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$K_2[Ga(B_5O_{10})]\cdot 4H_2O$: The First Chiral Zeolite-like Galloborate with Large Odd 11-Ring Channels

Zhi-Hong Liu,* Ping Yang, and Ping Li

School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, People's Republic of China

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The first chiral zeolite-like galloborate, $K_2[Ga(B_5O_{10})]\cdot 4H_2O$, has been synthesized by a mild solvothermal method and characterized by Fourier transform IR, energy-dispersive spectroscopy, thermogravimetric/differential thermal analysis, and single-crystal X-ray diffraction. This compound crystallizes in the orthorhombic system with space group $C222_1$. The structure possesses a 3D open framework constructed by B_5O_{10} clusters and GaO_4 units and contains large odd 11-ring channels.

Microporous materials have attracted considerable attention because of their widespread applications in catalysis, ion exchange, and adsorption.[1] The discovery of aluminophosphate analogues of zeolites[2] has greatly stimulated interest in designing other novel inorganic microporous materials with different topological structures. In recent years, much of this work has been largely focused on the following systems: Al−O−P,[3] Al−O−B,[4] Zn−O−P,[5] B−O−P,[6] Ga−O−P,[7] Ge−O,[8] and B−O−Ge.[9]

Boron is a unique element, which can be coordinated by oxygen with triangular or tetrahedral geometries. Its heavier congener gallium can also have flexible coordination geometries, as exemplified by tetrahedral GaO_4, trigonal-bipyramidal GaO_5, and octahedral GaO_6. It is expected that the combination of the B and Ga atoms in the same crystalline material may generate a new class of materials with novel structures and useful properties. However, very little research has been carried out on the B−O−Ga system. This is, in part, due to the large difference in the radii of B and Ga atoms, which makes it difficult for their compounds to react. Previous studies, to explore new nonlinear optical materials, have focused on the synthesis of galloborates by a high-temperature solid-state reaction, such as $K_2Ga_2O(BO_3)_2$,[10] $Sr_3Ga_3(BO_3)_4O(OH)$,[11] and $Ba_4Ga_2B_8O_{18}Cl_2\cdot NaCl$.[12] In this Communication, we report the synthesis and structure of the first chiral zeolite-like galloborate, $K_2[Ga(B_5O_{10})]\cdot 4H_2O$ (denoted as **XA-1**). Single-crystal X-ray analysis revealed that the crystal structure of **XA-1** could be described as a 3D open framework constructed by B_5O_{10} clusters and GaO_4 units.

Colorless single crystals of **XA-1** were obtained by using a mild solvothermal route: 0.166 g of $K_2B_4O_5(OH)_4\cdot 2H_2O$ was dissolved in a mixture solution of 0.6 mL of H_2O, 0.5 mL of diethylenetriamine, and 3.5 mL of pyridine. After the mixture was briefly stirred, 0.141 g of Ga_2O_3 was added and stirring was continued for 6 h at room temperature. The final mixture with pH = 9.0 was heated in a Teflon-lined stainless steel autoclave at 160 °C for 9 days under autogenous pressure, and then it was cooled to room temperature. The resulting colorless crystals were obtained by filtration,

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* To whom correspondence should be addressed. E-mail: liuzh@snnu.edu.cn.

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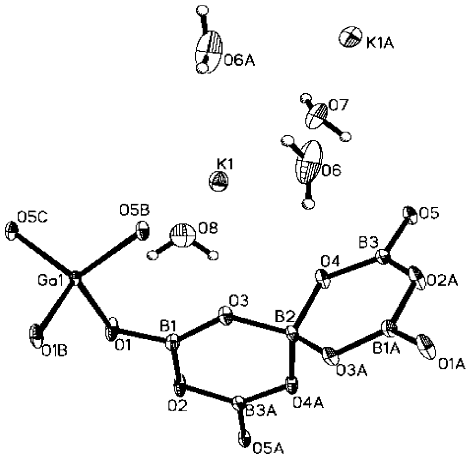

