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QD-2: A Novel Open-Framework Aluminoborate with Intersecting Three-Dimensional Helical Channels

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A novel open-framework aluminoborate, $[CH_3NH_2(CH_2)_3NH_3][AlB_5O_{10}]$ (QD-2), has been synthesized under hydrothermal conditions and characterized by IR, elemental analysis, thermogravimetric analysis, and powder and single-crystal X-ray diffractions. The compound crystallizes in the orthorhombic system, space group $P2_12_12_1$ (No. 19), $a = 9.4352(4)$ Å, $b = 10.2972(2)$ Å, $c = 13.7511(5)$ Å, $V = 1336.0(8)$ Å^3, and $Z = 4$. Its structure consists of AlO_4 tetrahedra and B_5O_{10} clusters, which are interconnected to form the first example of a three-dimensional aluminoborate with intersecting helical channels.

Microporous materials have attracted a lot of interest in the past decades, and a large number of new inorganic framework solids with novel structural features have been characterized to date.[1] Among them, porous materials with helical pores are particularly desirable for their promising applications in enantioselective separation and catalysis.[2] Chiral rhodium complexes supported on a zeolite matrix, for example, are recognized to give rise to asymmetric hydrogenation of *N*-acyldehydrophenylalanine derivatives with an enantioselectivity of >95%.[3] However, it is still a highly challenging task to design an inorganic structure with helical features because of the unclear mechanism by which such an inorganic framework is formed. Among the vast variety of zeolitic frameworks, only a small number of chiral microporous materials have been reported.[4–8] Notable examples include vanadium phosphate $[\{(CH_3)_2NH_2\}K_4\{V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7\}]$ with interpenetrating double helices,[5] zinc phosphates $[\{NH_3(CH_2)_2NH_2(CH_2)_2NH_3\}\{Zn_4(PO_4)_3(HPO_4)\}]\cdot H_2O$ and $[\{Zn_2(HPO_4)_4\}\{Co(dien)_2\}]\cdot H_3O$ with intersecting helical channels,[6] UCSB-7 frameworks with cross-linked helical pores,[7] as well as a few interesting metal borophosphates.[8] Recently, inorganic borates have been receiving particular attention because of their outstanding physical properties and fascinating structural diversity.[9] The ability of boron to adopt both BO_3 and BO_4 coordination modes, coupled with the tendency of such units to polymerize into a wide range of polyanions, has made inorganic borates a rapidly growing family. However, it is worth noting that only a very few microporous borates with helical characters have been reported so far.[10] Here, we present the synthesis and characterization of the first helical aluminoborate, $[CH_3NH_2(CH_2)_3NH_3][AlB_5O_{10}]$ (QD-2), in which B_5O_{10} and AlO_4 units are interconnected to form an unprecedented open framework with intersecting helical channels.

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(1) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268, and references cited therein.

(2) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.

(3) Corma, A.; Iglesias, M.; del Pina, C.; Sanchez, F. *J. Chem. Soc., Chem. Commun.* **1991**, 1235.

(4) (a) Treacy, M. M. J.; Newsam, J. M. *Nature* **1988**, *332*, 249. (b) Anderson, M. W.; Terasaki, O.; Ohsuna, T.; Philippou, A.; MacKay, S. P.; Ferreira, A.; Rocha, J.; Lidin, S. *Nature* **1994**, *367*, 347. (c) Bruce, D. A.; Wilkinson, A. P. *J. Chem. Soc., Chem. Commun.* **1995**, 2059. (d) Stalder, S. M.; Wilkinson, A. P. *Chem. Mater.* **1997**, *9*, 2168. (e) Feng, P.; Bu, X.; Tolbert, S. H.; Stucky, G. D. *J. Am. Chem. Soc.* **1997**, *119*, 2497. (f) Ayyappan, S.; Bu, X.; Cheetham, A. K.; Rao, C. N. R. *Chem. Mater.* **1998**, *10*, 3308. (g) Lin, Z. E.; Yao, Y. W.; Zhang, J.; Yang, G. Y. *J. Chem. Soc., Dalton Trans.* **2002**, 4527. (h) Medina, M. E.; Iglesias, M.; Snejko, N.; Gutierrez-Puebla, E.; Monge, M. A. *Chem. Mater.* **2004**, *16*, 594. (i) Zou, X. D.; Conradsson, T.; Klingstedt, M.; Dadachov, M. S.; O'Keeffe, M. *Nature* **2005**, *437*, 716.

