) can be found in **7** and **8**. Such interactions for **7** include $R_2^2(6)$ {Ni1-O8-H8 ··· O2 ··· H1AA-N1-} and {Ni1-O9-H9 ··· O3 ··· H2BD-N2-}, $R_4^4(8)$ {O21-H21B ··· O10H10 ··· O21′-H21B′ ··· O10′-H10′ ··· } and a reciprocal $R_2^2(12)$ {O12-H12 ··· O6′-B3′-O5′-B5′-O12′-H12′ ··· O6-B3-O5-B5-}. There are five interstitial H_2O's per $Ni^{(II)}$ centre in **8** and their main roles are to act as 'spacers' [28] by forming H-bond bridges between neutral $Ni^{(II)}$ oxidoborate complexes. Templating interactions occur when the oxidoborate ligand of one complex enters the second coordination sphere of another. This occurs in reciprocal oxidoborate ligand $R_2^2(12)$ interactions, {O11-H11 ··· O10′-B6′-O7′-B1′-O11′-H11′ ··· O10-B6-O7-B1-} and {O12-H12 ··· O9′-B5′-O4′-B2′-O12′-H12′ ··· O9-B5-O4-B2-}; these are that similar to one observed in **7** and in another heptaborate(2-) system [52]. A $R_2^2(8)$ {O8-H8 ··· O2′-B4′-O8′-H8′ ··· O2-B4-} interaction also links oxidoborate sections of neighbouring complexes.

*2.3. Magnetic, Spectroscopic, Thermal and p-XRD Characterization of Compounds **1–8***

Magnetic susceptibility measurements on **1–8** confirmed that all, excepting **5**, are paramagnetic with χ_m values ranging from 2500×10^{-6} to 3600×10^{-6} $cm^3{\cdot}mol^{-1}$ (μ_{eff} of 2.6–3.0 BM) corresponding to two unpaired electrons per formula unit. Compound **5** is diamagnetic ($\chi_m = -170 \times 10^{-6}$ $cm^3{\cdot}mol^{-1}$), and this value is in accord with the $Ni^{(II)}$ centre being square-planar. The χ_m values of **1–4**, **7** and **8** are typical of octahedral $Ni^{(II)}$ complexes [61] and have similar values to those obtained for the starting octahedral $Ni^{(II)}$ complexes. Compound **6** is unusual in that it has a μ_{eff} corresponding to two unpaired electrons but there are *two* $Ni^{(II)}$ centres in the formula unit; the XRD study confirmed that one $Ni^{(II)}$ centre is square planar and the other is octahedral.

Compound **5**, in D_2O solvent, gave ^1H and ^{13}C NMR signals for the AEN ligand at similar intensities and chemical shifts to those obtained for $[Ni(AEN)]Cl{\cdot}H_2O$ and other reported data [62]. ^1H and ^{13}C NMR signals for the organic ligands (in D_2O) were not observable for the other $Ni^{(II)}$ oxidoborates despite their apparent solubility, due to their paramagnetic properties. Despite the possible lability of the organic ligands the complexes the organic ligands are not sufficiently labile to be remote from the $Ni^{(II)}$ centres during the lifetime of the NMR experiment. ^{11}B NMR spectra for *all* D_2O solutions arising from

the $Ni^{(II)}$ oxidoborates were observed and a probable explanation for this being two-fold: (i) compounds with insular oxidoborate anions (**1–6**) are not coordinated to the $Ni^{(II)}$ centres and hence are not in close proximity and unaffected by the paramagnetic centres, and (ii) the coordinated hexaborate(2-) ligands are significantly more labile than the *N*-donor ligands in **7** and **8**. The ^{11}B spectra were not particularly characteristic of the specific oxidopolyborate anions in **1–8** since it is known that dissolution of oxidopolyborate anions in aqueous solution yields solutions containing equilibrium mixtures of various oxidopolyborate anions whose concentrations are pH are boron concentration dependent [19,20]. However, pentaborate(1-) salts often afford spectra in a characteristic pattern with three signals at ca. +17, +13 and +1 ppm which have been assigned to $B(OH)_3/[B(OH)_4]^-$, $[B_3O_3(OH)_4]^-$ and $[B_5O_6(OH)_4]^-$ species [5,27,28]; compounds **2–4** all showed this characteristic pattern. Dilute solutions often give just one signal, assigned to $B(OH)_3/[B(OH)_4]^-$, at a chemical shift which is variable [19] but can be calculated assuming fast exchange of $B(OH)_3/[B(OH)_4]^-$ according to their relative proportions present in the oxidopolyborate anion originally present [27]. Unsurprisingly, therefore, compounds **1** and **5–8** all gave single signals at +11.1, +16.3, +15.8, +17.7 and +15.8 ppm respectively. The observed chemical shifts for the tetraborate(2-) (**1**) and the pentaborate(-) (**5**) salts are as would be expected from this calculation (+11.0 and +16.1, respectively) but chemical shifts for the hexaborate(2-) (**7** and **8**) and the heptaborate(2-) (**6**) salts are ca. 2 ppm more downfield than expected (13.8 and 14.6 ppm calc., respectively), indicating that more $B(OH)_3$ might be present than expected. Similar behaviour has been observed before for hexaborate [34–38] and heptaborate [33] complexes.