Figure 1. Molecular structure of **XA-1**, drawn at the 30% probability level.

washed with deionized water and alcohol, and dried in a dryer to a constant mass at room temperature (48% yield based on Ga). Anal. Calcd: Ga, 16.06; K, 18.01. Found: Ga, 16.29; K, 17.68. IR (KBr pellet, cm^{-1}): 3444 (OH), 1646 (H_2O), 1395 (BO_3), 1244 (GaO_4), 1066 (BO_4), 940 (BO_3), 823 (BO_4), 645 (BO_3), 469 (BO_4).[13]

The crystal structure[14] of **XA-1** consists of two K^+ cations, one $[Ga(B_5O_{10})]^{2-}$ anion, and four lattice water molecules, as shown in Figure 1. The $[Ga(B_5O_{10})]^{2-}$ anion is made up of a B_5O_{10} cluster and a GaO_4 tetrahedron that are connected through an O atom. The B_5O_{10} cluster consists of two almost planar B_3O_3 rings linked by a common $B2O_4$ tetrahedron, and these two rings are nearly perpendicular to each other. Each ring is composed of two BO_3 triangles (B1, B1A, B3, and B3A) and a slightly distorted common BO_4 tetrahedron, which are linked through their vertexes. The B−O distances range from 1.304(3) to 1.428(3) Å (av 1.369 Å) and from 1.436(2) to 1.537(2) Å (av 1.487 Å), and the O−B−O bond angles are in the ranges of 113.6(2)−123.5(2)° and 101.75(8)−118.3(2)° for BO_3 and BO_4 units, respectively. The Ga−O distances range from 1.8035(15) to 1.8882(13) Å (av 1.8459 Å), and the O−Ga−O bond angles are in the range of 93.49(11)−113.42(8)°. The Ga−O−B bond angles are in the range of 127.96(13)−129.37(16)°. The analogous framework of B_5O_{10} clusters is also present in some hydrated pentaborates, such as $M[B_5O_6(OH)_4]\cdot 2H_2O$ (M = K, Rb, Cs, NH_4^+).[15] In these pentaborates, the $B_5O_6(OH)_4^-$ polyborate anion only exists in isolated form because the four terminal protonated O atoms prevent the unit from further connections. However, in **XA-1**, each B_5O_{10} cluster is connected to four GaO_4 units by four shared μ_2-O atoms (Figure S2 in the Supporting Information) and further connected to 12 other B_5O_{10} clusters through four bridging GaO_4 units. Thus, there are no Ga−O−Ga connections in the structure. Like the B_5O_{10} cluster, each GaO_4 unit is also connected to 12 other GaO_4 units through four bridging B_5O_{10} clusters. The alternate connectivity between the B_5O_{10} clusters and the GaO_4 units through their vertex O atoms gives rise to the 3D macroanionic $[Ga(B_5O_{10})]_n^{2n-}$ open framework with two different kinds of channels along the [100], [010], and [001] directions, respectively. One is the 8-ring channel with a $GaO_4-BO_3-BO_4-BO_3-GaO_4-BO_3-BO_4-BO_3$ sequence, and the other is the smaller 6-ring channel with a $GaO_4-2(BO_3)-GaO_4-2(BO_3)$ sequence. Moreover, each kind of channel displays the symmetrical distribution (Figure S3 in the Supporting Information).

