

An open-framework zincoborate formed by  $Zn_6B_{12}O_{24}$  clustersAmitava Choudhury,<sup>a,b</sup> S. Neeraj,<sup>a</sup> Srinivasan Natarajan<sup>a</sup> and C. N. R. Rao<sup>\*a,b</sup><sup>a</sup> Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in<sup>b</sup> Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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A novel zincoborate,  $Zn(H_2O)B_2O_4 \cdot xH_2O$  ( $x \approx 0.12$ ), **I**, with open architecture has been synthesized hydrothermally. The 3-dimensional structure is built up of  $Zn_6B_{12}O_{24}$  clusters formed by the capping of the polycyclic borate anion,  $B_{12}O_{24}^{12-}$ , by  $Zn_3O_3$  clusters. The open-framework structure of **I** has one-dimensional 8-membered channels wherein the water molecules reside. Formation of trimeric  $Zn_3O_3$  clusters as well as the presence of boron in dual coordination, both triangular and tetrahedral, are important structural features of this new zincoborate.

## Introduction

Borolite,  $Zn_4O(BO_2)_6$ , is a zincoborate<sup>1</sup> with a direct analogy to the sodalite type aluminosilicate.<sup>2</sup> In their effort to prepare a microporous zincoborate, Harrison *et al.*<sup>3</sup> isolated a neutral zincoborate framework constructed by vertex-sharing tetrahedral  $ZnO_4$  units and triangular  $BO_3$  units. This zincoborate was prepared hydrothermally from an alkaline solution of borax and  $Zn(NO_3)_2$ . In many of the boron containing compounds, the boron–oxygen linkages form cyclic polyborates.<sup>4</sup> The investigations by various researchers on the M–B–O system (M = metal), under hydrothermal conditions, invariably lead to the formation of unusual clusters. Thus, two types of situations have been commonly encountered. In the first instance, the borate clusters (polyborates) are sandwiched by metal–oxygen clusters,<sup>5,6</sup> and in the second, the metal–oxygen clusters are sandwiched by cyclic polyborates.<sup>7</sup> A zinc vanadoborate consisting of  $Zn_6V_{12}B_{18}$  clusters formed by sandwiching a 12-membered ring of  $B_{18}O_{39}(OH)_3$  between two alternating edge-sharing  $V_6O_{15}$  clusters has been prepared under hydrothermal conditions.<sup>6</sup> On the other hand, Warren *et al.*<sup>7</sup> have established the formation of metalborate clusters in which the vanadium–oxygen clusters sandwich the polyborate clusters. During our investigations of open-framework materials, we have isolated an unusual zincoborate of the composition  $Zn(H_2O)B_2O_4 \cdot xH_2O$   $x \approx 0.12$ , **I**, resulting from the addition of  $Zn^{2+}$  ions to the polycyclic  $B_{12}O_{24}^{12-}$  anion and involving the formation of  $Zn_3O_3$  clusters. The Na-salt of this borate polyanion has been prepared hydrothermally and described in the literature.<sup>8</sup> Connectivity between the polycyclic  $[B_{12}O_{24}]$  clusters and the  $[Zn_3O_3]$  clusters, through the Zn–O–B bonds gives rise to a 3-dimensional open-framework structure with channels, in which the extra-framework water molecules reside along with terminal ones. To our knowledge, **I** is the first zincoborate with an extended framework structure containing boron in both triangular and tetrahedral coordinations. In most transitional metal borates, specially in the oxovanadium–borate system, the metalborate clusters are present as isolated units.<sup>5,6,7</sup>

## Experimental

The title compound, **I**, was prepared under mild hydrothermal conditions. In a typical synthesis, 0.40 g of ZnO was dispersed in 4.6 ml of water and 1.008 g of boric acid was added under constant stirring. To this mixture, 0.60 g of guanidium