(5) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596.

(6) (a) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **1999**, 165. (b) Wang, Y.; Yu, J. H.; Guo, M.; Xu, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 4089.

(7) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154.

(8) (a) Kniep, R.; Will, H. G.; Boy, I.; RThr, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 1013. (b) Yilmaz, A.; Bu, X.; Kizilyalli, M.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 3243. (c) Boy, I.; Stowasser, F.; Schäfer, G.; Kniep, R. *Chem.*−*Eur. J.* **2001**, *7*, 834. (d) Huang, Y. X.; Schäfer, G.; Carrillo-Cabrera, W.; Cardoso, R.; Schnelle, W.; Zhao, J. T.; Kniep, R. *Chem. Mater.* **2001**, *13*, 4348. (e) Li, M. R.; Liu, W.; Ge, M. H.; Chen, H. H.; Yang, X. X.; Zhao, J. T. *Chem. Commun.* **2004**, 1272.

(9) (a) Heller, G. *Top. Curr. Chem.* **1986**, *39*, 131. (b) Burns, P. C.; Grice, J. D.; Hawthorne, F. C. *Can. Mineral.* **1995**, *33*, 1131. (c) Burns, P. C. *Can. Mineral.* **1995**, *33*, 1167. (d) Grice, J. D.; Burns, P. C.; Hawthorne, F. C. *Can. Mineral.* **1999**, *37*, 731. (e) Becker, P. *Adv. Mineral.* **1999**, *37*, 979.

(10) (a) Rowsell, J. L. C.; Taylor, N. J.; Nazar, L. F. *J. Am. Chem. Soc.* **2002**, *124*, 6522. (b) Lin, Z. E.; Zhang, J.; Yang, G. Y. *Inorg. Chem.* **2003**, *42*, 1797. (c) Zhang, H. X.; Zhang, J.; Zheng, S. T.; Wang, G. M.; Yang, G. Y. *Inorg. Chem.* **2004**, *43*, 6148. (d) Li, Y. F.; Zou, X. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 2012. (e) Zhang, H. X.; Zhang, J.; Zheng, S. T.; Wang, G. M.; Yang, G. Y. *Cryst. Growth Des.* **2005**, *5*, 157. (f) Liu, Z. H.; Yang, P.; Li, P. *Inorg. Chem.* **2007**, *46*, 2965. (g) Liu, G. Z.; Zheng, S. T.; Yang, G. Y. *Inorg. Chem. Commun.* **2007**, *10*, 84.

10.1021/ic800593q CCC: $40.75

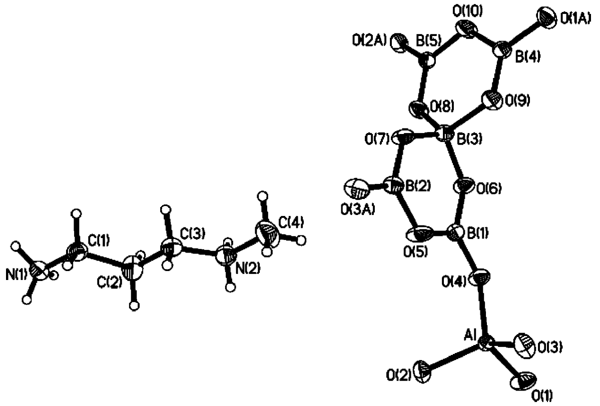

Figure 1. Labeled ORTEP plot of the asymmetric unit of QD-2 (50% probability ellipsoid).

