

# Syntheses and crystal structures of two new pentaborates

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## Abstract

Two new pentaborates,  $[\text{Zn}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$  (DIEN = diethylenetriamine) (**I**) and  $[\text{B}_5\text{O}_7(\text{OH})_3\text{Zn}(\text{TREN})]$  (TREN = tris(2-aminoethyl)amine) (**II**), have been hydrothermally synthesized and characterized by single crystal X-ray diffraction, FTIR, elemental analysis and thermogravimetric analysis. Compound **I** crystallizes in the monoclinic system, space group  $P2_1/c$  (No. 14),  $a = 8.5686(2) \text{ \AA}$ ,  $b = 11.7883(3) \text{ \AA}$ ,  $c = 14.5407(6) \text{ \AA}$ ,  $\beta = 91.259(2)^\circ$ ,  $V = 1468.39(8) \text{ \AA}^3$ ,  $Z = 2$ . The structure consists of isolated borate polyanion  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  and zinc complex cation  $[\text{Zn}(\text{DIEN})_2]^{2+}$ . The anionic units,  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ , are linked by hydrogen bonds to form a 3D supramolecular network containing large channels, in which the templating  $[\text{Zn}(\text{DIEN})_2]^{2+}$  cation are located. **II** is monoclinic,  $P2_1/c$  (No. 14),  $a = 8.9969(2) \text{ \AA}$ ,  $b = 20.6903(6) \text{ \AA}$ ,  $c = 9.2878(3) \text{ \AA}$ ,  $\beta = 99.635(2)^\circ$ ,  $V = 1704.52(8) \text{ \AA}^3$ ,  $Z = 4$ . The structure of **II** is constructed from two distinct motifs, a usual  $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$  cluster and a supporting zinc complex  $[\text{Zn}(\text{TREN})]^{2+}$ , which are integrated through Zn–O–B linkage. This compound represents the first example of the combination of B–O cluster with transition-metal complex.

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**Keywords:** Borates; Crystal structure; Hydrothermal synthesis; Zinc; Pentaborate

## 1. Introduction

Borate compounds are of considerable interest due to their rich structural chemistry and potential applications in mineralogy and industry [1–5]. From a structural point of view, boron atoms can form planar or non-planar  $\text{BO}_3$  groups, and also tetrahedral  $\text{BO}_4$  groups. The  $\text{BO}_3$  and  $\text{BO}_4$  groups may be further linked by sharing common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks [4,6–12]. Over the past decade, Burns et al. [2,4] have developed a comprehensive description based on fundamental building blocks (FBBs) to have a clearer nomenclature for the borates with more complicated borate anions.

So far, many borate systems concerning alkali metal, alkaline earth metal, rare earth and transition metal have been widely studied. And a number of structurally complex hydrated and anhydrous boron-containing materials have been prepared by hydrothermal syntheses and high temperature solid-state syntheses. In contrast, much less work has been carried out on metallo-organically templated borates [13,14]. Understanding how metal cations direct borate structural units is fundamental to the synthetic strategies for novel borates having useful properties. During our investigations of such borate materials, we apply a self-assembly process under solvothermal conditions. Herein, we first describe the syntheses and crystal structures of two new pentaborates,  $[\text{Zn}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$  (**I**) and  $[\text{B}_5\text{O}_7(\text{OH})_3\text{Zn}(\text{TREN})]$  (**II**). Compound **I** is a new pentaborate templated by a transition-metal complex, and **II** provides the first instance of the combination of B–O cluster with transition-metal complex.

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Table 1  
Crystal data and structure refinement for **I** and **II**

Compounds	<b>I</b>	<b>II</b>
Empirical formula	C <sub>8</sub> H <sub>34</sub> N <sub>6</sub> B <sub>10</sub> O <sub>20</sub> Zn	C <sub>6</sub> H <sub>21</sub> N <sub>4</sub> B <sub>5</sub> O <sub>10</sub> Zn
Formula weight	707.88	428.69
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	8.5686(2)	8.9969(2)
<i>b</i> /Å	11.7883(3)	20.6903(6)
<i>c</i> /Å	14.5407(6)	9.2878(3)
$\beta$ /°	91.259(2)	99.635(2)
<i>V</i> /Å <sup>3</sup>	1468.39(8)	1704.52(8)
<i>Z</i>	2	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.601	1.671
$\mu$ (MoK $\alpha$ )/mm <sup>-1</sup>	0.927	1.497
Reflection collected	4539	5013
Independent reflections	2530	2959
Parameters refined	221	246
$\theta$ range for data collection/deg.	2.22–25.03	2.51–25.01
Limiting indices	$-10 \leq h \leq 8$ , $-13 \leq k \leq 13$ , $-13 \leq l \leq 17$	$-10 \leq h \leq 10$ , $-24 \leq k \leq 22$ , $-6 \leq l \leq 11$
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.063	1.078
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0594, 0.1061	0.0690, 0.1318
Largest diff. peak and hole (eÅ <sup>-3</sup> )	0.360 and -0.418	0.605 and -0.434