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

Empirical formula	$Zn(H_2O)B_2O_4 \cdot xH_2O$ ( $x \approx 0.12$ )
Crystal system	Rhombohedral (hexagonal setting)
Space group	$R\bar{3}m$
$T/K$	293
$a/\text{\AA}$	11.4101(6)
$c/\text{\AA}$	17.1556(11)
$V/\text{\AA}^3$	1934.3(2)
$Z$	36
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.610
$\mu/\text{mm}^{-1}$	5.620
Total data collected	2759
Unique data	627
Observed data [ $\sigma > 2\sigma(I)$ ]	371
$R_{\text{int}}$	0.102
$R$ indices [ $\sigma > 2\sigma(I)$ ]	$R_1 = 0.0300$ , $wR_2 = 0.0692^a$
$R$ (All data)	$R_1 = 0.0450$ , $wR_2 = 0.0757$

<sup>a</sup>  $W = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$  where  $P = [F_o^2 + 2F_c^2]/3$ ;  $a = 0.00347$  and  $b = 0$ .

carbonate was added and the resulting thick gel was homogenized for 30 min at room temperature. The final mixture of the composition  $ZnO : 3.3H_3BO_3 : 68GC : 52H_2O$  was transferred to a 23 ml PTFE-lined acid digestion bomb and heated at 453 K for 48 h. The resulting crop of large colorless rod-like single crystals was filtered, washed thoroughly with deionized water and dried under ambient conditions. The total yield of **I** was about 45%. Thermogravimetric analysis under the flow of nitrogen ( $50 \text{ ml min}^{-1}$ ) in the range 25–800 °C, indicated two distinct steps at 120 °C and a broad one at 250 °C corresponding to the loss of extra-framework water and bound water respectively. The final calcined product was found to be a condensed zincoborate  $Zn(BO_2)_2$  [JCPDS: 39–1126] by powder XRD.

Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer. A hemisphere of intensity data was collected in 1321 frames with  $\omega$  scans (width of 0.30° and exposure time of 10 s per frame). Pertinent details of crystal structure determination are presented in Table 1. The structure was solved and refined using the SHELXTL-PLUS suite of programs.<sup>9</sup> The direct methods solution readily revealed the heavy atom position (Zn) and enabled us to locate the other non-hydrogen positions (B and O) from the Fourier difference maps. Hydrogen positions for both the bonded [O(3)] as well as the extra-framework water

**Table 2** Selected bond distances and bond angles in **I**

Moiety	Distance/Å	Moiety	Angle/°
Zn(1)–O(1)	1.953(4) [0.51] <sup>a</sup>	O(4) <sup>#2</sup> –B(1)–O(4)	121.4(6)
Zn(1)–O(2)	1.979(2) [0.47]	O(4)–B(1)–O(2)	119.3(3)
Zn(1)–O(3)	2.004(6) [0.44]	O(4) <sup>#3</sup> –B(2)–O(4) <sup>#4</sup>	107.4(5)
B(1)–O(4)	1.365(5) [1.012]	O(4) <sup>#3</sup> –B(2)–O(1)	110.7(2)
B(1)–O(2)	1.378(9) [0.98]	O(4) <sup>#4</sup> –B(2)–O(1)	107.7(2)
B(2)–O(4) <sup>#3</sup>	1.477(5) [0.75]	O(1)–B(2)–O(1) <sup>#5</sup>	112.6(6)
B(2)–O(1)	1.479(5) [0.74]	B(2) <sup>#6</sup> –O(1)–B(2)	122.3(3)
Moiety	Angle/°	B(2) <sup>#6</sup> –O(1)–Zn(1)	118.0(2)
O(1)–Zn(1)–O(2)	112.24(13)	B(2)–O(1)–Zn(1)	118.1(2)
O(2)–Zn(1)–O(2) <sup>#1</sup>	100.9(2)	B(1)–O(2)–Zn(1)	122.15(10)
O(1)–Zn(1)–O(3)	114.5(2)	Zn(1)–O(2)–Zn(1) <sup>#7</sup>	115.7(2)
O(2)–Zn(1)–O(3)	108.0(2)	B(1)–O(4)–B(2) <sup>#8</sup>	123.4(4)