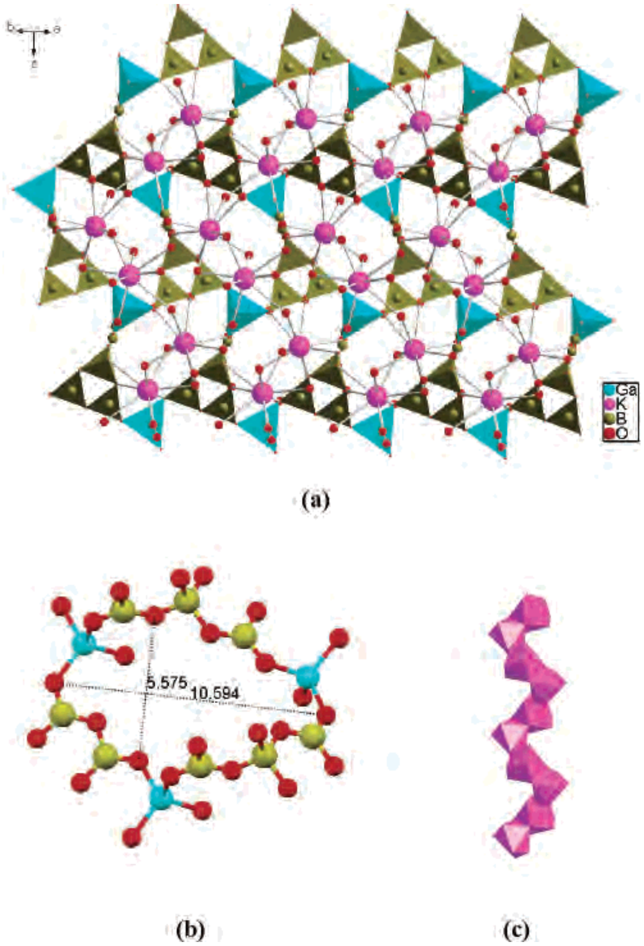

Figure 2. (a) Polyhedral view of **XA-1** along the [110] direction. (b) Pore aperture and 11-ring size (Å). (c) Polyhedral view of the helical KO_9 chain.

Among the known zeolite topologies, odd rings are rare, with the exception of the 5-ring,[9a] and the highest odd ring number to date is 11, found only in ICMM6.[16] It is worth noting that there also exist such largest odd 11-ring channels extending along the crystallographic [110] direction (Figure 2a and Figure S4 in the Supporting Information) with the $GaO_4-BO_3-BO_4-BO_3-GaO_4-2(BO_3)-GaO_4-BO_3-BO_4-BO_3$ sequence. The pore aperture and size are shown in Figure 2b. The wall of the 11-ring channel has two 11-ring windows with the same sequence as was mentioned above (in fact, the two 11-ring windows form the other 11-ring

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(14) The crystal data were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 291 K. Crystal data for **XA-1** (CSD No. 417397): $H_8B_5GaK_2O_{14}$, M_r = 434.03, orthorhombic, $C222_1$, T = 291(2) K, a = 10.3798 (7) Å, b = 9.3934 (7) Å, c = 13.8051(10) Å, β = 90°, V = 1346.02 (17) $Å^3$, Z = 4, D_c = 2.142 Mg/m^3, GOF = 1.078, R1 = 0.0210, wR2 = 0.0555.

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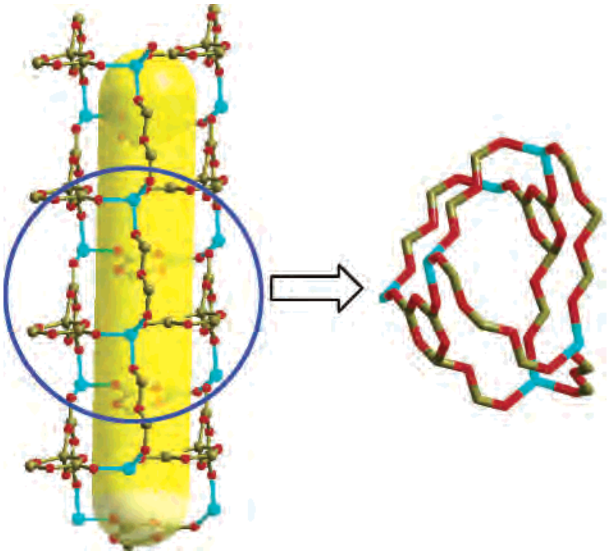

Figure 3. 11-ring channel and its three windows.

