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ARTICLE TYPE

Two novel metal borates with three-dimensional open-framework layers constructed from the $[M_2B_8O_{20}(OH)_2]$ ($M = Al, Ga$) cluster units

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Two novel metal borates with three-dimensional open-framework layer, $Ba[MB_4O_8(OH)] \cdot H_2O$ ($M=Al/Ga$), were made under hydro(solvo)thermal conditions, in which the Al^{3+}/Ga^{3+} ions have been successfully introduced into the oxoboron cluster backbone and further linked together to form the open-framework layer made of the $[M_2B_8O_{20}(OH)_2]$ cluster units, of which the half-unit $[MB_4O_{11}(OH)]$ can be viewed as the analogous to known $[B_5O_9(OH)]$ cluster. Interestingly, the rare M-O-M linkages play a crucial role in forming the open-framework layer.

Borates are usually formed by oxo boron (B-O) clusters or B-O-M clusters as the structural building units (SBUs), which have made considerable progress up to now. Introducing main group atoms P/Ge into B-O cluster backbone or B-O anionic framework leading to two large subclasses of the heteroborate family, borophosphates¹ and borogermanates² with novel architectures and unusual properties. Whereas borates contain other main group atoms, such as Al,³⁻⁶ and Ga⁷ atoms, are still limited. Recently, our group employed hydro(solvo)thermal synthetic route to obtain some exciting results in open framework aluminoborates (ABOs) templated by protonated amines or transition metal complexes,⁴ and most of them display non-linear optical properties. However, the group IIIA metal borates templated by alkaline-earth metal cations have not been systematically investigated under hydro(solvo)thermal conditions. Thus, we extend the hydro(solvo)thermal systems from the amine templates to the alkaline-earth-metal templates. In addition, the alkaline-earth-metal cations have flexible coordination environments and higher transparency in the UV region, which result in the novel structures and potential application in nonlinear optical materials. Herein, two new IIIA metal borates $Ba[MB_4O_8(OH)] \cdot H_2O$ ($M = Al$ **1**, Ga **2**) have been successfully made, in which a unique cluster $M_2B_8O_{20}(OH)_2$ was firstly observed in the borate chemistry.

Over the past decades, according to the unique coordination modes of boron (triangular BO_3 and tetrahedral BO_4), Burns et al. developed a comprehensive description based on fundamental building blocks (FBBs) to have a clearer nomenclature for more complicated polyanions.⁸ Generally, the pentaborate cluster $B_5(O,OH)_n$ ($n = 10-14$) with the characteristic of two nearly perpendicular B_3O_3 rings is preferred obtained to other units in trivalent metal borates. So far, a series of non-metal

pentaborates and ABOs with $B_5(O,OH)_n$ have been made under hydro(solvo)thermal conditions, such as $[H_3N(C_6H_{10})-NH_3][B_5O_8(OH)]$,^{9a} $KB_5O_7(OH)_2 \cdot H_2O$,^{9b} $K_2Al[B_5O_{10}] \cdot 4H_2O$,^{4b} and $(CH_3NH_3)_2(H_2O)_2[Al(B_5O_{10})]$.^{4d}

Compared with the B atom, Al and Ga atoms exhibit more flexible coordination geometry (tetrahedral MO_4 , trigonal-bipyramidal/square-pyramidal MO_5 , and octahedral MO_6). To our knowledge, they tend to adopt MO_4 tetrahedral mode in borates under hydro(solvo)thermal condition except two AlO_6 octahedral examples of QD-6^{3a} and $C_5H_{18}AlB_{12}NO_{26}$.^{3b} However, the AlO_6 -based ABOs have often been made by boric acid flux method, such as PKU-n ($n=1,2,5,8$),⁵ only one AlO_5 -containing ABO was identified as square-pyramidal AlO_5 geometry in PKU-6.⁶ So far, the Al/Ga centres with trigonal-bipyramidal O_2MO_3 ($M=Al/Ga$) geometry in borates are rarely made by hydro(solvo)thermal or boric acid flux method. Only a $Ga_4B_2O_9$ ^{8c} with O_2GaO_3 trigonal-bipyramid is reported so far. Here two novel metal borates **1** and **2** with 3-D porous layer^{2b,10} containing the distorted O_2MO_3 trigonal-bipyramids (Fig. 1a) have been made.¹¹ Notice that the $B_4O_8(OH)$ (B_4)