Symmetry transformations used to generate equivalent atoms: #1  $-y + 1, x - y + 1, z$ ; #2  $-x + y, y, z$ ; #3  $x - 1/3, x - y + 4/3, z + 1/3$ ; #4  $y - 1, -x + y, -z$ ; #5  $x - y + 2/3, x + 1/3, -z + 1/3$ ; #6  $y - 1/3, -x + y + 1/3, -z + 1/3$ ; #7  $-x + y, -x + 1, z$ ; #8  $x - y + 1, x + 1, -z$ . <sup>a</sup> Calculated bond valence sum values.

molecule [O(100)] were not included in the final refinement as they were unstable during the refinement cycles in spite of soft constraints for the distances and angles. The extra-framework water molecule, O(100), occupies a special position with  $3m$  symmetry. The free refinement for the occupancy of the extra-framework water [O(100)] has been attempted, resulting in a stable occupancy of 0.36. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms. Full-matrix least-squares structure refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS<sup>9</sup> package of programs. Details of the final refinements are given in Table 1. Selected bond distances and angles for **I** are presented in Table 2.

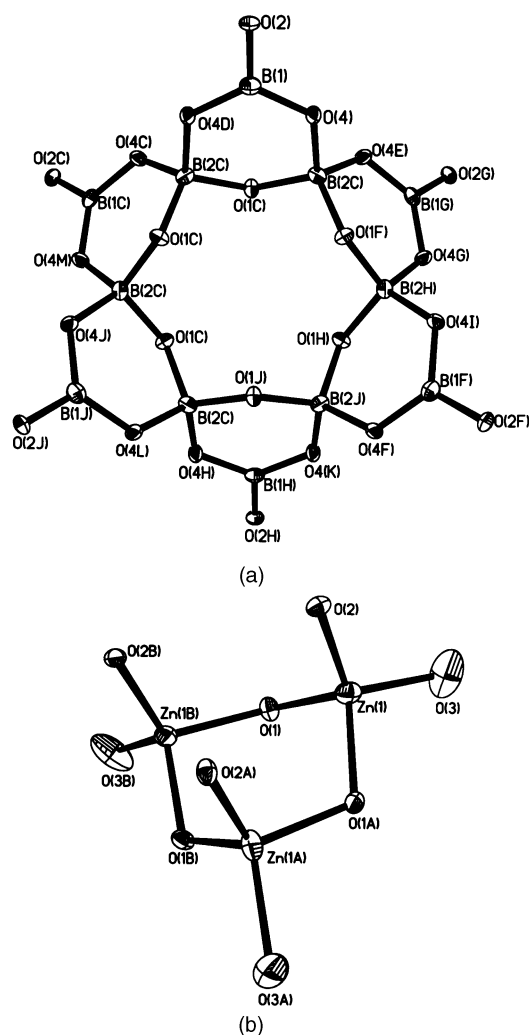
CCDC reference number 156617.

See <http://www.rsc.org/suppdata/dt/b1/b108047b/> for crystallographic data in CIF or other electronic format.

