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COMMUNICATION

# A pillared-layered zincoborate with an anionic network containing unprecedented zinc oxide chains†

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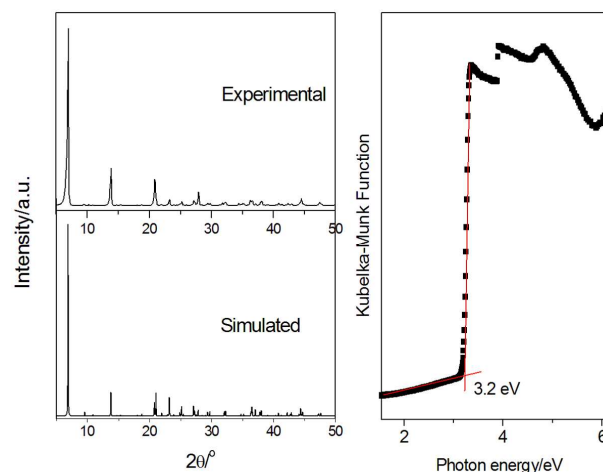
**A semiconducting zincoborate with a pillar-layered structure, has been made under solvothermal conditions, showing the first example of an inorganic-organic hybrid zincoborate with an anionic network based on the interesting zinc oxide chains linked by boron atoms and B<sub>3</sub>O<sub>7</sub>H<sub>2</sub> clusters, which are further pillared by diamine molecules to form the 3-D framework.**

The synthesis of boron-containing open-framework materials has long been a topic of interest due to their potential applications in ion-exchange, separation, and catalysis. Several approaches have been developed for producing such materials. A common strategy is to incorporate boron atoms into zeolite structures. However, it seems that boron could not fit well into tetrahedral zeolite frameworks. So far, only a limited number of aluminium/silicon sites in zeolitic structures could be replaced by boron atoms.<sup>1</sup> To increase the density of boron in the frameworks, new open-framework compounds containing boron as one of the main framework cations is highly desired. During the past years, a great deal attention has been paid to combine borate and phosphate groups in the same crystalline framework.<sup>2</sup> As a result, a new class of molecular sieves, namely metal borophosphates, have been developed and structurally characterized. It is noteworthy that the connection between borate and phosphate groups often result in the formation of helical chains, which offer exciting opportunities for the design and synthesis of chiral open-framework structures. Very recently, open-framework metal borates are of particular interest since these materials may integrate zeolitic porosity with extraordinary optical properties of borate materials. In contrast to tetrahedrally coordinated silicon in zeolite chemistry, boron can be surrounded by three or four oxygen atoms to form a unique BO<sub>3</sub> triangle or a typical BO<sub>4</sub> tetrahedron. The BO<sub>3</sub> and BO<sub>4</sub> groups may be further linked via common oxygen atoms to form different polyanionic clusters (e.g. B<sub>3</sub>O<sub>7</sub>H<sub>4</sub><sup>-</sup>, B<sub>4</sub>O<sub>9</sub>H<sub>4</sub><sup>2-</sup>, and B<sub>5</sub>O<sub>10</sub>H<sub>4</sub><sup>-</sup>) with ring- and cage-like apertures. These polyanionic clusters have active hydroxy groups and can serve as the secondary build-

ing units for the construction of new open-framework structures containing boron at relatively high concentrations.<sup>3</sup>

It's long been known that oxo boron clusters are often polymerized into low-dimensional structures. To obtain three-dimensional (3-D) open-framework structures, heteroatoms are usually added as the linking centers between oxo boron clusters. Many exciting results have been achieved in some systems, such as B–Al–O<sup>4</sup>, B–Ge–O<sup>5</sup>, B–V–O<sup>6</sup> and B–Zn–O<sup>7</sup>. In contrast to the rapid increasing amounts of the first three series of compounds listed above, only a limited number of zincoborates have been reported to date because of the difficulty in growing crystals suitable for structural determination.

Recently, we made a novel 3-D zincoborate in the presence of 1,4-diaminebutane.<sup>8</sup> The amine molecules bond directly to zinc centers and extend the inorganic chains of B<sub>4</sub>O<sub>9</sub>H<sub>2</sub> polyanions into a 3-D structure. As a continuous work, in our great effort to explore the structure-directing and extending effect of 1,6-diaminehexane (dah), a new zincoborate, formulated as Zn<sub>4</sub>(dah)(BO<sub>3</sub>)<sub>2</sub>(B<sub>3</sub>O<sub>7</sub>H<sub>2</sub>)·H<sub>3</sub>O·1.5H<sub>2</sub>O (**1**), was isolated under solvothermal conditions. **1** is a novel framework structure with zincoborate layers pillared by dah molecules. As far as we know, it represents the first example of inorganic-organic hybrid zincoborate with an anionic network.