Vibration spectroscopy is often used to help characterize oxidopolyborate species since strong, and often diagnostic, B-O stretches can be observed by IR spectroscopy between 1600 and 600 cm^{-1} [63]. In particular, diagnostic bands have been reported for pentaborate(1-) [5,27,28,64], hexaborate (2-) [35,37,63], and heptaborate(2-) [28,33,52] anions. Compounds **1–8** all displayed such diagnostic bands with the diagnostic band for the pentaborate(1-) anion (*ca.* 1925 cm^{-1}) clearly present in **1- 5**. Likewise, the diagnostic bands for hexaborate(2-) anion (*ca.* 960 and 810 cm^{-1}) and the heptaborate(2-) anion (*ca.* 860 cm^{-1}) were observed in IR spectra of **6** and **7**, and **8**, respectively.

Selected $Ni^{(II)}$ oxidoborates (**2**, **4–7**) were thermally decomposed air and insights into these decompositions were obtained through TGA/DSC studies. The $Ni^{(II)}$ oxidoborates all yielded green glassy residues by 700 °C with masses consistent with anhydrous $Ni^{(II)}$ oxidoborates being produced with Ni:B stochiometries in the elemental ratios of their precursors. Thus, the pentaborates **2** and **4** were decomposed to $NiB_{10}O_{16}$ whilst **5** gave $Ni_2B_{10}O_{17}$, the heptaborate (**6**) gave $Ni_2B_{14}O_{23}$ and the hexaborate (**7**) yielded NiB_6O_{10}. These decomposition reactions are generally two-step processes with the first steps being a lower temperature (<280 °C) endothermic dehydration (loss of interstitial H_2O and condensation reactions of the hydrated oxidoborates) followed by higher temperature (280–700 °C) exothermic oxidations of the organic ligands. Details for individual compounds (**2**, **4–7**) are given in the experimental section. This type of decomposition behaviour has been observed previously for other hydrated $Ni^{(II)}$ oxidoborates [33,42–48] and more generally applies to the thermolysis of many hydrated transition-metal oxidopolyborates [30,33,35,37]. Powder XRD data were also obtained for this selection of $Ni^{(II)}$ oxidoborates (*viz.* **2**, **4–7**). The data obtained were good matches with data calculated from the single-crystal XRD data indicating that these samples were crystalline and homogeneous.

3. Experimental Methods

3.1. General

The $Ni^{(II)}$ complexes *s-fac*-$[Ni(dien)_2]Cl_2{\cdot}H_2O$ [65] $[Ni(dmen)_2]Cl_2{\cdot}4H_2O$ [66] , $[Ni(HEen)_2]$ Cl_2 [67], $[Ni(AEN)]Cl{\cdot}H_2O$ [62], *trans*-$[Ni(dach)_2(H_2O)_2]Cl_2$ [68] were prepared by modified literature procedures. FTIR spectra were obtained as KBr pellets on a Perkin–Elmer 100FTIR spectrometer (Perkin–Elmer, Seer Green, UK). ^{11}B NMR spectra were obtained on a Bruker Avance-400 spectrometer (Bruker, Coventry, UK) on samples

dissolved in D_2O at 128 MHz. TGA and DSC were performed on an SDT Q600 instrument (TA Instruments, New Castle DE, USA) using Al_2O_3 crucibles with a ramp rate of 10 °C per minute (RT to 1000 °C in air). X-ray crystallography was performed at the EPSRC national crystallography service centre at Southampton University. Magnetic susceptibility measurements were performed on a Johnson–Matthey magnetic susceptibility balance. (Johnson–Matthey, UK). CHN analyses were obtained from OEA Laboratories (Callingham, Cornwall).