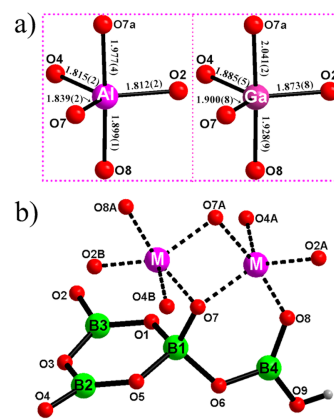


Fig 1. (a) The ball-and-stick representations of AlO_5 and GaO_5 distorted trigonal bipyramid with bond lengths, respectively. (b) Linkage of the $[B_4O_8(OH)]$ unit and M_2O_8 dimer ($M = Al, Ga$), showing the structure of the $MB_4O_{11}(OH)$ half-unit.

unit links the O_2MO_3 group via two O(7,8) atoms to form a very unique $MB_4O_{11}(OH)$ (MB_4) half-unit (Fig. 1b) in borate chemistry. Furthermore, The MB_4 can be viewed as that a O_2MO_3 group substitutes a BO_3 triangle of the well known $B_5O_9(OH)$ (B_5) unit (Fig. S1).

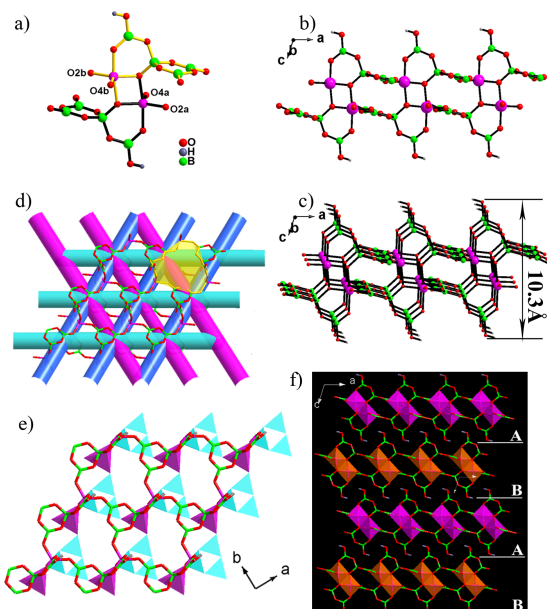


Fig 2. (a) View of the SBU. (b) Side view of 1-D chain along the *a*-axis. (c) Side view of the 3-D bilayer. (d) View of the intersecting 6-MR channels (cyan, purple and blue) in 3-D bilayer along the [010], [110] and [1-10] directions, respectively. (e) Top view of 3-D bilayer, showing the interlaced 9-MR windows along the *c*-axis. Color code: M/MO₅, purple; BO₄/BO₃, cyan. (f) View of the stacking mode of the 3-D bilayers in -ABAB- along the *c*-axis. Layer A/B, purple/orange.

Single crystal X-ray analysis reveals **1** and **2** are isostructural,¹² hence only structure of **1** will be discussed in detail. The asymmetrical unit contains 14 unique atoms, 1 Al, 4 B, 1 OH, and 8 O atoms, which make up of 1 O₂AlO₃ trigonal-bipyramid, 1 BO₄ tetrahedron and 3 B(O,OH)₃ triangles, respectively (Fig. 1b). In O₂AlO₃ group, five O atoms come from adjacent two B₄ units, its basal positions are occupied by three O(2a,4a,7) atoms (Al-O, 1.812(2)-1.839(2) Å) and the axial positions are located by two O(7a,8) atoms (Al-O, 1.899(1)-1.977(4) Å), showing the axial elongation. The ∠O7a-Al-O8 of 171.4° is close to the ideal value of 180°, the other longitudinal ∠O-Al-O angles of 91.6-94.2° (except ∠O7a-Al-O7 = 78.1°) and the equatorial ∠O-Al-O angles of 115.8-127.8° deviate only from the ideal 90° and 120°, respectively. In the B-centred groups, the B-O bond lengths are in the range of 1.343(3)-1.414(8) Å and 1.4731(7)-1.495(4) Å, and the ∠O-B-O angles span from 115.0 to 123.8° and 104.3 to 112.2° for the B(O,OH)₃ triangles and BO₄ tetrahedron, respectively.