**Fig. 1** (Left) Simulated and experimental powder X-ray diffraction patterns of **1**. (Right) The solid-state UV/Vis absorption spectrum of **1**.

Colorless single crystals of **1** were made by solvothermal reactions of Zn(OH)<sub>2</sub>, H<sub>3</sub>BO<sub>3</sub>, H<sub>2</sub>O, pyridine, and dah at 180°C for 7

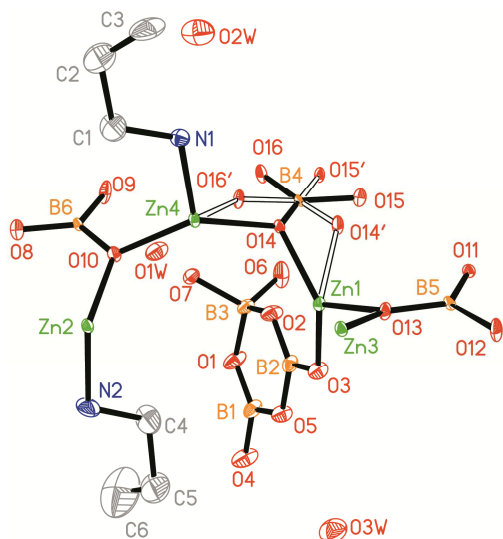
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† Electronic Supplementary Information (ESI) available: X-ray data in CIF format, experimental details, additional structural figures, IR spectrum, TGA curve. CCDC 961211. See DOI: 10.1039/b000000x/

days.<sup>‡</sup> The experimental powder X-ray diffraction pattern is in good agreement with the simulated one on the basis of single crystal data, indicating the phase purity of as-synthesized product (Fig. 1). IR spectrum of the polycrystalline sample indicates the presence of  $\text{BO}_3$  triangles and  $\text{BO}_4$  tetrahedra in the structure (Fig. S1, ESI<sup>†</sup>). The band at  $1255\text{ cm}^{-1}$  is due to the asymmetric stretch of  $\text{BO}_3$  units, and the bands for  $\text{BO}_4$  units appears at  $1046\text{ cm}^{-1}$  and  $1005\text{ cm}^{-1}$ . Diffuse-reflectance UV/Vis spectrum of **1** was measured in solid state at room temperature. As shown in Fig. 1, the optical absorption data derived from the reflectance show an optical transition with a band gap of  $3.2\text{ eV}$ , indicating that compound **1** is a wide-gap semiconductor.

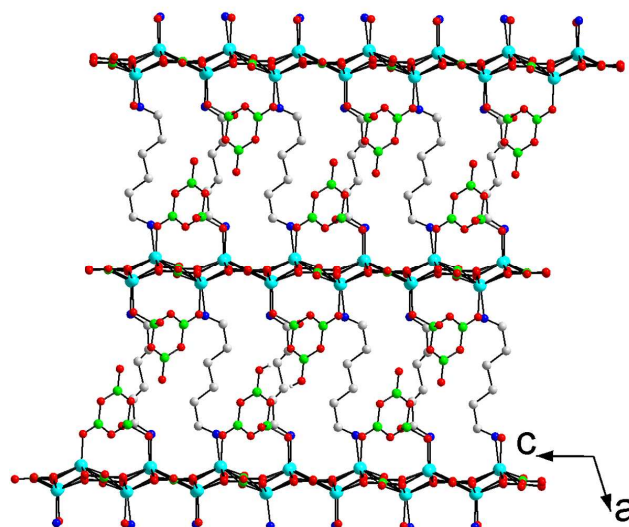
The structure of **1** was solved from single-crystal X-ray diffraction data collected at room temperature on an Agilent SuperNova Dual diffractometer.<sup>§</sup> It crystallizes in the monoclinic space group  $C2/c$  (no. 15). The asymmetric unit contains 32.5 crystallographically independent non-hydrogen atoms, including 4 zinc atoms, 5 boron atoms, 6 carbon atoms, 2 nitrogen atoms and 15.5 oxygen atoms (Fig. 2). All the four Zn atoms have tetrahedral coordination geometry. Zn1 and Zn3 are coordinated with four O atoms, while Zn2 and Zn4 are coordinated with three O atoms and one N atom. Of the five independent B atoms, B3 is tetrahedrally coordinated by four O atoms, and the remaining B atoms each coordinate with three O atoms to form a triangular geometry. The Zn–O bond lengths are in the region of  $1.918(10)$ – $1.988(10)\text{ \AA}$ , and the B–O bond lengths vary from  $1.342(11)\text{ \AA}$  to  $1.487(10)\text{ \AA}$ . Bond valence sum values indicate that B(1)–O(4) and B(3)–O(6) with the bond lengths of  $1.373(11)\text{ \AA}$  and  $1.469(12)\text{ \AA}$  are B–OH units. The framework of  $\text{Zn}_4(\text{dah})(\text{BO}_3)_2(\text{B}_3\text{O}_7\text{H}_2)$  would result in a net charge of  $-1$ , which is balanced by one extraframework  $\text{H}_3\text{O}^+$  cation per formula unit.



