

## Conference paper

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# Transition-metal complexes with oxidoborates. Synthesis and XRD characterization of $[(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Zn}\{\kappa^3\text{O},\text{O}',\text{O}''-\text{B}_{12}\text{O}_{18}(\text{OH})_6-\kappa^1\text{O}'''\}\text{Zn}(\text{en})(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)] \cdot 8\text{H}_2\text{O}$ ( $\text{en} = 1,2\text{-diaminoethane}$ ): a neutral bimetallic zwiterionic polyborate system containing the ‘isolated’ dodecaborate(6–) anion

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**Abstract:** The title compound,  $[(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Zn}\{\kappa^3\text{O},\text{O}',\text{O}''-\text{B}_{12}\text{O}_{18}(\text{OH})_6-\kappa^1\text{O}'''\}\text{Zn}(\text{en})(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)] \cdot 8\text{H}_2\text{O}$  ( $\text{en} = 1,2\text{-diaminoethane}$ ) (1), was prepared as a crystalline solid in moderate yield from the reaction of  $\text{B}(\text{OH})_3$  with  $[\text{Zn}(\text{en})_3][\text{OH}]_2$  in aqueous solution (15:1) ratio. The structure contains a neutral bimetallic complex comprised of a unusual dodecaborate(6–) anion ligating two  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2\text{Zn}(\text{en})]^{3+}$  centers in a monodentate ( $n = 1$ ) or tridentate ( $n = 0$ ) manner.

**Keywords:** dodecaborate(6–); IMEBORON-16; oxidoborate; polyborate; self-assembly; X-ray structure; zinc(II).

## Introduction

Oxidoborates (or more correctly hydroxyoxidoborates) are anionic boron species with boron atoms linked solely to oxygen atoms and such compounds are commonly referred to as ‘borates’ [1]. Polyborate anions can be readily categorized as ‘isolated’ or ‘insular’, containing discrete anionic moieties, or ‘condensed’ with more condensed 2D or 3D polymeric chains, sheets or networks [2–4]. These anions contain numerous fused B–O rings and cages with the ‘boroxole’  $\{\text{B}_3\text{O}_3\}$  ring system a very common structural motif. Salts containing polyborate anions have attracted recent attention due to their applications as bulk chemicals and possible applications as luminescent, second harmonic generation, ferroelectric, flame retardant and non-linear optical materials [5–16].

Polyborates are readily synthesized by solvothermal methods or the addition of  $\text{B}(\text{OH})_3$  to a basic aqueous solution containing templating cations: polyborate salts containing isolated anions are generally obtained from aqueous solution, whereas solvothermal methods often give the more condensed species [17]. Polyborates crystallize from aqueous solution as cation templated self-assembled solids [18] since in basic aqueous solution  $\text{B}(\text{OH})_3$  exists as a dynamic combinatorial library (DCL) [19, 20] of numerous polyborate anions [21–25]. Polyborate salts containing the pentaborate(1–) anion,  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ , are very common and this is because

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these salts have a strong three-dimensional H-bonded anionic lattice and this lattice is sufficiently flexible to accommodate many medium sized non-metal uncharged cations [26, 27].

We are interested in the synthesis of structurally novel polyborate anions and have adopted a strategy of templating such anions by the use of non-innocent (sterically demanding or multi H-bond donating) and/or more highly charged transition-metal cations. We have recently reported the synthesis of salts containing isolated polyborate anions partnered with inert cobalt(3+) complexes and have described the synthesis and structures of two previously unobserved isolated polyborate anions: heptaborate(3-) and octaborate(2-) [28, 29]. We have also prepared a series of salts and neutral complexes containing more labile copper(2+) centers where pentaborate(1-) or hexaborate(2-) ions are found coordinated to the metal center [30].

We now report an unusual neutral zwitterionic bizinc complex,  $[(H_3NCH_2CH_2NH_2)Zn\{\kappa^3O,O',O''-B_{12}O_{18}(OH)_6-\kappa^1O'''\}Zn(en)(NH_2CH_2CH_2NH_2)] \cdot 8H_2O$  (en = 1,2-diaminoethane) (**1**), derived from a self-assembly in methanolic aqueous solution of  $B(OH)_3$  and components of the labile complex salt,  $[Zn(en)_3](OH)_2$ .