3.2. X-ray Crystallography

Crystallographic data for **1–8** are given in the experimental section. The crystallographic data collection of compounds were performed on a Rigaku FR-E+ diffractometer (**1, 3–8**) equipped with an AFC12 goniometer, an HG Saturn 724+ detector and either HF varimax confocal mirrors (**1, 3, 4, 6–8**) or VHF varimax confocal mirrors (**5**). Data for **2** were obtained on DLS synchronous beamtime 119 equipped with a crystallographic goniometer and a Rigaku HG Saturn 724 detector. Data for all compounds were obtained at 100(2)K. Cell determinations and data collections were carried out using either CrysAlisPro [69] (**1**) or CrystalClear [70] (**2–8**). Data reduction, cell refinement and absorption correction were carried out using either CrysAlisPro [69] (**1–3, 5–8)** or CrystalClear [70] (**4**). Using Olex2 [71] the structures were solved using SHELXT [72] and models or refined with SHELXL [73]. Structure refinement details are given in the Supplementary Material. CCDC 2101911-2101918 (**1–8** respectively), contains 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 CCDC, 12 Union Road, Cambridge, CB2 1EZ. Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk)

3.3. Preparation of Trans-$[Ni(NH_3)_4(H_2O)_2][B_4O_5(OH)_4]\cdot H_2O$ (*1*)

$NiCl_2\cdot 6H_2O$ (1.00 g, 4.0 mmol) dissolved in ethanol (25 mL) and gave a clear green solution. Aqueous NH_3 solution (2.2 mL, 25%, 24 mmol) was added dropwise to the green solution with stirring and then was left to stir for a further 5 min to give a dark blue solution. Ag_2O (0.926 g, 4 mmol) was rapidly added and stirred at room temperature for 5 min and the precipitate which had formed (AgCl) was removed by filtration. $B(OH)_3$ (1.23 g, 20 mmol) was added to the dark blue filtrate and left to stir for a further 10 min. The reaction mixture was filtered into vials and left to allow for slow evaporation of the solvent. After 2 weeks a light blue solid (**1**) had formed in the bottom of a vial and this was collected by filtration. (0.6 g, 40%). M.p. $\geq$ 300 °C. $\chi_m = 2500 \times 10^{-6}$ $cm^3\cdot mol^{-1}$. $H_{22}B_4N_4NiO_{12}$. Anal. Calc.: H = 6.0%, N = 15.1%. Found: H = 5.7%, N = 15.3. ^{11}B/ppm: 11.1. IR (KBr/cm^{-1}): 3375(s), 3245(s), 1634(m), 1450(s), 1402(s), 1345(s), 1230(m), 1152(m), 1059(m), 1002(s), 936(m), 828(m). sc-XRD crystal data: M_r = 372.16, monoclinic, $P2_1/c$ (No. 14), a = 8.27730(10) Å, b = 20.5277(3) Å, c = 8.01330(10) Å, β = 91.2830(10)°, $\alpha = \gamma = 90°$, V = 1361.23(3) $Å^3$, T = 100(2) K, Z = 4, Z' = 1, $\mu(MoK_\alpha)$ = 1.492 mm^{-1}, 15,477 reflections measured, 3128 unique (R_{int} = 0.0329) which were used in all calculations. The final wR_2 was 0.0528 (all data) and R_1 was 0.0216 ($I > 2\sigma(I)$).

3.4. Preparation of *s-fac*-$[Ni(dien)_2][B_5O_6(OH)_4]_2$ (*2*)

s-fac-$[Ni(dien)_2]Cl_2\cdot H_2O$ (1.05 g, 3.0 mmol) was dissolved in H_2O (10 mL) and added to a suspension of excess DOWEX® monosphere 550A OH^- activated anion exchange resin (Dupont, Wilmington, DE, USA) (40 g) in H_2O (40 mL). The mixture was left to stir for 30 h at RT and then filtered to remove the resin. The filtrate, containing *s-fac*-$[Ni(dien)_2](OH)_2$, was reduced in volume to 15 mL and MeOH (15 mL) was added. $B(OH)_3$ (1.83 g, 29.7 mmol) was added to the H_2O/MeOH solution which was then gently warmed with stirring for 3 h. The solution was concentrated to 5 mL under reduced pressure and the concentrated solution was left for a few days for crystallization. Purple crystals of **2** were carefully recovered by filtration and dried in air (0.70 g, 34%). M.p. = 287–289 °C (dec.). $\chi_m = 3516 \times 10^{-6}$ cm^3 mol^{-1}. $C_8H_{34}B_{10}N_6NiO_{20}$. *Anal.* Calc.: C = 13.7%, H = 4.9%,