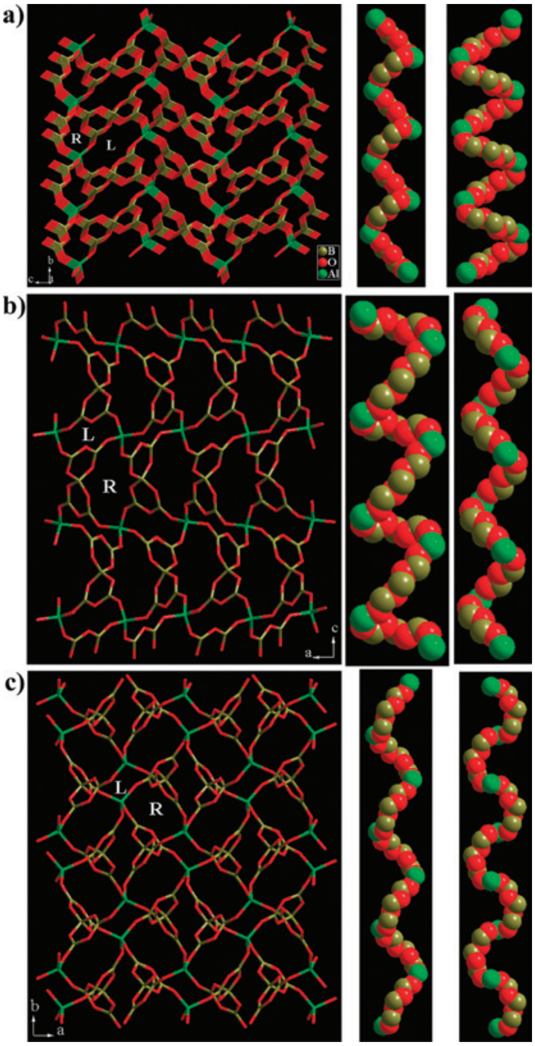

Figure 2. Framework of QD-2 viewed along the [100] (a), [010] (b), and [001] (c) directions showing intersecting helical channels (left), the right-handed channels (middle), and the left-handed channels (right).

QD-2 was prepared by heating a mixture of Al_2O_3, H_3BO_3, *N*-cyclohexyl-1,3-diaminopropane, pyridine, and H_2O in the molar ratio of 1:3:3:54:30 in a Teflon-lined autoclave at 170 °C for 10 days under autogenous pressure. The pH of the resulting mixture did not show any appreciable change during the hydrothermal reaction and remained at ~8.0. The homogeneous product consisting of large colorless block-shaped crystals was separated from the solution by filtration, washed with distilled water, and then dried in air (18% yield based on Al). Notably, the solvent pyridine played an important role for the crystallization of the desirable product. Attempts to synthesize QD-2 with high crystallinity by using other solvents such as ethylene glycol and *N*,*N*-dimethylformamide were unsuccessful. The experimental and simulated powder X-ray diffraction patterns are in good accordance with each other, indicating the phase purity of the sample (Figure S1 in the Supporting Information). The elemental chemical analysis is consistent with the present structural study. Anal. Calcd (found, %) for QD-2: C, 14.50 (14.42); H, 4.26 (4.21); N, 8.46 (8.40). IR (KBr pellet, cm^{-1}): 1552 cm^{-1} ($CH_3NH(CH_2)_3NH_2$), 1380 cm^{-1} (BO_3), 1225 cm^{-1} (AlO_4), 1050 cm^{-1} (BO_4) (Figure S2 in the Supporting Information).