## 2. Experimental section

### 2.1. Synthesis

Single crystals of the title compounds were obtained from a mixture of ZnO, H<sub>3</sub>BO<sub>3</sub>, organic amine (DIEN for **I**, triethylenetetramine (TETA) for **II**), Pyridine and H<sub>2</sub>O in the molar ratio of 1:3:2:40:30 and 1:4:2:32:24, respectively. The final mixture was stirred for several hours at room temperature and then crystallized in a Teflon-lined autoclave at 160 °C for 7 days. The prismatic colorless single crystals were easily separated by sonication from a mixture phase containing a small amount of white powder and further washed by distilled water and then air-dried. The white powder is an unknown phase and no further characterization. (72.5% yield based on boron for **I** and 36.2% for **II**).

Elemental analyses (wt%) **I**: C, 13.52; H, 4.81; N, 11.83 (found); C, 13.57; H, 4.84; N, 11.87 (calcd). For **II**: C, 16.84; H, 4.91; N, 13.03 (found); C, 16.81; H, 4.94; N, 13.07 (calcd). All the experimental results are consistent with the calculated values based on the formula given by X-ray single crystal diffraction.

### 2.2. Characterization

Infrared spectra were obtained from sample powder pelletized with KBr on an ABB Bomen MB 102 series FTIR spectrophotometer over a range 400–4000 cm<sup>-1</sup>. The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N<sub>2</sub> atmosphere with a heating rate of 10 °C/min. The elemental analysis of C, H, and N was carried out using

the combustion method on an Elemental Vario EL III CHNOS elemental analyzer.

### 2.3. Determination of crystal structure

Crystals of **I** (prism, dimensions 0.50 × 0.22 × 0.10 mm<sup>3</sup>) and **II** (prism, dimensions 0.40 × 0.18 × 0.12 mm<sup>3</sup>) were carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073$  Å) in the  $\omega$  and  $\phi$  scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program [15]. The structures were both solved by direct methods using SHELXS-97 [16]. The zinc atom was first located, and the boron, oxygen, carbon and nitrogen atoms were found in the successive Fourier difference maps. The C(2) atom in **I** and C(1) atom in **II** are both disordered over two positions (SOF of C(2) and C(2') are 0.70 and 0.30, and C(1) and C(1') are 0.80 and 0.20, respectively). The hydrogen atoms of the OH groups were found in Fourier difference maps and the remaining hydrogen atoms were placed geometrically. The structures were refined on *F*<sup>2</sup> by a full-matrix least-squares methods using the SHELXL-97 program package [16]. All non-hydrogen atoms, except C(2) atom in **I** and C(1) atom in **II**, were refined anisotropically. Crystallographic data for **I** and **II** are presented in Table 1. The final atomic coordinates and the selected bond distances are listed in Tables 2 and 3, respectively. CCDC 248623 and 248524

Table 2

Final atomic coordinates ( $\times 10^4$ ) and equivalent thermal isotropic Displacement  $U_{eq}$  ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in Parentheses of **I** and **II**