N = 12.0%. Found: C = 14.0%, H = 5.4%, N = 12.1%. ^{11}B/ppm: 1.5 (1%), 13.3 (13%), 17.4 (86%). IR (KBr/cm $^{-1}$): 3362(s), 3333(s), 3297(s), 3263(s), 1412(s), 1330(s), 1303(s), 1135(m), 1059(m), 1042(m), 1028(m), 964(m), 931(m), 915(s), 774(s), 772(m), 707(s). TGA: 100-200 °C, condensation of polyborate which loss of four H_2O 14.9% (10.2% calc.); 200–650 °C, oxidation of organic content 40.3% (39.7% calc.); residual NiB_8O_{13} 59.7% (60.3% calc.). p-XRD d-spacing/Å (% rel. int.): 6.22 (24), 5.88 (100), 5.57 (94), 4.27 (15), 3.79 (19), 3.71 (28), 2.94 (17). sc-XRD crystal data: M_r = 701.22, triclinic, *P*-1 (No. 2), a = 8.5763(5) Å, b = 9.2902(6) Å, c = 9.3493(6) Å, α = 78.098(5)°, β = 89.108(5)°, γ = 89.110(5)°, V = 728.75(8) Å^3, T = 100(2) K, Z = 1, Z' = 0.5, μ(Synchrotron$_{0.6889Å}$) = 0.702 mm $^{-1}$, 6342 reflections measured, 3152 unique (R_{int} = 0.0476) which were used in all calculations. The final wR_2 was 0.2109 (all data) and R_1 was 0.0767 (I > 2σ(I)).

*3.5. Preparation of Trans-[Ni(dmen)$_2$(H$_2$O)$_2$][B$_5$O$_6$(OH)$_4$]$_2$·2H$_2$O (**3**)*

[Ni(dmen)$_2$]Cl$_2$·4H$_2$O (0.97 g, 3.0 mmol), and Ag_2O (0.75 g, 3.2 mmol) were rapidly stirred in H_2O (30 mL) at room temperature for 40 min and the precipitate which had formed (AgCl) was removed by filtration. $B(OH)_3$ (1.85 g, 30 mmol) was added to the dark blue filtrate and left to stir for a further 40 min. The reaction mixture was filtered into vials and then left to allow for slow evaporation of solvent. After 3 weeks a light blue solid **(3**) had formed in the bottom of a vial and this was collected by filtration. (0.9 g, 40%). M.p. ≥ 300 °C. χ_m = 3600 × 10^{-6} cm^3·mol^{-1}. $C_8H_{40}B_{10}N_4NiO_{24}$. Anal. Calc.: C = 12.9%, H = 5.4%, N = 7.5%. Found: C = 13.0%, H = 5.5%, N = 7.5. ^{11}B/ppm 16.6 (85%), 13.9 (14%), 1.2 (1%). IR (KBr/cm $^{-1}$): 3510 (m), 3348(s), 3285(s), 1608(m), 1415(s), 1310(s), 1129(m), 1043(m), 1015(m), 920(s), 780(s), 707(m), 486(m). sc-XRD crystal data: M_r = 743.25, triclinic, *P*-1 (No. 2), a = 8.6570(3) Å, b = 9.7443(3) Å, c = 10.2101(3) Å, α = 107.087(3)°, β = 102.747(3)°, γ = 95.002(3)°, V = 792.23(5) Å^3, T = 100(2) K, Z = 1, Z' = 0.5, μ(MoK$_\alpha$) = 0.708 mm^{-1}, 12,978 reflections measured, 3628 unique (R_{int} = 0.0163) which were used in all calculations. The final wR_2 was 0.0731 (all data) and R_1 was 0.0270 (I > 2σ(I)).