## Results and discussion

### Synthesis and characterization

The title compound,  $[(H_3NCH_2CH_2NH_2)Zn\{\kappa^3O,O',O''-B_{12}O_{18}(OH)_6-\kappa^1O'''\}Zn(en)(NH_2CH_2CH_2NH_2)] \cdot 8H_2O$  (**1**), was prepared in moderate yield (40 %) as a colorless crystalline material by a self-assembly process involving a prolonged (30 days) recrystallization period of an aqueous methanolic reaction mixture originally containing  $B(OH)_3$  and  $[Zn(en)_3](OH)_2$  (eq. 1). The  $[Zn(en)_3](OH)_2$  was obtained from  $[Zn(en)_3]Cl_2$  by use of an ion exchange resin.



Compound **1** was characterized primarily by single-crystal XRD study (see below) and its structure is fully consistent with other characterization data that we were able to obtain. Compound **1** is formulated as a neutral molecule although it is zwitterionic with several atoms possessing formal charges and it contains some interesting features (see below). The bulk sample gave satisfactory elemental analysis and its powder XRD pattern was consistent with that derived from the single-crystal XRD analysis, confirming homogeneity. Compound **1** is diamagnetic with a molar magnetic susceptibility of  $-414.2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  and its IR spectrum shows several strong absorptions in the B–O stretching region which are further assigned as follows:  $1355 \text{ cm}^{-1}$  (asymmetric  $B_{\text{tri}}-O$  stretch),  $1163 \text{ cm}^{-1}$  and  $1041 \text{ cm}^{-1}$  (asymmetric  $B_{\text{tet}}-O$  stretch),  $951 \text{ cm}^{-1}$  and  $900 \text{ cm}^{-1}$  (symmetric  $B_{\text{tri}}-O$  stretch), and  $856 \text{ cm}^{-1}$  (symmetric  $B_{\text{tet}}-O$ ) [31]. Compound **1** is decomposed by dissolution in aqueous solution with ( $^1H$  and  $^{13}C$ ) NMR consistent with the ethylenediamine species and  $^{11}B$  NMR showing a single peak (+16.1 ppm) indicative of one signal arising from rapid  $B(OH)_3/OH^-$  exchange equilibria [21–25].

### Solid-state structure

Crystallographic data for compound **1** are given in Table 1, and the structure of **1**, together with associated atomic numbering scheme is given in Fig. 1. Its structure is best represented as comprised of a  $[B_{12}O_{18}(OH)_6]^{6-}$  ligand coordinated to, and bridging two zinc(II) centers.

Compound **1** contains a dodecaborate(6-) anion. This anion was first reported in 1990 in  $Ag_6[B_{12}O_{18}(OH)_6] \cdot 3H_2O$  [32] and was described as an ‘insular’ polyborate anion. The anion is comprised of six boroxole rings linked together in such a way as to produce a larger central 12-membered  $\{B_6O_6\}$  ring (Fig. 2), with each boron atom within this ring being 4-coordinate and carrying a formal negative charge. These six 4-coordinate boron centers (B1–B6) have B–O bond lengths ranging from 1.435(5) to 1.499(6) Å and the O–B–O

Table 1: Crystallographic data for compound 1.