**Fig. 2** ORTEP plot of the asymmetric unit of **1**, showing the labelling scheme and the 30% probability displacement ellipsoid.

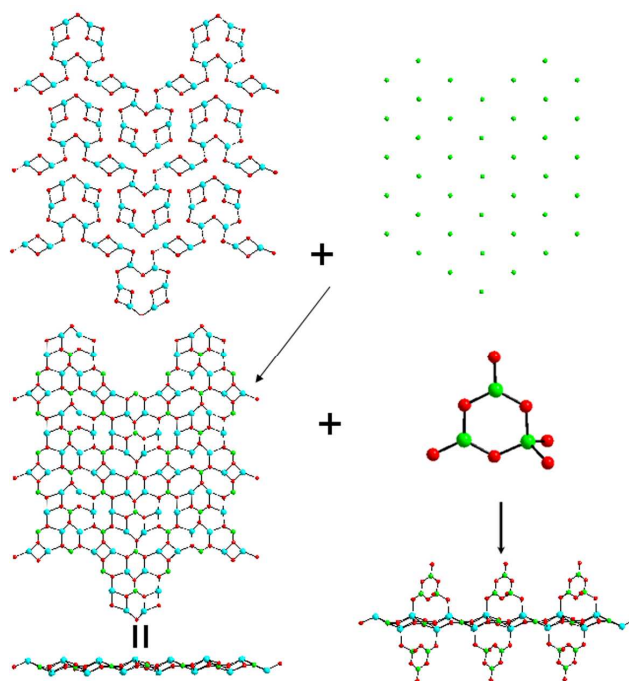
The structure of **1** features a 3-D framework with zincoborate layers pillared by dah molecules (Fig. 3). There are two different types of borate units in the structure: an isolated  $\text{BO}_3$  triangle and a cyclic  $\text{B}_3\text{O}_7\text{H}_2$  cluster (Fig. 2). Each triangular  $\text{BO}_3$  unit makes six B–O–Zn connections to adjacent zinc atoms, result in the formation of planar zincoborate layers parallel to the  $bc$  plane. The  $\text{B}_3\text{O}_7\text{H}_2$  cluster is made up of one  $\text{BO}_2(\text{OH})$  triangle, one  $\text{BO}_3$  tri-

angle, and one  $\text{BO}_3(\text{OH})$  tetrahedron. Although this cyclic cluster is a common structural building unit for different metal borate frameworks, it is first observed in zincoborate structures. The cyclic  $\text{B}_3\text{O}_7\text{H}_2$  clusters hang from zinc centers on both sides of the zincoborate layers as pendants (Fig. 3).



**Fig. 3** View of the framework structure of **1** with zincoborate layers pillared by dah molecules (all hydrogen atoms and water molecules are omitted for clarity). Color code: zinc, cyan; boron, green; oxygen, red; nitrogen, blue; carbon, gray.

The most striking structural feature of **1** is the presence of infinite zinc oxide chains (Fig. S2, ESI<sup>†</sup>) constructed from strictly alternating heart-like  $\text{Zn}_6\text{O}_8$  clusters and  $\text{Zn}_2\text{O}_4$  dimers along the  $[001]$  direction (Fig. 4). Prior to this work, only isolated zinc-



**Fig. 4** View of the inorganic zincoborate layer based on zinc oxide chains linked by boron atoms and  $\text{B}_3\text{O}_7\text{H}_2$  clusters. Color code: zinc, cyan; boron, green; oxygen, red.

centered polyhedra have been found in the structures of inorganic-organic hybrid zincborates. The linkages between oxo boron clusters (i.e.  $B_4O_9H_2$  clusters) in these structures generate 1- or 2-D substructures, which act as the backbones of zincborate frameworks. However, in the case of **1**, the zincborate layers are based on zinc oxide chains linked through boron atoms and  $B_3O_7H_2$  clusters (Fig. 4). Compared with other zincborates, it seems that the role of boron and zinc in the construction of the framework structure is reversed.