*3.6. Preparation of [Ni(HEen)$_2$][B$_5$O$_6$(OH)$_4$]$_2$ (**4**)*

The preparation of [Ni(HEen)$_2$](OH)$_2$ was carried out as described previously for **2** from [Ni(HEen)$_2$]Cl$_2$ (1.00 g, 2.95 mmol) and Dowex (40 g). $B(OH)_3$ (1.83 g, 29.6 mmol) was added with stirring. The reaction mixture was stirred for a further 2 h at room temperature. The solvent was then evaporated to 5 mL using a rotary evaporator, then the resulting solution was left for 10 d in several NMR tubes for crystallization to yield purple crystals of **4** (0.76 g, 37%). M.p. = 288–289 °C (dec.). χ_m = 3430 × 10^{-6} cm^3 mol^{-1} $C_8H_{32}B_{10}N_4NiO_{22}$. *Anal.* Calc.: C = 13.7%, H = 4.6%, N = 8.0%. Found: C = 13.7%, H = 4.7%, N = 8.0%. ^{11}B/ppm: 1.2 (3%), 13.4 (23%), 18.0 (74%). IR (KBr/cm $^{-1}$): 3375(s), 3288(s), 3322(s), 1410(s), 1321(s), 1196(m), 1141(s), 1022(s), 919(s), 774(s), 706(s). TGA: 230–290 °C, condensation of polyborate which loss of four H_2O 10.3% (10.2% calc.); 290–700 °C, oxidation of organic content 37.9% (39.9% calc.); residual $NiB_{10}O_{16}$ 62.1% (60.1 calc.). p-XRD d-spacing/Å (% rel. int.): 6.18 (40), 5.88 (75), 5.50 (100), 3.94 (26), 3.78 (38), 3.66 (25). sc-XRD crystal data: M_r = 703.18, Monoclinic, $P2_1/c$, a = 8.3891(2) Å, b = 11.6666(3) Å, c = 14.3092(4) Å, $\alpha = \gamma$ = 90°, β = 90.035(2)°, V =1400.47(6) Å^3, T = 100(2) K, Z = 2, Z' = 0.5, μ(MoK$_\alpha$) = 0.791 mm^{-1}, 6239 reflections measured, 6239 unique (R_{int} = 0) which were used in all calculations. The final wR_2 was 0.1124 (all data) and R_1 was 0.0499 (I > 2σ(I)).

*3.7. Preparation of [Ni(AEN)][B$_5$O$_6$(OH)$_4$]·H$_2$O (**5**)*

The preparation of [Ni(AEN)](OH) was carried out as described previously for **2** from [Ni(AEN)]Cl·H$_2$O (2.10 g, 7.0 mmol) and Dowex (25 g). $B(OH)_3$ (2.22 g, 36 mmol) was added to the aqueous solution which was gently warmed with stirring for 3 h, and then its volume was reduced to 5 mL under reduced pressure. The solution was then distributed in several NMR tubes for crystallization and left for 10 days to yield dark red crystals of **5** (1.30 g, 38%). M.p. = 279–280 °C (dec.). χ_m = −170 × 10^{-6} cm^3 mol^{-1}. $C_9H_{25}B_5N_4NiO_{11}$. *Anal.* Calc.: C = 22.6%, H = 5.3%, N = 11.7%. Found: C = 22.7%, H = 5.4%, N = 11.7%. ^{1}H/ppm: 2.0 (s,

6H, CH_3), 2.5 (t, 4H, J = 6 Hz, CH_2 of en), 3.2 (t, 4H, J = 6 Hz, CH_2 of en), 4.8 (s, 11H, NH_2, H_2O, OH, CH). ^{13}C/ppm: 19.9, 43.0, 53.6, 160.5. ^{11}B/ppm: 16.3. IR (KBr/cm^{-1}): 3377(s), 3326(s), 3288(s), 3246(s), 3169(s), 1615(m), 1566(m), 1536(m), 1476(s), 1442(s), 1416(s), 1393(s), 1333(s), 1295(s), 1129(m), 1094(s), 1072(m), 1019(m), 924(s), 778(m). TGA: 100–180 °C, loss of one interstitial H_2O 2.5% (3.7% calc.); 180–280 °C, condensation of polyborate which loss of two further H_2O 10.0% (11.3% calc.); 280–700 °C, oxidation of organic content 46.1% (48.0% calc.); residual $Ni_2B_{10}O_{17}$ 53.9% (52.0% calc.). p-XRD d-spacing/Å (% rel. int.): 5.65 (69), 5.38 (100), 4.14 (46), 3.89 (33), 3.81 (53), 3.65 (58), 2.03 (41), 1.43 (33). sc-XRD crystal data: M_r = 478.09, Triclinic, P-1, a = 8.5386(2) Å, b = 11.3328(3) Å, c = 11.8717(3) Å, α = 115.914(3)°, β = 101.626(2)°, γ = 99.670(2)°, V = 968.39(5) Å^3, T = 100(2) K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 1.065 mm^{-1}, 16,639 reflections measured, 4433 unique (R_{int} = 0.0216) which were used in all calculations. The final wR_2 was 0.0765 (all data) and R_1 was 0.0278 (I > 2σ(I)).