Atoms	x	y	z	$U_{eq}^a$
<b>[Zn(DIEN)<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub></b>				
Zn	0	0	0	34(1)
B(1)	-7197(6)	-144(4)	-4613(3)	31(1)
B(2)	-9022(6)	-189(4)	-3399(3)	33(1)
B(3)	-6217(5)	-152(4)	-2994(3)	30(1)
B(4)	-4411(7)	-1174(5)	-1925(4)	37(1)
B(5)	-4418(6)	845(5)	-1889(4)	37(1)
O(1)	-7017(4)	-98(3)	-5534(2)	44(1)
O(2)	-6006(3)	-109(3)	-3998(2)	32(1)
O(3)	-8720(3)	-228(3)	-4324(2)	45(1)
O(4)	-10533(3)	-181(3)	-3125(2)	41(1)
O(5)	-7864(3)	-169(3)	-2762(2)	34(1)
O(6)	-5450(3)	-1180(2)	-2632(2)	33(1)
O(7)	-5477(3)	871(2)	-2588(2)	35(1)
O(8)	-3775(5)	-2128(3)	-1561(3)	60(1)
O(9)	-3940(4)	-176(3)	-1510(2)	50(1)
O(10)	-3783(5)	1790(3)	-1505(3)	56(1)
C(1)	1267(9)	2356(6)	-333(4)	85(2)
C(2)	1069(12)	1864(8)	-1228(6)	58(2)
C(2')	240(20)	2033(16)	-1224(13)	48(4)
C(3)	1841(8)	-1971(5)	-734(5)	71(2)
C(4)	210(9)	-2098(5)	-1090(4)	72(2)
N(1)	-270(5)	971(4)	-1272(3)	53(1)
N(2)	2168(5)	-791(4)	-560(3)	57(1)
N(3)	934(5)	1595(4)	452(3)	49(1)
H(1)	-6110(30)	10(60)	-5670(40)	80(20)
H(2)	-11240(50)	-120(50)	-3550(30)	64(17)
H(3)	-4070(70)	-2720(30)	-1790(40)	70(20)
H(4)	-3880(70)	2360(30)	-1830(30)	70(20)
<b>[B<sub>5</sub>O<sub>7</sub>(OH)<sub>3</sub>Zn(TREN)]</b>				
Zn	1323(1)	5909(1)	6002(1)	27(1)
B(1)	-500(9)	6108(4)	3142(8)	23(2)
B(2)	-1500(9)	6885(4)	1315(10)	32(2)
B(3)	-3174(9)	6471(4)	2985(9)	25(2)
B(4)	-4799(10)	6896(4)	4692(9)	33(2)
B(5)	-5795(9)	6081(4)	3007(9)	27(2)
O(1)	706(5)	5788(2)	3840(5)	26(1)
O(2)	-337(6)	6502(3)	1960(6)	43(1)
O(3)	-1214(6)	7284(3)	220(7)	51(2)
O(4)	-1893(5)	6073(2)	3561(5)	31(1)
O(5)	-2856(5)	6883(2)	1767(5)	29(1)
O(6)	-4483(5)	6064(2)	2454(5)	32(1)
O(7)	-3497(5)	6912(2)	4158(5)	31(1)
O(8)	-5089(6)	7282(3)	5805(7)	55(2)
O(9)	-5953(5)	6483(3)	4142(6)	40(1)
O(10)	-6924(6)	5667(3)	2499(6)	38(1)
C(1)	1541(13)	7087(5)	7834(12)	48(3)
C(1')	2480(40)	7091(18)	7720(40)	33(8)
C(2)	2343(12)	6613(4)	8925(11)	63(3)
C(3)	-746(10)	5801(5)	8140(9)	53(2)
C(4)	749(10)	5640(5)	9064(9)	55(2)
C(5)	4272(9)	5553(4)	7561(9)	48(2)
C(6)	3427(10)	5534(5)	8829(9)	51(2)
N(1)	1678(7)	6902(3)	6262(8)	43(2)
N(2)	-681(7)	5635(3)	6618(6)	35(2)
N(3)	3250(7)	5338(3)	6240(6)	33(1)
N(4)	2029(8)	5929(3)	8489(7)	44(2)
H(1)	-1900(80)	7520(40)	-130(110)	90(40)
H(2)	-4310(60)	7520(30)	6130(90)	60(30)
H(3)	-7730(60)	5750(40)	2880(90)	60(30)