Formula	C <sub>6</sub> H <sub>48</sub> B <sub>12</sub> N <sub>6</sub> O <sub>32</sub> Zn <sub>2</sub>
D <sub>calc.</sub> /g cm <sup>-3</sup>	1.870
μ/mm <sup>-1</sup>	1.505
Formula weight	976.96
Color	Colorless
Shape	Block
Size/mm <sup>3</sup>	0.100×0.090×0.040
T/K	100(2)
Crystal system	Monoclinic
Flack parameter	−0.006(7)
Hoofit parameter	−0.019(7)
Space group	Cc
a/Å	17.2990(5)
b/Å	12.5264(3)
c/Å	16.6091(4)
α/°	90
β/°	105.358(3)
γ/°	90
V/Å <sup>3</sup>	3470.58(16)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK <sub>α</sub>
Θ <sub>min</sub> /°	2.436
Θ <sub>max</sub> /°	27.484
Measured Refl.	21 551
Independent Refl.	7310
Reflections used	7109
R <sub>int</sub>	0.0253
Parameters	536
Restraints	3
Largest peak	1.054
Deepest hole	−0.455
GoF	1.048
wR <sub>2</sub> (all data)	0.0865
wR <sub>2</sub>	0.0856
R <sub>1</sub> (all data)	0.0334
R <sub>1</sub>	0.0322

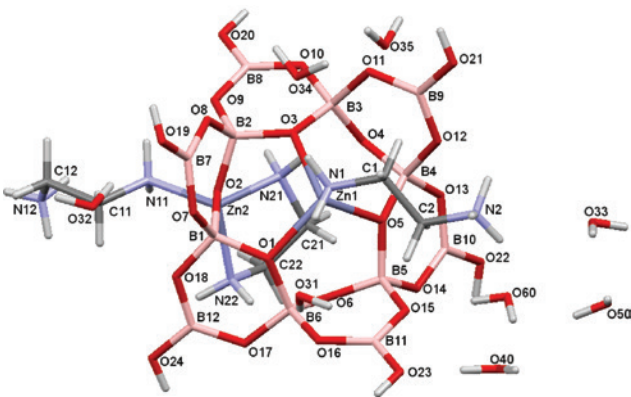
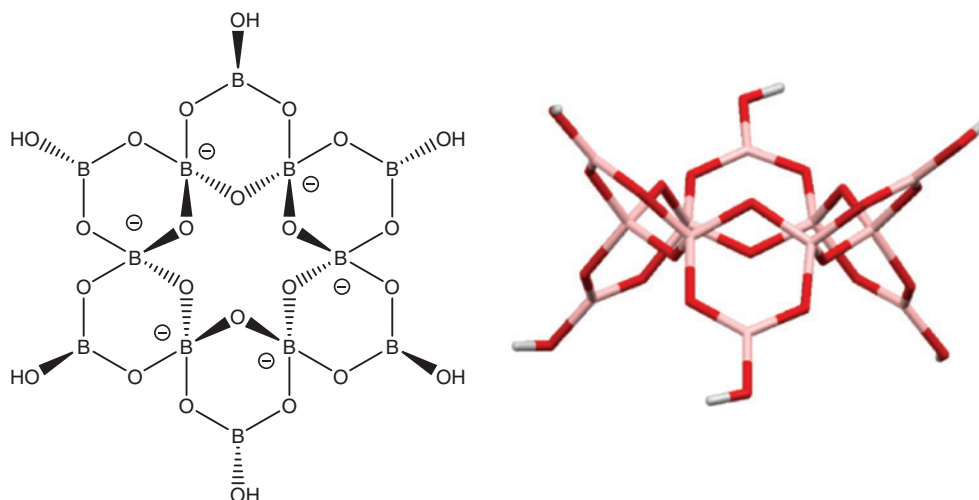


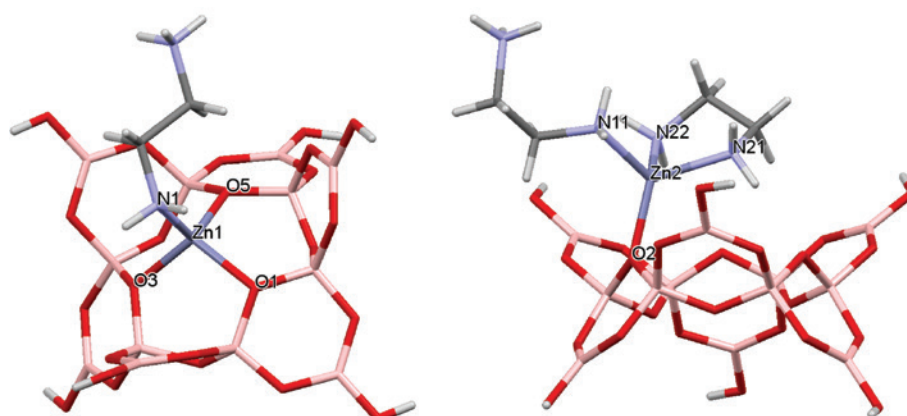
Fig. 1: Diagram showing atomic numbering scheme for [(H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)Zn{κ<sup>3</sup>O,O',O''-B<sub>12</sub>O<sub>18</sub>(OH)<sub>6</sub>-κ<sup>1</sup>O'''}Zn(en)(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)] (1).