Three B(O,OH)₃ triangles are bridged by a BO₄ tetrahedron to form a lacunary B₄ polyanion (the shorthand notation ‘4:<2 Δ+T>+Δ,isolated’)⁸ and further acts as a bidentate ligand to chelated a Al atom, forming a novel AlB₄ half-unit with two types of 3-membered rings (MRs), B₃O₃ and AlB₂O₃ (Fig. 1b); the AlB₄ is derived from the B₅O₉(OH)⁷ (B₅) cluster by replacing a BO⁺ group with AlO₃³⁻ group (Fig. S1), i.e. it is an Al-substituted AlB₄ cluster (B₅-like) and firstly made in borates. Compared with the B₅ cluster observed frequently in borates, the AlB₄ shows some structural differences that caused by the substituted Al atom: the ∠O7-Al-O8 in **1** corresponding to the ∠O7⁻-B₅⁻-O8⁻ in B₅ unit is 93.5°, which is much less 120°, owing to triangle BO₃ is replaced by O₂AlO₃ trigonal-bipyramid (Fig. 1b,S1,S2). Generally, Al atom occurs in a

tetrahedron or an octahedron and rarely in a distorted trigonal bipyramid, but a distorted O₂AlO₃ trigonal bipyramid is observed in **1** (Fig. 1a). So far, the reported ABOs containing B-O clusters are usually arranged by the alternate connection between AlO₄ tetrahedra and B-O clusters, and no Al-O-Al linkages in the structure. Thus, the trigonal-bipyramidal O₂AlO₃ groups and Al-O-Al linkages are firstly observed in ABOs.

Two AlB₄ link together via two Al-O-Al bonds to form the SBU of Al₂B₈O₂₀(OH)₂ (Al₂B₈) dimeric cluster, resulting in forming the edge-shared Al₂O₈ units (Fig. 2a). The SBUs are joined each other by two O(2,2a) atoms into an 1-D chain along the *a*-axis (Fig. 2b). Such chains are further linked by two O(4,4a) atoms along the *b*-axis to form the novel open-framework bilayer with the thickness of 10.3 Å in the *ab* plane (Fig. 2c), showing intersecting 6-MR channels along the [010], [110] and [1-10] directions (Fig. 2d), and interlaced 9-MR windows along the *c*-axis (Fig. 2e). Such bilayers are arranged in the -ABAB- mode along the *c*-axis (Fig. 2f). Notice that the known 1-D chainlike or 2-D layered borates are usually joined by single bridging O atoms. Here, the 2-D borate layer containing double bridging chains (Fig. 2b) and double bridges (Fig. 2c) is first observed in **1**. The bilayer can also be understood as adjacent two sheets, {AlB₄O₁₀(OH)}_n, with 3-/9-MR windows (Fig. 3e,S3). Adjacent sheets, formed by 180° rotation along the *c*-axis, are bridged by Al-O-Al bonds to form bilayer (Fig. 2c-e). This kind of 3-D open-framework bilayer was first found in AMH-3, in which the 8-MR limiting apertures run along the thickness of the silicate layer as well as in the plane of the layers.^{10a} Such 3-D bilayers are rare in metal borates, only three ones are known, i.e. K₄[B₈Ge₂O₁₇(OH)₂]^{2b} (**3**) Ba₃M₂[B₃O₆(OH)]₂[B₄O₇(OH)₂]^{10b} (M = Al **4**, Ga **5**). Compared **1/2** with AHM-3 and **3-5**, the remarkable differences are their linkages: in **1/2**, the adjacent MBO layers are linked by double bridging M₂O₈ dimers containing M-O-M linkages, in which the Al/Ga centres are trigonal-bipyramidal geometries; in **4/5**, adjacent ABO layers are linked by the B₄O₇(OH)₂ clusters to form the Al-[B₄O₇(OH)₂]-Al linkages, in which the Al/Ga centres are tetrahedral geometries; while adjacent Si-O layers in AHM-3 and adjacent B-Ge-O layers in **3** are connected by Si-O-Si and double bridging Ge₂O₇ dimers containing Ge-O-Ge linkages, in which the Si/Ge centres also possess tetrahedral geometries.

The topology of **1** can be simplified by considering the Al₂B₈ clusters and O(2,4) atoms as nodes and linkers, respectively. As a result, a layer of *sql* topological net with double edges is formed (Fig. S3). The Schläfli symbol of this net is {4⁴-6²}. The *sql* topological net with double edges is rare and only observed in [Co₃(dca)₆(H₂O)₄]·2(2,3,5-tmpdo)^{13a} and [Cd(dien)]₂[Cd(dien)(H₂O)]₂[As₄V₁₆O₄₂(H₂O)]·2H₂O.^{13b}