channel along the [1$\bar{1}$0] direction, as shown in Figure S4c in the Supporting Information) and one 12-ring window with the GaO_4−2(BO_3)−GaO_4−2(BO_3)−GaO_4−2(BO_3)−GaO_4−2(BO_3) sequence, which results in an unprecedented 3D intersecting-channel system (Figure 3). In addition, the unique 11-multirings have two tropisms, in which the K^+ cations and lattice water molecules are located (the H_2O6 molecules reside in the other 11-ring channels along [1$\bar{1}$0]). The charge of the $[Ga(B_5O_{10})]_n^{2n-}$ framework is balanced by K^+ cations. Interestingly, the two K^+ cations are both nine-coordinate, with five framework O atoms and four bridging water molecules (Figure S5 in the Supporting Information), of which the bridging H_2O8 and H_2O8A connect the two pairs of K^+ ions in two adjacent rings, forming the helical chain structure (Figure 2c), which makes the 11-multirings display helical chain topologies and further leads to the chirality of the crystal. The K−O distances range from 2.7485(16) to 3.3320(17) Å (av 3.000 Å). Moreover, there exist weak hydrogen bonds not only between the water molecules (O8-H···O6) but also between the water molecules (H_2O6 and H_2O7) and the B_5O_{10} cluster O atoms (O3, O4, and O5), with the O···O distances from 2.637(2) to 3.455(3) Å and the O−H···O angles from 129.0 to 161.4°.

The structure of **XA-1** is closely related to that of $Li_2AlB_5O_{10}$ synthesized by a solid-state reaction.[17] Similar to the case in **XA-1**, the $[AlB_5O_{10}]^{2-}$ anion consists of a B_5O_{10} group linked by a AlO_4 tetrahedron. The B−O bond lengths for BO_3 and BO_4 units in $Li_2AlB_5O_{10}$ are in accordance with those found in **XA-1**. As compared to the chiral orthorhombic space group $C222_1$ in **XA-1**, $Li_2AlB_5O_{10}$ crystallized in the monoclinic space group $P2_1/c$. In addition, the asymmetric unit of $Li_2AlB_5O_{10}$ is different from that of **XA-1** (Figure S6 in the Supporting Information). In a word, the structure of $Li_2AlB_5O_{10}$ can be characterized as a 3D network,[17] whereas the structure of the title compound is characterized as a 3D open framework with 8-, 8-, 8-, and 11-multiring channels along the [100], [010], [001], and [110] directions, respectively.

Simultaneous thermogravimetric/differential thermal analysis (TG-DTA) curves show that the four water molecules in the channel can be removed between 30 and 200 °C (found, 15.93%; calcd, 16.59%) and the formed $K_2[Ga(B_5O_{10})]$ melts at 630 °C, which implicates a stable framework up to this temperature. More importantly, the anhydrous sample takes up almost completely the lost water molecules when exposed to air at room temperature for about 1 day. This reversible dehydration and rehydration behavior shows that the framework can be retained, which was testified by TG-DTA and X-ray diffraction (XRD) (Figures S7 and S8 in the Supporting Information).

In summary, the first chiral zeolite-like galloborate, $K_2[Ga(B_5O_{10})]\cdot 4H_2O$, with large odd 11-ring channels has been synthesized. This is the first mild synthesis route and single-crystal structure reported on the galloborate microporous materials. This result enriches the field of molecular sieves and has a great significance for the new class of galloborate microporous materials. The successful synthesis of **XA-1** provides possibilities to synthesize other novel galloborates using B−O clusters in combination with Ga−O units. Further research on this work is in progress.

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Supporting Information Available: Crystallographic files in CIF format and figures of the FT-IR spectrum, a view of the linkages of the B_5O_{10} cluster and GaO_4 unit, a view along the *a*, *b*, or *c* axis and [110] and [1$\bar{1}$0] directions, the coordination environments of K^+, TG-DTA curves, and XRD. This material is available free of charge via the Internet at http://pubs.acs.org.

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