<sup>a</sup> $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3

Selected bond length ( $\text{\AA}$ ) for **I** and **II**

<b>[Zn(DIEN)<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub></b>			
Zn–N(1)	2.182(4)	B(3)–O(5)	1.458(5)
Zn–N(2)	2.247(4)	B(3)–O(6)	1.472(5)
Zn–N(3)	2.141(4)	B(3)–O(7)	1.479(5)
B(1)–O(1)	1.354(5)	B(4)–O(6)	1.344(6)
B(1)–O(2)	1.341(5)	B(4)–O(8)	1.352(6)
B(1)–O(3)	1.383(5)	B(4)–O(9)	1.379(6)
B(2)–O(3)	1.377(6)	B(5)–O(7)	1.347(6)
B(2)–O(4)	1.362(6)	B(5)–O(9)	1.383(6)
B(2)–O(5)	1.342(5)	B(5)–O(10)	1.355(6)
B(3)–O(2)	1.476(5)		
<b>[B<sub>5</sub>O<sub>7</sub>(OH)<sub>3</sub>Zn(TREN)]</b>			
Zn–O(1)	2.007(4)	B(3)–O(4)	1.445(9)
Zn–N(1)	2.087(6)	B(3)–O(5)	1.482(9)
Zn–N(2)	2.061(6)	B(3)–O(6)	1.465(9)
Zn–N(3)	2.078(6)	B(3)–O(7)	1.485(9)
Zn–N(4)	2.292(6)	B(4)–O(7)	1.347(10)
B(1)–O(1)	1.341(9)	B(4)–O(8)	1.366(10)
B(1)–O(2)	1.395(9)	B(4)–O(9)	1.376(10)
B(1)–O(4)	1.375(9)	B(5)–O(6)	1.364(9)
B(2)–O(2)	1.368(9)	B(5)–O(9)	1.368(9)
B(2)–O(3)	1.368(10)	B(5)–O(10)	1.351(9)
B(2)–O(5)	1.355(9)		

contain the supplementary crystallographic data for this paper.

### 3. Results and discussion

#### 3.1. Infrared (IR) spectra

The IR spectra of **I** and **II** showed typical peaks, with little differences between the spectra, as shown in Fig. 1. The strong bands at  $\sim 1406$  and  $1330 \text{ cm}^{-1}$  in the spectra are characteristic of trigonally coordinated boron, while the bands at  $\sim 1050$  and  $960 \text{ cm}^{-1}$  are characteristic of tetrahedral boron. [17] In addition, the stretching vibration of the O–H, N–H, and C–H bands are observed at  $\sim 3435$ ,  $3213$  and  $2930 \text{ cm}^{-1}$ , respectively.

#### 3.2. Crystal structures

##### 3.2.1. Structure of **I**

As shown in Fig. 2, the asymmetric unit of **I** consists of one crystallographically distinct zinc atom and five unique boron atoms. The Zn atom is octahedrally coordinated by six nitrogen atoms from two DIEN molecules, with Zn–N bond lengths in the range of 2.141(4)–2.247(4)  $\text{\AA}$ . Of the five independent B atoms, B(3) adopts tetrahedral oxygen coordination (B–O (av.) 1.471  $\text{\AA}$ ), and other four B atoms adopt trigonal oxygen coordination (B–O (av.) 1.360  $\text{\AA}$ ). The connectivity of the triangular  $\text{BO}_3$  and tetrahedral  $\text{BO}_4$  units creates the borate polyanion of the formula  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ . It is