**Fig. 2:** The dodecaborate(6–) ligand as found in **1**. The central  $\{B_6O_6\}$  ring as shown on the left is non-planar with oxygen atoms (red) alternating ‘up’ and ‘down’ as shown in the side-on view (right). Boron atoms are pale pink.

angles ranging from  $106.3(3)$  to  $112.6(3)^\circ$ . The other six boron centers in the anion, B7–B12, are 3-coordinate and have significantly shorter B–O bonds  $\{1.349(6)–1.389(6) \text{ \AA}\}$  and larger O–B–O angles which range from  $116.1(4)$  to  $123.9(4)^\circ$ . These distances and angles are very similar to distances and angles observed in the previously reported  $Ag_6[B_{12}O_{18}(OH)_6] \cdot 3H_2O$  [32] and in acyclic polyboroxole ‘chain’ species,  $[B_5O_6(OH)_4]^-$  [33–38],  $[B_7O_9(OH)_5]^{2-}$  [39–43],  $[B_9O_{12}(OH)_6]^{3-}$  [44–46], and related boroxole systems [47–49] containing both 3- and 4-coordinate boron centers bound to oxygen. The dodecaborate(6–) in **1** is closely related to deprotonated structures  $Na_8[B_{12}O_{20}(OH)_4]$  [50] and  $Zn_6[B_{12}O_{24}]$  [51] and is an alternative (but not isomeric) to the hydrated dodecaborate found in  $K_4[B_{12}O_{16}(OH)_8]$  [52] which has four 4-coordinate boron atoms and carries a charge of 4–.

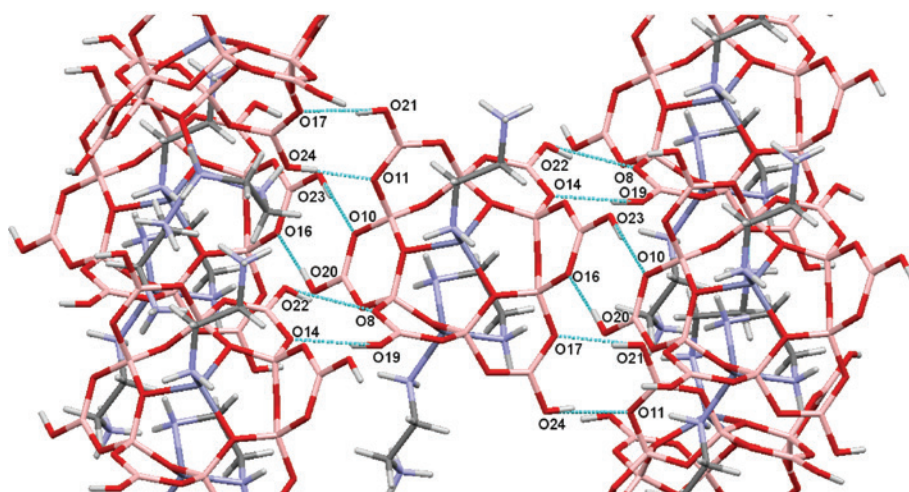
The dodecaborate(6–) anion in **1** utilizes its ‘inner’ ring oxygen atoms to coordinate to the Zn(II) centers and due to their stereochemistry the dodecaborate(6–) anion is ideally set up to bridge metal centers. The dodecaborate(6–) anion has been previously observed coordinated tridentate to metal centers in the following compounds:  $Na_2Cs_4Ba_2[B_{12}O_{18}(OH)_6](OH)_4$  [53],  $K_7[(BO_3)Mn\{B_{12}O_{18}(OH)_6\}] \cdot H_2O$  [54], and  $K_7[(BO_3)Zn\{B_{12}O_{18}(OH)_6\}] \cdot H_2O$  [55] with the latter also containing a zinc(II) ion. The coordination modes of the dodecaborate(6–) ligand towards the Zn centers are separated out in Fig. 3. Both Zn atoms in **1** are 4-coordinate and Zn1 is coordinated by the dodecaborate(6–) ligand in a tridentate fashion through oxygen donors O1, O3 and