In addition to possessing an unique structure, **1** also represents high stability, powder X-ray diffraction patterns indicate it is stable in air for more than one and a half years and the fundamental packing is retained up to about 450°C (Fig. S4). The optical diffuse reflectance studies reveal that the band gaps for **1** and **2** are 5.57 and 5.33 eV and have ultraviolet cutoff edge below 209 and 220 nm respectively, suggesting the potential for UV applications (Fig. S5). In order to test its porosity, we attempted to exchange Ba²⁺ with Ca²⁺, Mg²⁺,

NH₄⁺ or Cs⁺ cations. Unfortunately, the results are disappointing, owing to the strong interactions between the Ba₂O₁₈ dimers and the host framework, as well as the pore sizes and shapes in the bilayers can not be adjusted by the above cations, either in radius (Ca²⁺, Mg²⁺) or in charge (NH₄⁺ or Cs⁺).

To further explore the chemical bonding and electronic structures of **1/2**, herein, we calculate the band structures and density of states (DOS) for them. The calculation was performed utilizing the density functional theory^{14,15} with the plane-wave pseudopotential in CASTEP code,¹⁶ the generalized gradient approximation functional by Perdew and Wang (PW91) was employed.^{17,18} The calculated band structures of **1/2** (Fig. S6a,c) show that the top of the valence bands (VBs) is nearly flat meanwhile the bottom of the conduction bands (CBs) displays some dispersion. Both of the lowest energy (5.05/4.92 eV for **1/2**) of CBs and the highest energy (-0.04/-0.02 eV for **1/2**) of VBs are located at the G point. Therefore, **1/2** have direct band gaps of about 5.09/4.94 eV, respectively. As we expect that less orbital overlap for **1** containing the smaller Al³⁺ ion, leading to a larger band gap. The band can be assigned according to the total and partial DOS plotted (Fig. S6b,d). It is clear to see that the VBs from -20.0 to -18.0 eV for **1/2** are mainly derived from B-2s and O-2s states. The bands from the -11.0 eV to the Fermi level are mainly contributions of B-2p, O-2p and Ba-6p states and localized around -12.0 eV is contribution of Ga-3d for **2**. The CBs are dominated by unoccupied of B-2p and Ba-5d states. Overlap among the bands indicates the strong covalent interactions among the elements in the system.

In summary, two novel open-framework layered metal borates have been made under hydro(solvo)thermal conditions, in which the M₂B₈ (M=Al/Ga) cluster with O₂MO₃ trigonal-bipyramids is first observed in inorganic-templated metal borates and provides useful information to understand the coordination behavior of Al/Ga atoms in various solid-state materials. The frameworks **1** and **2** firstly exhibit 3-D open-framework bilayers with the M-O-M linking modes in metal borates, which not only enriches the structural chemistry of borates, but also extends the cluster chemistry from borates to metal borates. Further study on novel metal borate cluster open frameworks is in progress.

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Notes and references

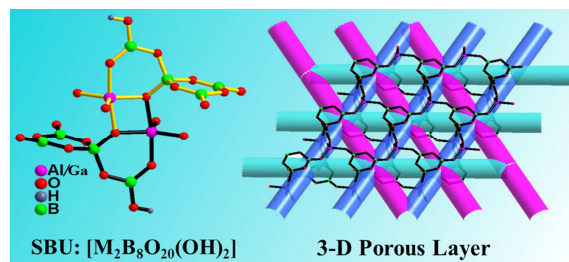
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† Electronic Supplementary Information (ESI) available: Synthesis, additional structural plots, power XRD, IR, TG, UV-vis diffuse-reflectance. ICSD-426545 (**1**) and 426546 (**2**). See DOI: 10.1039/b000000x/

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- 105 11 Compounds **1** and **2** were made by hydrothermal reactions of aluminium/gallium isopropoxide, H₃BO₃, Ba(OH)₂·8H₂O, pyridine and H₂O in a 25 ml Teflon autoclave. After heating at 260 °C for 6 days, single crystal was obtained as a colorless irregular polygonal flaky.
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Two metal borates with 3-D porous layers, $Ba[MB_4O_8(OH)] \cdot H_2O$ ($M = Al, Ga$), have been made under hydro(solvo)thermal conditions, in which two half-units $MB_4O_{11}(OH)$ link via Al-O-Al linkages to form the dimeric $M_2B_8O_{20}(OH)_2$ cluster unit that further connect each other to produce 3-D porous layers with thickness of 10.3 Å, showing the three types of intersecting 6-membered ring channels. Also, the edge-shared $O_2M_2O_3$ trigonal bipyramids are first observed in inorganic-templated metal borates.