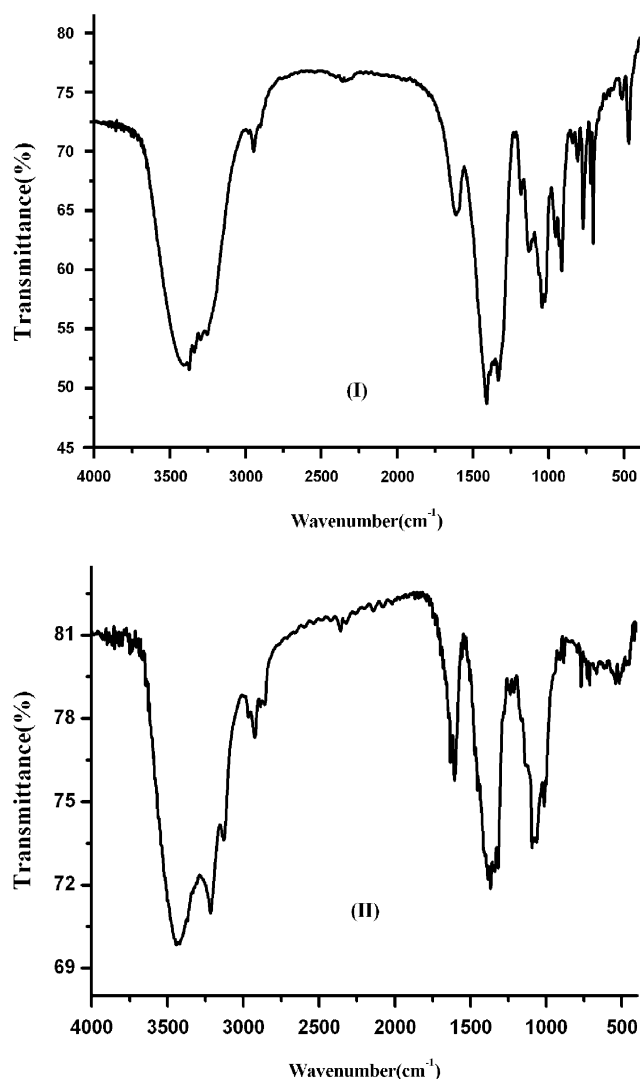


Fig. 1. IR spectra of I and II.

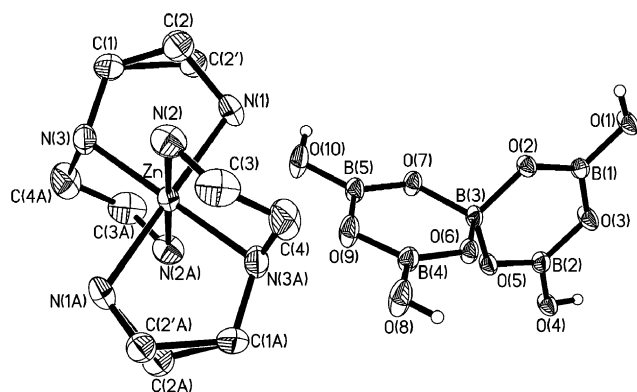
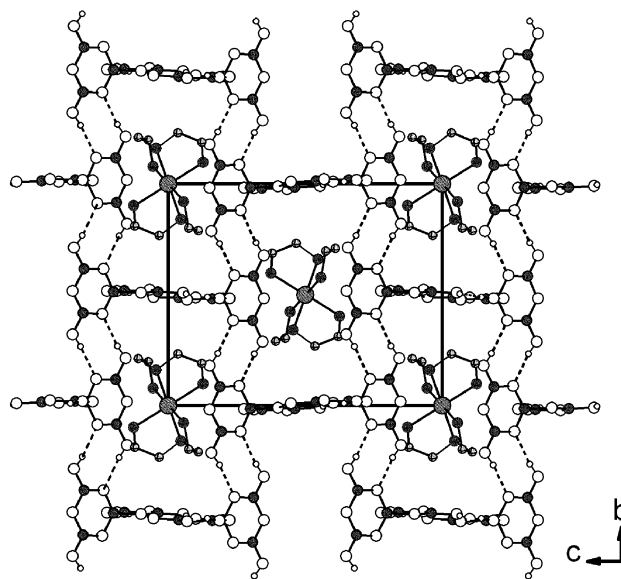
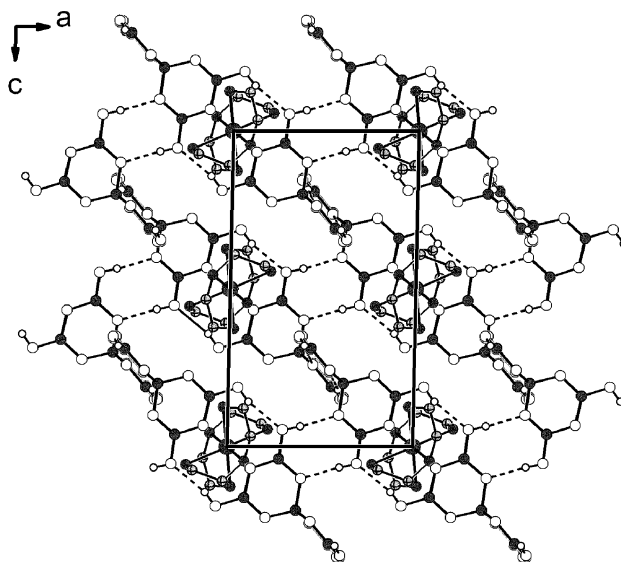


Fig. 2. ORTEP view of the asymmetric unit of I, showing the labeling Scheme 1 and the 30% probability displacement ellipsoids; atom labels with "A" refer to symmetry-generated atoms.

composed of one  $\text{BO}_4$  tetrahedron (B(3)) and four  $\text{BO}_2(\text{OH})$  triangles (B(1), B(2), B(4) and B(5)), which forms two  $\text{B}_3\text{O}_3$  cycles linked by the common  $\text{BO}_4$  tetrahedron. Such an anion is a basic unit of hydrous

pentaborates  $\text{LiB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$  [18],  $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$  [19],  $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  [20],  $\text{CsB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  [21],  $(\text{NH}_4)\text{B}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  [22], and anhydrous pentaborate  $\text{NaB}_5\text{O}_6(\text{OH})_4$  [23] etc.