*3.8. Preparation of Trans-[Ni(dach)$_2$(H$_2$O)$_2$] [Ni(dach)$_2$] [B$_7$O$_9$(OH)$_5$]$_2$·4H$_2$O (**6**)*

The preparation of $[Ni(dach)_2(H_2O)_2](OH)_2$ was carried out as previously described for **2** from *trans*-$[Ni(dach)_2(H_2O)_2]Cl_2$ (1.00 g, 2.53 mmol) and Dowex (40 g). $B(OH)_3$ (1.56 g, 25.2 mmol) was added to the solution which was then gently warmed with stirring for 3 h. The solution volume was reduced to 5 mL under reduced pressure. The product (**6**) was isolated by filtration, and then allowed to dry in an oven at 40 °C for 3 h to afford orange prismatic crystals (0.78 g, 47%). M.p. = 270–272 °C (dec.). $\chi_m = 3030 \times 10^{-6}$ cm^3 mol^{-1}. $C_{24}H_{78}B_{14}N_8Ni_2O_{34}$. *Anal*. Calc.: C = 22.3%, H = 6.1%, N = 8.7%. Found: C = 21.8%, H = 6.3%, N = 8.4%. ^{11}B/ppm: 15.8. IR (KBr/cm $^{-1}$): 3663(s), 3271(s), 2929(m), 2863(m), 1468(m), 1453(s), 1350(s), 1180(s), 1125(m), 1066(s), 986(w), 854(m), 807(m). TGA: 100190 °C, loss of four interstitial and two coordinated H_2O 7.5% (8.4% calc.); 190–270 °C, condensation of polyborate which loss of five further H_2O 15.0% (15.3% calc.); 270–720 °C, oxidation of organic content 48.2% (50.7% calc.); residual $Ni_2B_{14}O_{23}$ 51.8% (49.3% calc.). p-XRD d-spacing/Å (% rel. int.): 10.67 (100), 9.81 (89), 6.25 (58), 5.35 (70), 4.26 (48), 3.74 (55), 2.03(59). sc-XRD crystal data: M_r = 645.85, Monoclinic, $C2/c$, a = 22.3539(4) Å, b = 11.0192(2) Å, c = 22.8834(4) Å, $\alpha = \gamma = 90°$, β = 107.630(2)°, V = 5371.94(18) Å^3, T = 100(2) K, Z = 8, Z' = 1, μ(MoK$_\alpha$) = 0.806 mm^{-1}, 33628 reflections measured, 6154 unique (R_{int} = 0.0281) which were used in all calculations. The final wR_2 was 0.1087 (all data) and R_1 was 0.0384 (I > 2σ(I)).

*3.9. Preparation of Trans-[Ni(en)(H$_2$O)$_2${B$_6$O$_7$(OH)$_6$}]·H$_2$O (**7**)*

