Inorg. Chem. **2008**, *47*, 1270−1272

Inorganic Chemistry
Communication

Synthesis and Characterization of QD-3: The First Organically Templated Aluminoborate with 11-, 12-, and 14-Ring Intersecting Channels

Guo-Ming Wang,* Jin-Hua Li, Zeng-Xin Li, Hai-Lan Huang, Shu-Yun Xue, and Hui-Luan Liu

Department of Chemistry, Teachers College of Qingdao University, Qingdao, Shandong 266071, China

Received December 18, 2007

QD-3, a novel aluminoborate $(\mathrm{TETA})_2[\mathrm{Al}_2\mathrm{B}_{10}\,\mathrm{O}_{20}]\cdot 0.25\mathrm{H}_2\mathrm{O}$ (TETA = triethylenetetramine), has been solvothermally synthesized and characterized by IR, thermogravimetric analysis, power X-ray diffraction, elemental analysis, and single-crystal X-ray diffraction. This compound crystallizes in the orthorhombic system, space group $Pna2_1$ (No. 33), $a = 25.9174(2)$ Å, $b = 7.4028(5)$ Å, $c = 17.013(4)$ Å, $V = 3264.2(2)$ Å^3, and $Z = 4$. Its structure consists of AlO_4 tetrahedra and $\mathrm{B}_5\mathrm{O}_{10}$ clusters, which are interconnected and form a three-dimensional framework with large 11-, 12-, and 14-ring channels.

Borate materials have long been a focus of research for their variety of structure types and potential applications in mineralogy, luminescence, and nonlinear optical materials.[1] The chemistry of inorganic borates is widely studied and quite complex. For example, versatile structural motifs in borate minerals, synthetic hydrated and anhydrous borates, were characterized in the past 50 years. This complexity arises, in part, from the flexibility of boron to adopt either trigonal or tetrahedral oxygen coordination. Especially, the BO_3 and BO_4 units may further link together by sharing common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets, and networks.[1b–d,2] Therefore, predicted or controlled synthesis of specific borate species is problematic.

In recent years, attempts to incorporate heteroatoms into a pure borate framework have resulted in some intriguing systems, such as B−O−Al,[3] B−O−P,[4] B−O−V,[5] B−O−Co,[2b] B−O−Zn,[6] B−O−Ga,[7] and B−O−Ge.[8] In the specific field of aluminoborates, it was expected that a series of new materials with novel topologies and useful properties would be realized by the combination of the borate group and aluminum in flexible coordination geometries (tetrahedral, trigonal bipyramidal, square-pyramidal, and octahedral). Unexpectedly, however, only a few aluminoborates and aluminum boron oxide chlorides were known[3] and almost identified as semicrystallites or polycrystallites thus far. This is, in part, due to synthetic difficulties associated with the

---

* To whom correspondence should be addressed. E-mail: gmwang_pub@163.com. Fax: +86-532-85956024.

(1) (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.

(2) (a) Touboul, M.; Penin, N.; Nowogrocki, G. *Solid State Sci.* **2003**, *5*, 1327. (b) Rowsell, J. L. C.; Taylor, N. J.; Nazar, L. F. *J. Am. Chem. Soc.* **2002**, *124*, 6522. (c) Huppertz, H.; von der Eltz, B. *J. Am. Chem. Soc.* **2004**, *24*, 9376. (d) Schubert, D. M.; Visi, M. Z.; Knobler, C. B. *Inorg. Chem.* **2004**, *39*, 2250. (e) Liu, Z. H.; Li, L. Q.; Zhang, W. J. *Inorg. Chem.* **2006**, *45*, 1430. (f) Wang, M. S.; Guo, G. C.; Chen, W. T.; Xu, G.; Zhou, W. W.; Wu, K. J.; Huang, J. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 5607.

(3) (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) Psycharis, V.; Kapoutsis, I. A.; Chryssikos, G. D. *J. Solid State Chem.* **1999**, *142*, 214. (f) He, M.; Chen, X. L.; Lan, Y. C.; Li, H.; Xu, Y. P. *J. Solid State Chem.* **2001**, *156*, 181. (g) He, M.; Chen, X. L.; Gramlich, V.; Baerlocher, C.; Zhou, T.; Hu, B. Q. *J. Solid State Chem.* **2002**, *163*, 369. (h) He, M.; Kienle, L.; Simon, A.; Chen, X. L.; Duppel, V. *J. Solid State Chem.* **2004**, *177*, 3213. (i) Yu, Y.; Wu, Q. S.; Li, R. K. *J. Solid State Chem.* **2006**, *179*, 429.

(4) (a) Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2630. (b) Bontchev, R.; Do, J.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1937. (c) Kniep, R.; Schafer, G.; Engellhardt, H.; Boy, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 3642.