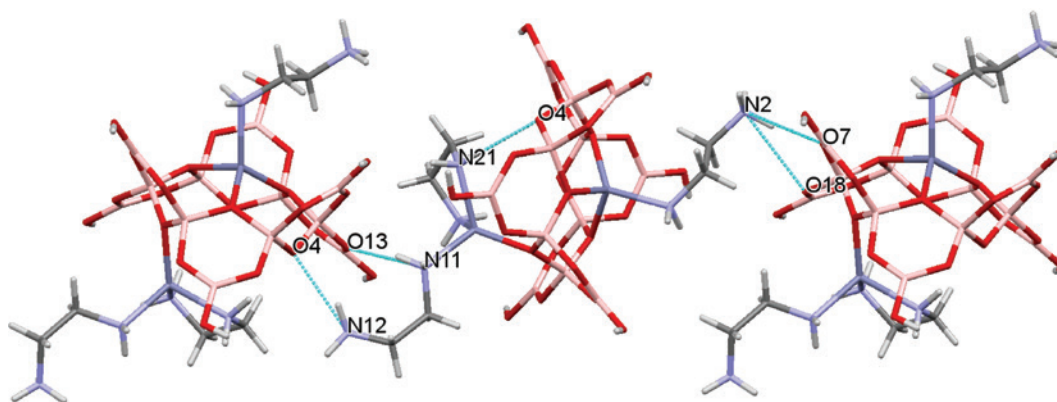
**Fig. 3:** Diagrams showing the two coordination modes of the dodecaborate(6–) ligand. The 4-coordinate Zn1 atom has a tridentate dodecaborate(6–) ligand and a monodentate protonated en ligand (left). The 4-coordinate Zn2 atom a monodentate dodecaborate(6–) ligand, a bidentate en ligand, and a monodentate protonated en ligand coordinated to it.

O5 with bond lengths to Zn1 of 1.971(3), 1.976(3) and 1.937(3) Å, respectively. The Zn2 atom is coordinated by the dodecaborate(6-) anion in a monodentate manner solely through O2 with a Zn2-O2 distance of 1.931(3) Å. The coordination number of four is completed on Zn2 by a bidentate en (ethylenediamine) ligand and a monodentate [enH]<sup>+</sup> group, whilst Zn1 just has one additional monodentate [enH]<sup>+</sup> group. The Zn-N distances range from 2.018(5) to 2.043(4) Å, whilst borate O-Zn atom distances (listed above) are significantly shorter and range from 1.937(3) to 1.976(3) Å, and are comparable to those observed elsewhere related zinc-borate species [56-63] which typically range from 1.919(2) to 2.0099(14) Å. The Zn-N distances are comparable to those observed in related zinc borate complexes with organoamino ligands [56-63] and ethylenediamine complexes such as [Zn(en)<sub>3</sub>]Cl<sub>2</sub> · 2H<sub>2</sub>O [64].