An aqueous solution of en (2.30 g, 70%, 26.79 mmol) was added to an aqueous solution (10 mL) of $NiSO_4{\cdot}6H_2O$ (2.12 g, 8.06 mmol). The reaction mixture was stirred for 5 min, and then an aqueous solution (10 mL) of $Ba(OH)_2{\cdot}8H_2O$ (2.54 g, 8.06 mmol) was added. The reaction mixture was stirred for 30 min and then filtered to remove the $BaSO_4$. A solution of $B(OH)_3$ (4.98 g, 80.6 mmol) in H_2O (10 mL) was added to the filtrate with stirring. The reaction mixture was stirred at room temperature for 2 h. The solution was then distributed in several vials and left for 10 d to yield faint blue crystals of **7** (1.20 g, 33%). M.p. = 245–247 °C (dec.). $\chi_m = 2588 \times 10^{-6}$ cm^3 mol^{-1}. $C_2H_{20}B_6N_2NiO_{16}$. *Anal.* Calc.: C = 5.3%, H = 4.5%, N = 6.2%. found: C = 5.4%, H = 4.5%, N = 6.2%. ^{11}B/ppm: 17.7. IR (KBr/cm $^{-1}$): 3400(s), 3350(s), 2924(w), 1420(m), 1380(s), 1360(s), 1133(s), 1095(s), 1044(s), 955(m), 908(m), 809(s). TGA: 100–180 °C, loss of one interstitial H_2O and two coordinated water molecules 0.8% (12% calc.); 180–280 °C, condensation of polyborate which loss of three further H_2O 24.3% (23.9% calc.); 280–700 °C, oxidation of organic content 38.6% (37.2% calc.); residual NiB_6O_{10} 61.4% (62.8% calc.). p-XRD d-spacing/Å (% rel. int.): 9.78 (100), 8.26 (24), 6.77 (53), 4.88 (48), 3.99 (34), 3.38 (30), 2.74 (47). sc-XRD crystal data: M_r = 451.77, triclinic, P-1 (No. 2), a = 8.5116(7) Å, b = 9.7946(5) Å, c = 9.8073(8) Å, α = 89.873(5)°, β = 82.901(7)°, γ = 74.372(6)°, V = 780.94(10) Å^3, T = 100(2) K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 1.333 mm $^{-1}$, 5883 reflections measured, 5883 unique (R_{int} = 0) which were used in all calculations. The final wR_2 was 0.1902 (all data) and R_1 was 0.0682 (I > 2σ(I)).

*3.10. Preparation of [Ni(dmen)(H_2O){$B_6O_7(OH)_6$}]·5H_2O (**8**)*

The preparation of [Ni(dmen)$_2$](OH)$_2$ was carried out as described for **2** from [Ni(dmen)$_2$]Cl$_2$·4H$_2$O (1.00 g, 2.6 mmol) and Dowex (30 g). B(OH)$_3$ (1.57 g, 25 mmol) was added to the filtrate and left to stir for 30 min. The turquoise solution was filtered into vials and left to allow for slow evaporation of the solvents. After 2 weeks, a blue-green solid (**8**) had formed in the bottom of a vial and this was collected by filtration. Yield: (0.5 g, 36%). M.p. $\geq$ 300 °C. χ_m = 3050 × 10^{-6} cm^3 mol^{-1}. $C_4H_{30}B_6N_2NiO_{19}$. Anal. Calc.: C = 9.0%, H = 5.7%, N = 5.2%. Found: C = 9.3%, H = 5.5%, N = 5.5. ^{11}B/ppm: 15.8. IR (KBr/cm $^{-1}$): 3399(s), 1642(m), 1416(s), 1355(s),1247(s), 1120(s), 1052(m), 1009(m), 962(m), 859(m), 813(s), 700(m). sc-XRD crystal data: M_r = 533.87, triclinic, *P*-1 (No. 2), a = 9.1508(4) Å, b = 9.8599(4) Å, c = 13.5971(4) Å, α = 88.525(3)°, β = 70.627(3)°, γ = 65.245(4)°, V = 1041.79(8) Å^3, T = 100(2) K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 1.023 mm $^{-1}$, 15537 reflections measured, 4713 unique (R_{int} = 0.0461) which were used in all calculations. The final wR_2 was 0.1048 (all data) and R_1 was 0.0403 (I > 2σ(I)).

4. Conclusions

Eight new oxidoborate Ni$^{(II)}$ compounds were prepared by self-assembly crystallization processes from aqueous solution starting from B(OH)$_3$ and selected Ni$^{(II)}$ complexes. Six of these compounds were salts containing *insular* oxidoborate anions, but two products were complexes containing *coordinated* oxidoborate(2-) anions, with energetically favourable Ni-O bonds. The two products that contained coordinated hexaborate(2-) ligands were neutral monomeric complexes, rather than the 1-D coordination polymers that we have occasionally observed in related Cu$^{(II)}$ and Zn$^{(II)}$ chemistry. The new compounds were templated in all cases by numerous strong structure-directing inter/intramolecular H-bonding interactions involving the oxidoborate ligands and many novel H-bonding motifs are noted and described. This work further demonstrates that in general the inclusion of labile metal complexes into aqueous solutions containing B(OH)$_3$ can lead to the self-assembly of novel species including those with coordinated oxidoborate ligands and that this synthetic strategy could be applied successfully to other systems.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/inorganics9090068/s1: single-crystal XRD data, including H-bond interactions.

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