As is well known, extensive hydrogen bond interactions are important in the formation and stability of low-dimensional structures involving molecules where such interactions are possible. In the present instance, the framework is stabilized by the extensive hydrogen bonds involving the borate polyanion  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  groups, forming a 3D supramolecular network with large channels in three directions:

Fig. 3. View of the packing structure of I along the *a*-axis. Hydrogen atoms of the Zn complex cations are omitted for clarity.Fig. 4. View of the packing structure of I along the *b*-axis. Hydrogen atoms of the Zn complex cations are omitted for clarity.

O(1)–H(1)···O(2) ( $d = 1.89 \text{ \AA}$ ), O(4)–H(2)···O(1) ( $d = 1.99 \text{ \AA}$ ), O(8)–H(3)···O(7) ( $d = 1.92 \text{ \AA}$ ) and O(10)–H(4)···O(6) ( $d = 1.97 \text{ \AA}$ ) (Figs. 3–5). The templating transition-metal complexes,  $[\text{Zn}(\text{DIEN})_2]^{2+}$ , locate in the inorganic channels and interact with the framework via hydrogen-bonding interactions. The details of H-bonds are given in Table 4.

### 3.2.2. Structure of II

The asymmetric unit of **II** contains 26 independent non-hydrogen atoms, including one zinc atom, five boron atoms, 10 oxygen atoms, six carbon atoms, and four nitrogen atoms (Fig. 6). The zinc atom is square-pyramidally coordinated, bonded to one oxygen atom [Zn–O 2.007 Å] from  $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$  cluster and four nitrogen atoms [Zn–N (av.) 2.129 Å] from TREN. It is worth noting that the TREN, which has the same chemical formula and different structure with TETA, was formed by the rearrangement of the TETA in the hydrothermal reaction (Scheme 1). All the independent B atoms are triangularly coordinated (B–O (av.) 1.364 Å) except for the B(3) atom, which is tetrahedrally coordinated (B–O (av.) 1.469 Å).

The structure of **II** exhibits a novel transition-metal complex supported pentaborate. As shown in Fig. 6,

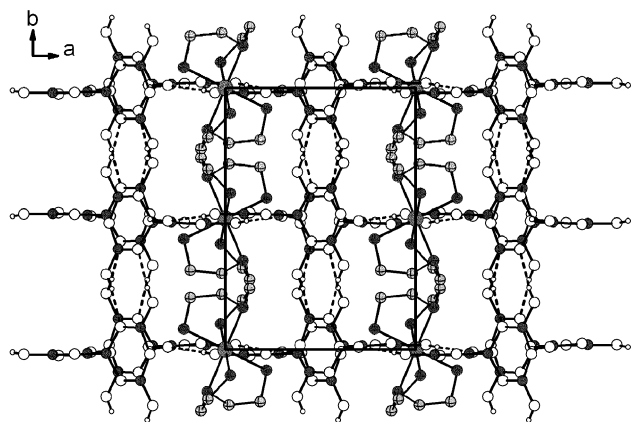


Fig. 5. View of the packing structure of **I** along the  $c$ -axis. Hydrogen atoms of the Zn complex cations are omitted for clarity.

Table 4  
Details of hydrogen bonds for **I**<sup>a</sup>

D–H···A	$d(\text{D–H})$ (Å)	$d(\text{H···A})$ (Å)	$d(\text{D···A})$ (Å)	$\angle(\text{DHA})$ (deg.)
O(1)–H(1)···O(2) [#2]	0.82(2)	1.89(2)	2.703(4)	174(7)
O(4)–H(2)···O(1) [#3]	0.86(2)	1.99(2)	2.853(4)	176(5)
O(8)–H(3)···O(7) [#4]	0.82(2)	1.92(2)	2.734(5)	173(6)
O(10)–H(4)···O(6) [#5]	0.83(2)	1.97(2)	2.774(5)	165(6)
N(3)–H(3C)···O(8) [#1]	0.91	2.14	2.958(5)	148.6

Symmetry transformations used to generate equivalent atoms: [#1]  $-x, -y, -z$ ; [#2]  $-x-1, -y, -z-1$ ; [#3]  $-x-2, -y, -z-1$ ; [#4]  $-x-1, y-1/2, -z-1/2$ ; [#5]  $-x-1, y+1/2, -z-1/2$ .