The hydroxyl hydrogen atoms of the  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  anion, the amino hydrogen atoms of the en ligands and protonated en ligands, and the waters of crystallization form multiple intramolecular H-bond donor interactions which are presumably responsible for the remarkable self-assembly of **1** from its component parts. In particular, all six hydroxyl groups in the polyborate anion of **1** are involved in energetically favorable  $\text{R}_2^2(8)$



**Fig. 4:** The  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  anion in **1** forms six H-bond donor interactions with six neighboring dodecaborate(6−) units. The interactions involve 8-membered rings  $R_2^2(8)$  with D···A oxygen atom distances as follows: O19H19···O14\*, 2.779(4) Å; O20H20···O16\*, 2.634(4) Å; O21H21···O17\*, 2.701(4) Å; O22H22···O8\*, 2.899(5) Å; O23H23···O10\*, 2.695(4) Å; O24H24···O11\*, 2.680(4) Å, where \* indicates an acceptor oxygen atom of a neighboring unit. H<sub>2</sub>O molecules omitted for clarity.



**Fig. 5:** Intermolecular H-bond interactions involving the amino hydrogen atoms link the dodecaborates(6-) anions into an extended chain. The D...A oxygen atom distances as follows: N2H2C...O7\*, 2.914(5) Å; N2H2C...O18\*, 3.068(5) Å; N11H11B...O13\*, 3.053(5) Å; N12H12A...O4\*, 2.903(5) Å, where \* indicates an acceptor oxygen atom of a neighboring unit. The intramolecular H-bond interaction is also shown: N21H21B...O4, 2.871(5) Å. H<sub>2</sub>O molecules omitted for clarity.



interactions (Etter nomenclature [65]) with six neighboring molecules of **1**, as shown in Fig. 4. Details of these H-bond interactions can be found in the caption to Fig. 4. In addition, the protonated ends of the monodentate  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_3$  ligands further H-bond to two more molecules of **1** forming a supramolecular chain (Fig. 5) giving an overall ‘coordination number’ of eight for each molecule of **1**. The amino hydrogens of the en ligand on Zn2 are involved in an intramolecular H-bond (Fig. 5) and H-bond donation to water molecules, and the waters of crystallization H-bond to each other and dodecaborate anions to further glue the structure together.

## Conclusion

The zwitterionic bimetallic complex,  $[(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2)\text{Zn}\{\kappa^3\text{O}, \text{O}', \text{O}''\text{-B}_{12}\text{O}_{18}(\text{OH})_6\text{-}\kappa^1\text{O}'''\}\text{Zn}(\text{en})(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)] \cdot 8\text{H}_2\text{O}$  has been synthesized in moderate yield from a self-assembly [18] process involving the basic labile zinc(II) complex salt  $[\text{Zn}(\text{en})_3](\text{OH})_2$  and a DCL of polyborate anions [19–25] derived from  $\text{B}(\text{OH})_3$ . The structure as determined by a single-crystal XRD study reveals that all six borate hydroxyl groups are involved in intermolecular H-bond donor interactions in pairwise  $\text{R}_2^2(8)$  rings. Intramolecular and intermolecular H-bonds emanating from the amino hydrogen atoms of the ethylenediamine ligands further template the formation of the self-assembled structure.

## Experimental

### General

NMR spectra were obtained on a Bruker Avance-400 spectrometer in  $\text{D}_2\text{O}$  Solution at 128, 400 or 101 MHz for  $^{11}\text{B}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$ , respectively, and referenced to either  $\text{BF}_3 \cdot \text{OEt}_2$  ( $^{11}\text{B}$ ) or TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ). FTIR spectra were obtained as KBr pellets on a Perkin Elmer 100FTIR spectrometer. Powder X-ray diffraction was carried out on a Phillips X'Pert 2040/60 XRD diffractometer with spectra obtained using the Phillips X'Pert Data Collector software. Single-crystal X-ray diffraction was performed at the EPSRC National Crystallographic Service at the University of Southampton. Magnetic susceptibility measurements were performed on a Johnson-Matthey magnetic susceptibility balance. CHN analyses were obtained from OEA Laboratories (Callingham, Cornwall).