Also interesting is to examine the roles of the amine molecules in the formation of various zincborate structures. It has been demonstrated that the amine molecules always act as the structure-directing agents in the synthesis of new open-framework inorganic solids, such as metal phosphates, phosphites, and germanates. The organic species locate within the inorganic channels and interact with the framework oxygen atoms through extensive hydrogen bonds. However, it is surprising to find that all the amine molecules in the structures of zincborates attach directly to zinc centers through Zn–N bonds. The organic species serve as bidentate ligands rather than the structure-directing agents. One of the main reasons for these organic species to coordinate with zinc centers is to avoid the formation of highly charged frameworks.

It has been demonstrated that oxo boron clusters with tetrahedra geometries (e.g.  $B_3O_7^{5-}$ ,  $B_4O_9^{6-}$ , and  $B_5O_{10}^{5-}$ ) are ideal secondary building units for the construction of new zeolitic structures. A number of open-framework structures based on tetrahedral oxo boron clusters have been produced in B–Al–O and B–Ge–O systems. However, the highly charged nature of oxo boron clusters make it a great challenge to use divalent zinc ions as the bridging cations to connect these oxo boron clusters. If every  $Zn^{2+}$  ion makes four Zn–O–B connections with adjacent oxo boron clusters, the  $ZnO_4$  unit would be unstable since the excess bond valence from four oxo boron clusters to the  $Zn^{2+}$  center. The presence of Zn-amine-Zn linkages would reduce Zn–O–B linkages and thus meet the local charge balance.<sup>9</sup>

In summary, a new inorganic-organic hybrid zincborate was synthesized under solvothermal conditions. The presence of Zn-amine-Zn linkages in its structure is explained by the local charge balance rule, which is extended for the first time from chalcogenide chemistry to metal borate frameworks. This compound represents a rare example of semiconducting zincborate with zinc oxide backbones linked by boron atoms and oxo boron clusters. Different from the reported inorganic-organic hybrid zincborates with neutral frameworks, this compound features a unique anionic network. This makes it possible to explore its cation exchange application. Further work on this subject is in progress.

## Acknowledgements

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## Notes and references

‡ Synthesis of compound **1**: A mixture of  $Zn(OH)_2$  (0.099 g),  $H_3BO_3$  (0.618 g), dah (0.5 ml),  $H_2O$  (1.0 ml), and pyridine (3.0 ml) were stirred at room temperature for 30 min. The resulting solution was sealed in a 30

ml Teflon-lined stainless steel reactor and heated at 180°C for 7 days. After cooling to room temperature, colorless thin sheet crystals of **1** were recovered by filtration, washed with water, and then dried in air. Yields: 32% based on  $Zn(OH)_2$ . Elemental analysis (%) calcd for **1**: C 10.48, N 4.07, H 3.52; found: C 10.39, N 4.01, H 3.71.

§ Data collection was performed on an Agilent SuperNova Dual diffractometer with graphite-monochromated  $CuK\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation at room temperature. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using the *SHELXTL* program package.<sup>10</sup> Crystal data for **1**:  $C_6H_{24}B_5N_2O_{15.5}Zn_4$ ,  $M = 687.80$ , monoclinic, space group *C2/c* (no. 15),  $a = 26.8486(6) \text{ \AA}$ ,  $b = 9.8558(2) \text{ \AA}$ ,  $c = 17.0824(2) \text{ \AA}$ ,  $\beta = 107.816(2)^\circ$ ,  $V = 4303.48(16) \text{ \AA}^3$ ,  $Z = 8$ ,  $D_c = 2.123 \text{ g cm}^{-3}$ ,  $\mu = 5.759 \text{ mm}^{-1}$ , 13628 reflections measured, 3855 unique ( $R_{int} = 0.0205$ ). Final  $wR_2$  (all data) = 0.2295, final  $R_1 = 0.0740$ . In the structure, atoms B5 and B6 lie on inversion centres, and O3W lies on a twofold axis.

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