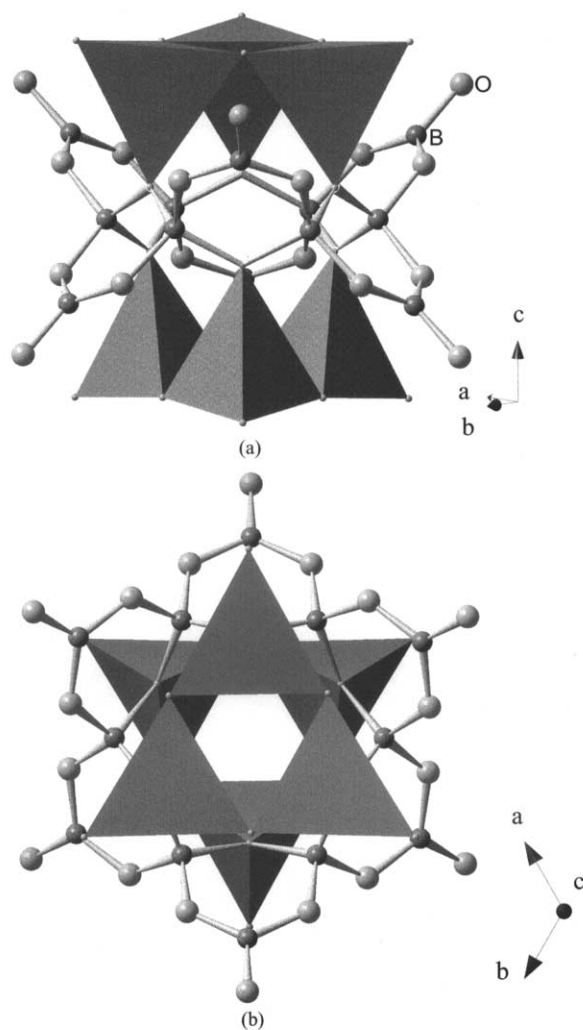
## Results and discussion

The asymmetric unit of **I** consists of 8 non-hydrogen atoms, of which 7 belong to the framework and the remaining oxygen to the guest water molecule. There are two crystallographically independent B atoms and one Zn atom in the asymmetric unit. A noteworthy feature of the zincoborate, **I**, is the presence of boron in both triangular and tetrahedral coordinations. In most of the known zincoborates, boron generally has triangular coordination.<sup>3,10</sup> Dual coordination of boron (*i.e.* both triangular and tetrahedral) seems to occur only in one other zincoborate.<sup>11</sup> The only example of a zincoborate where boron is solely tetrahedrally coordinated is boralite.<sup>1</sup>

The structure of **I** is constructed from the vertex linkages between the triangular B(1)O<sub>3</sub> unit and the tetrahedral B(2)O<sub>4</sub> and ZnO<sub>4</sub> units (Fig. 1). The connectivity between the triangular B(1)O<sub>3</sub> and the tetrahedral B(2)O<sub>4</sub> units creates the six-membered cyclic borate polyanion of the formula [B<sub>12</sub>O<sub>24</sub>]<sup>12-</sup> (Fig. 1a). The polyanion is formed by six B(2)O<sub>4</sub> tetrahedra and six B(1)O<sub>3</sub> triangles. The six B(2)O<sub>4</sub> tetrahedra are linked to one another *via* their corners forming the 6-membered ring. Each B(2)O<sub>4</sub> tetrahedron also shares two of its corners externally with the B(1)O<sub>3</sub> triangles as shown in Fig. 1a. The addition of Zn<sup>2+</sup> ions to the polyborate anion, [B<sub>12</sub>O<sub>24</sub>]<sup>12-</sup>, through Zn–μ<sub>3</sub>O(1)–B bonds gives rise to the zincoborate cluster Zn<sub>6</sub>B<sub>12</sub>O<sub>24</sub> as shown in Fig. 2. Such connectivity also leads to the formation of a 4-membered ring involving one Zn–O–Zn, one B–O–B and two Zn–O–B bonds. A terminal water molecule satisfies the fourth coordination needed for the tetrahedral connectivity of the Zn atom. The Zn atoms are also linked together through Zn–O–Zn linkages forming an unusual 3-membered Zn<sub>3</sub>O<sub>3</sub> cluster, as shown in Fig. 1b. To our knowledge, this is the first time such three-membered Zn–O clusters have been isolated,