The asymmetric unit of QD-2[11] consists of one diprotonated template cation $[CH_3NH_2(CH_2)_3NH_3]^{2+}$ and one $[Al(B_5O_{10})]^{2-}$ anion, as shown in Figure 1. It is noteworthy that the organic template $[CH_3NH(CH_2)_3NH_2]$ was not added in the initial mixture, with its presence derived from the decomposition of *N*-cyclohexyl-1,3-diaminopropane under the present hydrothermal conditions. This phenomenon was already observed during the synthesis of the earlier case, $AlPO_4$-GIS.[12] The $[Al(B_5O_{10})]^{2-}$ anion is composed of one usual B_5O_{10} cluster and one typical AlO_4 tetrahedron that are bridged by the common O(4) atom. The B_5O_{10} cluster, featuring two planar B_3O_3 rings that are approximately perpendicular to each other, is made up of one $B(3)O_4$ tetrahedron and four BO_3 triangles [B(1), B(2), B(4), and B(5)]. The B−O distances vary from 1.325(3) to 1.403(3) Å and from 1.456(3) to 1.474(3) Å, and the O−B−O bond angles are in the range of 115.8(2)−124.4(2)° and 107.5(2)−111.6(2)° for BO_3 and BO_4 units, respectively. The Al−O distances lie in the 1.719(2)−1.733(2) Å range, and the O−Al−O bond angles span from 106.5(9) to 111.8(8)°.

The alternate connectivity between the B_5O_{10} clusters and the AlO_4 tetrahedra through their vertices gives rise to a novel three-dimensional (3D) network with intersecting helical channels in the [100], [010], and [001] directions. Along the [100] direction, two different channels that appear to have 6- and 8-ring openings can be seen (Figure 2a). In fact, they are enclosed by two types of helices with opposite chirality. The right-handed helical chain is built from the infinite linkage of $-AlO_4-BO_3-BO_3-AlO_4-BO_3-BO_3-AlO_4-BO_3-BO_3-$, while the left-handed helical chain is constructed from the unclosed linkage of $-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_4-BO_3-$. The

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[11] Crystal data for QD-2: $C_4H_{14}N_2O_{10}B_5Al$, $M_r = 331.20$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 9.4352(4)$ Å, $b = 10.2972(2)$ Å, $c = 13.7511(5)$ Å, $V = 1336.0(8)$ Å^3, $Z = 4$, $\rho = 1.647$ mg·cm^{-3}, $\lambda = 0.710\,73$ Å, μ(Mo Kα) = 0.184 mm^{-1}, $F(000) = 680$. A total of 9322 reflections were collected in the range of $2.47° \leq \theta \leq 26.00°$, of which 2595 were unique ($R_{int} = 0.0225$) and 219 with $I \geq 2\sigma(I)$ were collected for the analysis. The structure was solved and refined by full-matrix least squares on F^2 values (*SHELXL-97*). Non-hydrogen atoms were refined anisotropically. The final indices were $R_1 = 0.0319$ and $wR_2 = 0.0881$ with GOF = 1.045. CCDC 681246.

[12] Paillaud, J.-L.; Marler, B.; Kessler, H. *J. Chem. Soc., Chem. Commun.* **1996**, 1293.

left- and right-handed helices couple with each other to form the 3D framework with helical channels. Furthermore, other helical channels can also be observed in the [010] and [001] directions (Figure 2b,c), which are similar to those in the [100] direction, only differing in their shape and size. Thus, QD-2 possesses a 3D helical pore system. To the best of our knowledge, it is for the first time that an open-framework aluminoborate with intersecting 3D helical channels is observed in the B−O−Al system.[13]

Another important structural feature of QD-2 is that it possesses regular 11-ring channels in the [110] direction (Figure 3a). Among the known crystallized microporous materials, the largest odd 11-rings are rare and are only found in ICMM6, XA-1, and QD-3.[10f,13e,14] The apertures of the 11-ring channels are elliptical in shape and are bound by three AlO_4, two BO_4, and six BO_3 units with the $AlO_4-BO_3-BO_3-AlO_4-BO_3-BO_4-BO_3-AlO_4-BO_3-BO_4-BO_3$ sequence. The wall of the 11-ring channels is composed of two 11-ring windows with the same sequence as that mentioned above and one puckered 12-ring window with the $AlO_4-2(BO_3)-AlO_4-2(BO_3)-AlO_4-2(BO_3)-AlO_4-2(BO_3)$ sequence (Figure 3b). The diprotonated organic molecules, residing in the 11-ring channels, compensate for the negative charge of the macroanionic $[Al(B_5O_{10})]_n^{2n-}$ framework and interact with the framework oxygen atoms through hydrogen bonding (Figure S3 in the Supporting Information), with N•••O distances in the range of 2.869(2)−3.078(2) Å.