### Preparation of $[\text{Zn}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

Tris(ethylenediamine)zinc(II) chloride dihydrate was prepared as described in the literature [64]. A slight excess of the ethylenediamine (en) (2.10 g, 70 %, 24.45 mmol) was added to an aqueous solution of zinc(II) chloride (3.0 g, 22.0 mmol) in distilled water (10 mL). The solution was concentrated by gentle evaporation in a warm water bath before being cooled in an ice bath to yield colorless crystals of tris(ethylenediamine)zinc(II) chloride dihydrate (5.4 g, 70 %). M.p. = 185–187 °C.  $\chi_m = -211.5 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .  $^1\text{H}/\text{ppm}$ : 2.7 (m, 12H,  $\text{CH}_2$  of en), 4.8 (s, 16 H,  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ ).  $^{13}\text{C}\{^1\text{H}\}/\text{ppm}$ : 39.1. IR (KBr/ $\text{cm}^{-1}$ ): 3383(s), 3261(s), 3154(s), 2949(s), 2933(s), 2885(s), 1651(m), 1587(s), 1458(s), 1331(s), 1275(s), 1147(m), 1023(s), 998(s), 976(m), 645(s), 511(s). [Lit. 3385, 3275, 3150, 2940, 2882, 1653, 1595, 1460, 1335, 1272, 1144, 1022, 996, 977, 644, 515] [66].

### Preparation of $[\text{Zn}_2(\text{en})(\text{enH})_2\{\text{B}_{12}\text{O}_{18}(\text{OH})_6\}] \cdot 8\text{H}_2\text{O}$ (**1**)

A solution of tris(ethylenediamine)zinc(II) chloride dihydrate (1.0 g, 2.8 mmol) in water (10 mL) was added to an aqueous suspension solution of excess activated Dowex 550A (50 g) monosphere anion exchange resin

in water (40 mL). 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 four times with a distilled water ( $4 \times 5$  mL). The solution of  $[\text{Zn}(\text{en})_3](\text{OH})_2$  was reduced to a volume of 15 mL using a rotary evaporator. Methanol (15 mL) was added to the concentrated solution, followed by boric acid (2.6 g, 42 mmol). The reaction mixture was gently warmed for 3 h. The solution volume was reduced to 5 mL using a rotary evaporator. The concentrated solution was left for 30 days in NMR tubes for crystallization to yield colorless crystals of  $[\text{Zn}_2(\text{en})(\text{enH})_2\{\text{B}_{12}\text{O}_{18}(\text{OH})_6\}] \cdot 8\text{H}_2\text{O}$  (0.55 g, 40 %). M.p.  $\geq 300$  °C.  $\chi_m = -414.2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .  $\text{C}_6\text{H}_{48}\text{B}_{12}\text{N}_6\text{O}_{32}\text{Zn}_2$ . Anal. Calc.: C = 7.4 %, H = 5.0 %, N = 8.6 %. Found: C = 6.9 %, H = 4.7 %, N = 8.3 %.  $^1\text{H}/\text{ppm}$ : 2.75 (m, 12H,  $\text{CH}_2$  of en), 4.8 (s, 34 H,  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ , OH).  $^{13}\text{C}\{^1\text{H}\}/\text{ppm}$ : 39.4.  $^{11}\text{B}/\text{ppm}$ : 16.1. IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3433(s), 3373(s), 3268(s), 2986(m), 1637(w), 1550(w), 1355(s), 1163(sh), 1041(s), 951(m), 900(s), 856(m), 758(w), 692(w), 646(w), 616(w), 519(w). p-XRD d-spacing/ $\text{\AA}$  (% rel. int.): 9.40 (68), 8.05 (39), 7.59 (100), 6.78 (75), 4.21 (22), 3.82 (22), 3.14 (28), 2.91 (45).

## X-ray crystallography

Crystallographic data for compound **1** is given in Table 1. A suitable crystal ( $0.10 \times 0.09 \times 0.04$ )  $\text{mm}^3$  was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer. The crystal was kept at  $T = 100(2)$  K during data collection. The data collection was carried out using CrystalClear [67] and cell determination and data reduction was carried out using CrysAlisPro [68]. Using Olex2 [69], the structure was solved and Superflip [70] structure solution program, using the Charge Flipping solution method. The model was refined with version 2014/7 of ShelXL [71] using Least Squares minimisation.

## Electronic supplementary information

CCDC1571610 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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