<sup>a</sup>D and A signify donor and acceptor oxygens, respectively.

four trigonal  $\text{BO}_2(\text{OH})$  and  $\text{BO}_3$  units and one tetrahedral  $\text{BO}_4$  unit are linked together through their vertexes to form the  $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$  cluster with the “hanging” zinc complex  $[\text{Zn}(\text{TREN})]^{2+}$  attached to the O(1) atom. The overall sheet-like structure shown in Fig. 7 is formed by extensive multipoint hydrogen bonding involving the  $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$  cluster like O(3)–H(1)···O(7) ( $d = 1.89 \text{ \AA}$ ), O(8)–H(2)···O(5) ( $d = 1.82 \text{ \AA}$ ) and O(10)–H(3)···O(1) ( $d = 1.79 \text{ \AA}$ ). Adjacent layers are further connected by the “hanging” zinc complex  $[\text{Zn}(\text{TREN})]^{2+}$  moieties through intermolecular interactions between the N–H group of  $[\text{Zn}(\text{TREN})]^{2+}$  and  $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$  cluster, forming a three-dimensional supramolecular network (Fig. 8). The details of H-bonds are given in Table 5. To the best of our knowledge, this compound is the first example of the

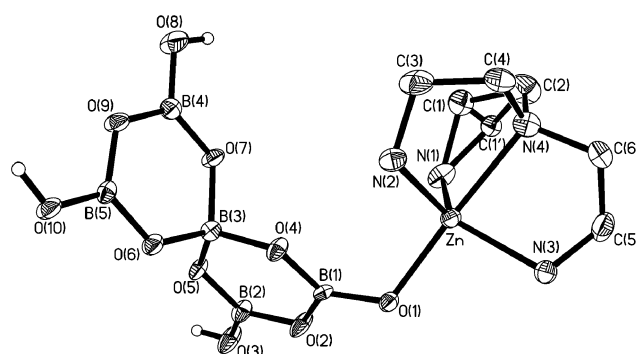
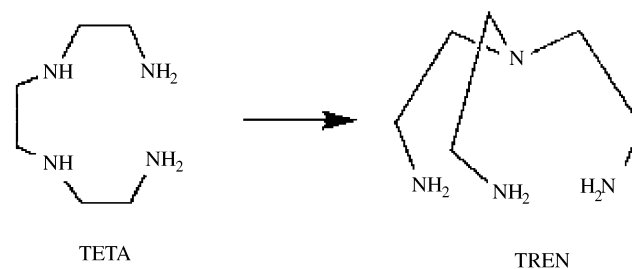


Fig. 6. ORTEP view of the asymmetric unit of **II**, with 30% thermal ellipsoids and the atom-labeling Scheme 1.



Scheme 1. TREN was formed by the rearrangement of the TETA.



combination of B–O cluster with transition metal complex.

### 3.3. Thermal properties

Thermogravimetric (TG) analysis of **I** and **II** was carried out in N<sub>2</sub> atmosphere from 40 to 1000 °C with a heating rate of 10 °C/min. As shown in Fig. 9, the TG curve of **I** showed that the compound was stable up to

about 170 °C, then a continuous weight loss between 170 and 750 °C, corresponding to the removal of two DIEN and two water molecules from the dehydration of hydroxyls (found: 39.16%; calcd: 39.33%). The TG curve of **II** showed a continuous weight loss between 200 and 630 °C, which was attributed to the removal of the TREN and the dehydration of hydroxyls (Found: 40.22%; calcd: 40.41%). The residue after the calcination for **I** and **II** is amorphous, respectively, and its phase is unidentified.

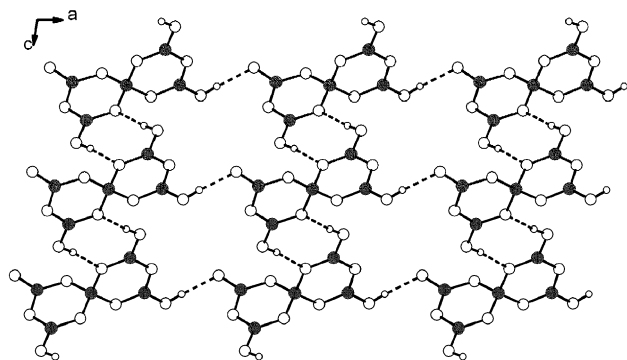


Fig. 7. View along the *b*-axis of **II** showing the 2D sheet structure.