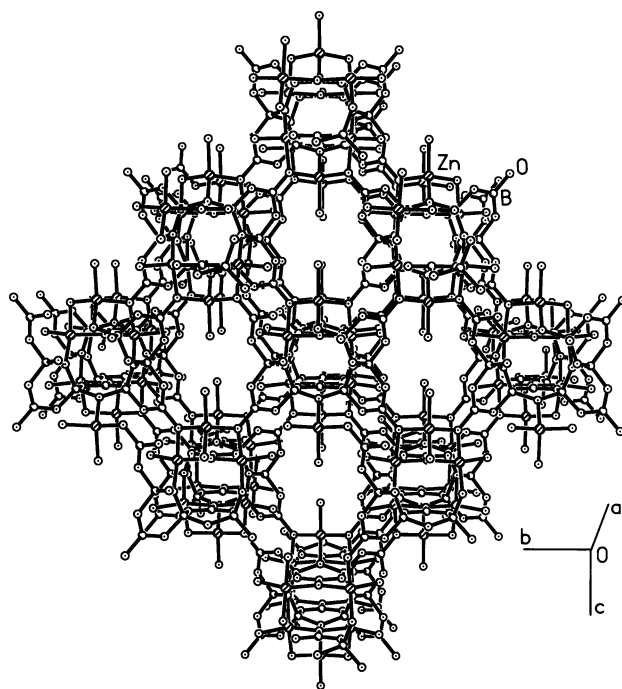
**Fig. 1** (a) Figure showing the six-membered polyborate B<sub>6</sub>O<sub>24</sub> anion with the thermal ellipsoids given at 50% probability. Note that the trigonally coordinated B atoms are positioned on the outside of the 6-membered ring. All the atoms are labelled with their symmetry indicators. Atoms labelled with C, D, E, F, G, H, I, J, K, L and M are at the symmetry positions  $(4/3 + x - y, 2/3 + x, 2/3 - z)$ ,  $(-x + y, +y, +z)$ ,  $(-2/3 + y, 2/3 + x, -1/3 - z - 1)$ ,  $(-x + y, -x + 2, +z)$ ,  $(-2/3 + y, 2/3 - x + y, -1/3 - z)$ ,  $(4/3 - x, 8/3 - y, -1/3 - z)$ ,  $(+x, +x - y + 2, +z)$ ,  $(-y + 2, +x - y + 2, +z)$ ,  $(4/3 + x - y, 8/3 - y, -1/3 - z)$ ,  $(-y + 2, -x + 2, +z)$  and  $(4/3 - x, 2/3 - x + y, -1/3 - z)$ , respectively. (b) Figure showing the trimeric Zn<sub>3</sub>O<sub>3</sub> cluster with the thermal ellipsoids given at 50% probability. All the atoms are labelled with their symmetry indicators. Atoms labelled with A and B are at the symmetry positions  $(-x + y, -x + 1, +z)$  and  $(-y + 1, +x - y + 1, +z)$ , respectively.



**Fig. 2** The zincoborate cluster,  $Zn_6B_{12}O_{24}$ . Note the capping of the polyborate ring by  $Zn_3O_3$  clusters on either side. (a) side view and (b) top view.

though three-membered rings involving two Zn and one P atom have been encountered in many open-framework zinc phosphates.<sup>12</sup> The zincoborate clusters, thus formed, are interconnected through  $Zn-\mu_3O(2)-B$  bonds. The covalent connectivity between the  $Zn_6B_{12}O_{24}$  clusters creates a bifurcated 6-membered ring involving two B–O–B and four Zn–O–B linkages. In other words, this 6-membered ring does not contain any Zn–O–Zn linkages. The connectivity between the zincoborate clusters is such that it forms an 8-membered one-dimensional channel of width  $4.3 \times 5.1$  Å (nearest O–O contacts not including the van der Waals radii) along the [102] direction (Fig. 3). The framework  $H_2O(3)$  molecule linked to the Zn atoms along with the free extra-framework  $H_2O(100)$  protrude into this channel as shown in Fig. 3 rendering it hydrophilic.