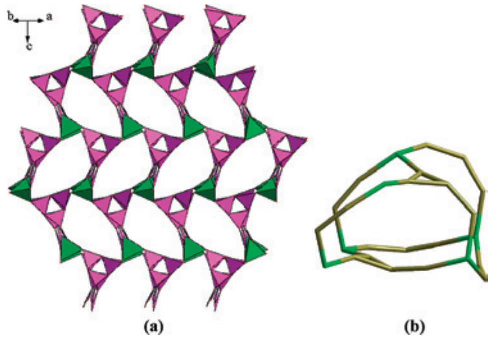

Figure 3. (a) Polyhedral view of QD-2 along the [110] direction: AlO_4, green; BO_3 and BO_4, purple. (b) Three windows of the 11-ring channel.

Although the 3D frameworks of QD-2 and QD-3[13e] are constructed from the same building blocks (AlO_4 and B_5O_{10} groups), the structures are completely different. In QD-2, each B_5O_{10} group is linked to 12 other B_5O_{10} groups through 4 bridging AlO_4 units, and each AlO_4 unit is also connected to 12 others by 4 bridging B_5O_{10} groups, forming a 3D chiral framework containing intersecting helical channels as mentioned above. In QD-3, however, each B_5O_{10}/AlO_4 unit links 10 others by 4 bridging AlO_4/B_5O_{10} units (Figure S4 in the Supporting Information), forming an interesting 3D framework with zeolitic topology (ABW). The formation of QD-2 and QD-3 suggests that it is possible to construct different framework structures from the same structural building units by using different structure-directing agents. The thermogravimetric analysis of QD-2 (in N_2) shows that it is stable up to 320 °C, and then a sharp weight loss of 27.86% occurred between 320 and 500 °C, corresponding to the removal of the organic templates (Calcd: 27.22%). The structure collapsed and converted to an amorphous phase, suggesting that the framework was not stable to the thermal removal of the template.

In summary, a novel open-framework aluminoborate QD-2 has been synthesized and structurally characterized. The compound is unique in that, among the vast number of synthetic borates and naturally occurring borate materials, it is the first example in which three intersecting helical channels are present. This fascinating structure enriches the borate family, and it is also expected that more novel aluminoborates might be synthesized by using organic templates with different shapes and sizes, as well as transition-metal complexes. Further investigations on the synthesis of microporous aluminoborates are underway.

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Supporting Information Available: Crystal data in CIF format, an IR spectrum, X-ray diffraction data, and a thermogravimetric analysis plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Yu, J.; Xu, R.; Chen, J.; Yue, Y. *J. Mater. Chem.* **1996**, *6*, 465. (b) Yu, J.; Lin, J. H.; Li, G. B.; Yang, T.; Li, H. M.; Liao, F. H.; Loong, C. K.; You, L. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 5607. (c) Yu, J.; Yang, T.; Li, G. B.; Liao, F. H.; Wang, Y. X.; You, L. P.; Lin, J. H. *Chem.—Eur. J.* **2004**, *10*, 3901. (d) Yang, T.; Ju, J.; Li, G. B.; Liao, F. H.; Zou, X. D.; Deng, F.; Chen, L.; Wang, Y. X.; Lin, J. H. *Inorg. Chem.* **2007**, *46*, 4772. (e) Wang, G. M.; Li, J. H.; Li, Z. X.; Huang, H. L.; Xue, S. Y.; Liu, H. L. *Inorg. Chem.* **2008**, *47*, 1270.

(14) Medina, M. E.; Iglesias, M.; Snejko, N.; Gutierrez-Puebla, E.; Monge, M. A. *Chem. Mater.* **2004**, *16*, 594.