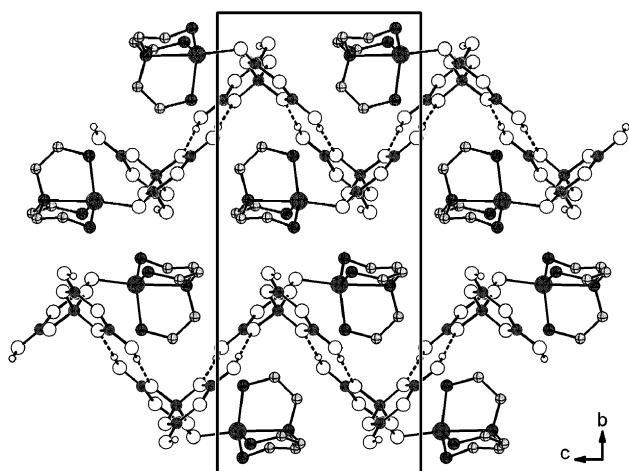


Fig. 8. The crystal packing of **II**, projected along the *a*-axis.

## 4. Conclusions

In summary, this work describes the syntheses, structures, and thermal properties of two new pentaborates, [Zn(DIEN)<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub> (**I**) and [B<sub>5</sub>O<sub>7</sub>(OH)<sub>3</sub>Zn(TREN)] (**II**). Compound **I** provides a new example of pentaborate templated by a transition-metal complex; while **II** describes for the first time a novel borate supported by transition-metal complex under hydrothermal conditions. The successful synthesis of this compound provides the possibility for preparing other structurally complex 1D, 2D and 3D borates in

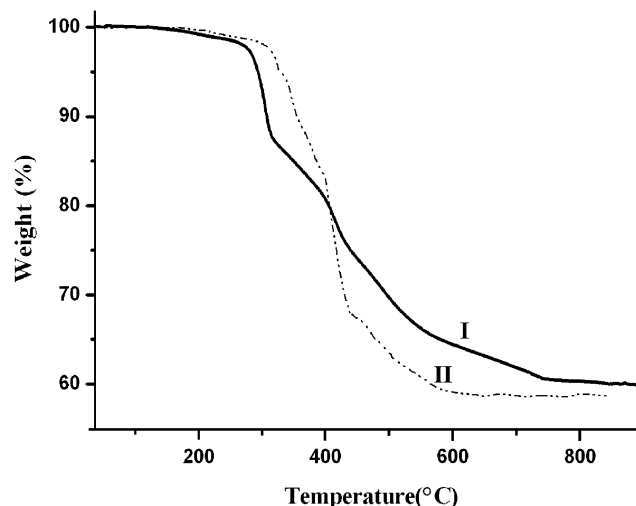


Fig. 9. TG curve of compounds **I** and **II**.

Table 5  
Details of hydrogen bonds for **II**<sup>a</sup>

D–H···A	<i>d</i> (D–H) (Å)	<i>d</i> (H···A) (Å)	<i>d</i> (D···A) (Å)	∠(DHA) (deg)
O(3)–H(1)···O(7) [#4]	0.81(5)	1.89(2)	2.698(7)	176(2)
O(8)–H(2)···O(5) [#2]	0.87(2)	1.82(2)	2.688(7)	172(8)
O(10)–H(3)···O(1) [#3]	0.88(2)	1.79(2)	2.655(6)	170(9)
N(2)–H(2D)···O(1) [#1]	0.90	2.08	2.974(8)	170.6
N(2)–H(2C)···O(4)	0.90	2.32	3.006(8)	133.1
N(3)–H(3C)···O(4) [#1]	0.90	2.29	3.182(8)	168.5

Symmetry transformations used to generate equivalent atoms: [#1]  $-x, -y+1, -z+1$ ; [#2]  $x, -y+3/2, z+1/2$ ; [#3]  $x-1, y, z$ ; [#4]  $x, -y+3/2, z-1/2$ .

<sup>a</sup>D and A signify donor and acceptor oxygens, respectively.

metal-boron-amine system, and further work on this subject is in progress.

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