Some of the unusual structural features of **I** deserve further discussion. The presence of the cyclic polyborate anions itself is an important feature. Though cyclic polyborate anions have been observed previously,<sup>4–8</sup> this is the first instance where such polyborates are linked to form extended structures. The cyclic borate  $[B_{12}O_{20}(OH)_4]^{8-}$  anion observed earlier,<sup>8</sup> possesses terminal –OH groups attached to the triangular boron atoms. In the present case, the presence of  $Zn^{2+}$  ions, appears to facilitate the condensation of the terminal hydroxyl linkages through Zn–O–B linkages leading to the formation of an extended open-framework structure. It is also to be noted that the polyborate anions are sandwiched by trimeric  $Zn_3O_3$  clusters, similar to the isolated vanadoborate<sup>5</sup> and the isolated zincoborate<sup>6</sup> clusters reported previously. This contrasts with the vanadoborates,<sup>7b</sup> where the polyborate anions,  $[B_{10}O_{16}(OH)_6]^{8-}$ ,



**Fig. 3** Structure of **I** along the [102] direction showing the 8-membered channels. Note that the  $H_2O$  molecules bound from the Zn centre protrude into the channel. The extra-framework water molecules are not shown.

sandwich the  $[(VO)_6]$  clusters forming discrete  $[(VO)_6(B_{10}O_{16}(OH)_6)_2]$  units. Formation of the  $Zn_3O_3$  clusters is an important feature, as this is the first instance of such trimeric Zn–O clusters. Such unusual clusters owe their occurrence to the presence of oxygen atoms in three-fold coordination. In many of the known Zn phosphates,<sup>12</sup> the formation of the three-membered ring normally involves one P and two Zn atoms. The  $Zn_3O_3$  trimers found here fill the gap in the ring systems involving Zn and O atoms in open-framework materials.<sup>13</sup>

The distinct Zn atom in **I** is tetrahedrally coordinated by the oxygen neighbors with Zn–O bond lengths in the range 1.953(4)–2.004(6) Å [av. 1.978 Å]. The O–Zn–O bond angles are in the range  $100.9(2)^\circ$ – $114.5(2)^\circ$  [av. =  $109.3^\circ$ ]. Of the four oxygen atoms that are connected to Zn, two are connected to two distinct B atoms via  $Zn(1)-O(2)-B(1)$  and  $Zn(1)-O(1)-B(2)$  linkages with an average Zn–O–B bond angle of  $120.1^\circ$ , one oxygen makes a Zn–O(2)–Zn bond and the remaining is a terminal [O(3)] linkage. Bond valence sum calculations<sup>14</sup> clearly indicate that this oxygen [O(3)] is a water molecule. The bond valence sum for the various species of the framework is as follows: Zn(1) [1.91], B(1) [3.01], B(2) [2.99], O(1) [2.00], O(2) [1.93], O(3) [0.44] and O(4) [1.77]. Of the four framework O atoms, two [O(1) and O(2)] have three-fold coordination, one is terminal [O(3)] and the remaining one [O(4)] connects two B atoms. The oxygen atom O(4), in fact, forms the polyborate cluster by linking with the B atoms. The B atoms have both triangular and tetrahedral coordination. The triangularly coordinated B(1) has B–O distances in the range 1.365(5)–1.375(9) Å [av. = 1.369 Å] and the tetrahedral B(2) has longer B–O distances in the range 1.477(5)–1.479(5) Å [av. = 1.478 Å]. The O–B(1)–O bond angles are in the range  $119.3(3)^\circ$ – $121.4(6)^\circ$  [av. =  $120^\circ$ ] and O–B(2)–O in the range  $107.7(2)^\circ$ – $112.6(2)^\circ$  [av. =  $109.4^\circ$ ]. The B atoms are also linked together through B–O–B linkages forming the cyclic cluster,  $[B_{12}O_{24}]$ , with an average B–O–B bond angle of  $122.8^\circ$ . The various geometric parameters observed in **I** are comparable to those in the two zincoborates reported in the literature.<sup>1,3</sup> Selected bond distances and angles in **I** are presented in Table 2.

In conclusion, a new zincoborate of the composition  $Zn(H_2O)B_2O_4 \cdot xH_2O$   $x \approx 0.12$ , **I**, has been synthesized under

hydrothermal conditions. Besides providing the first example of a zincoborate with an extended structure, **I** also possesses one-dimensional channels. In addition to boron being present in both triangular and tetrahedral coordination, the presence of the unusual  $Zn_3O_3$  trimeric clusters is noteworthy.

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