(5) (a) Rijssenbeek, J. T.; Rose, D. J.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1008. (b) Warren, C. J.; Rose, D. J.; Haushalter, R. C.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 1140. (c) Wu, M. M.; Law, T. S.-C.; Sung, H. H.-Y.; Cai, J. W.; Williams, I. D. *Chem. Commun.* **2005**, *14*, 1827.

(6) (a) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 724. (b) Choudhury, A.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Chem. Soc., Dalton Trans.* **2002**, *7*, 1535. (c) Schubert, D. M.; Alam, F.; Visi, M. Z.; Knobler, C. B. *Chem. Mater.* **2003**, *15*, 866. (d) Yu, Z. T.; Xu, J. J.; Jiang, Y. S.; Shi, Z.; Guo, Y.; Wang, D. J.; Chen, J. S. *J. Mater. Chem.* **2003**, *13*, 2227.

(7) (a) Smith, R. W.; Kennard, M. A.; Dudik, M. J. *Mater. Res. Bull.* **1997**, *32*, 649. (b) Barbier, J.; Park, H. *Acta Crystallogr.* **2000**, *C56*, 1057. (c) Liu, Z. H.; Yang, P.; Li, P. *Inorg. Chem.* **2007**, *46*, 2965.

(8) (a) Dadachov, M. S.; Sun, K.; Conradsson, T.; Zou, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 3674. (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) Wang, G. M.; Sun, Y. Q.; Yang, G. Y. *Cryst. Growth Des.* **2005**, *5*, 313. (f) Xiong, D. B.; Chen, H. H.; Li, M. R.; Yang, X. X.; Zhao, J. T. *Inorg. Chem.* **2006**, *45*, 9301.

10.1021/ic702448g CCC: $40.75

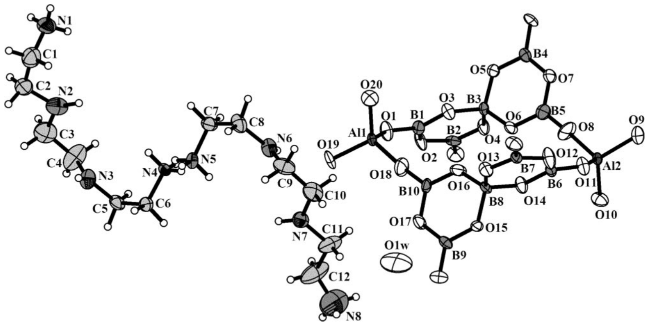

Figure 1. Labeled ORTEP plot of the asymmetric unit of **QD-3** (50% probability ellipsoid).

very low solubility of aluminum oxide and the subsequent problem of preparing a homogeneous starting mixture, which is essential to the formation of desirable crystalline materials. By using hydrothermal methods analogous to those employed for production of zeolites and related crystalline materials, here we report the synthesis and structure of the first organically templated aluminoborate, $(TETA)_2[Al_2B_{10}O_{20}]\cdot 0.25H_2O$ (**QD-3**; TETA = triethylenetetramine). X-ray diffraction (XRD) analysis revealed that the crystal structure of **QD-3** could be described as a three-dimensional open framework constructed by B_5O_{10} clusters and AlO_4 units.

QD-3 was solvothermally synthesized under autogenous pressure. In a typical synthesis, 0.104 g of Al_2O_3 and 0.186 g of H_3BO_3 were dissolved in a mixture solution of 0.54 mL of H_2O and 4.40 mL of pyridine; then, 0.76 mL of TETA was slowly added under constant stirring. The final mixture with a pH of 8.0 and a composition of 1:3:5:54:30 Al_2O_3/H_3BO_3/TETA/pyridine/H_2O was sealed in a Teflon-lined autoclave, heated at 170 °C for 8 days, and then cooled to room temperature. Colorless prismlike crystals were obtained by filtration, washed with distilled water, and dried in air (26% yield based on Al). Anal. Calcd (found) for **QD-3**: C, 18.42 (18.38); H, 5.15 (5.09); N, 14.32 (14.27). IR (KBr pellet, cm^{-1}): 3447, 3288 (H_2O), 1556 (TETA), 1364 (BO_3), 1230 (AlO_4), 1054 (BO_4) cm^{-1} (Figure S1 in the Supporting Information).

XRD analysis[9] reveals that the crystal structure of **QD-3** contains two diprotonated template cations $[H_2TETA]^{2+}$, one $[Al_2B_{10}O_{20}]^{4-}$ anion, and one-quarter lattice–water molecule, as shown in Figure 1. The $[Al_2B_{10}O_{20}]^{4-}$ anion, featuring one large cyclic eight-membered ring with internal dimensions of 8.320(2) × 4.215(5) Å, is composed of two B_5O_{10} groups and two AlO_4 tetrahedra that are connected alternately by common oxygen atoms. Each B_5O_{10} group is made up of one BO_4 tetrahedron and four BO_3 triangles, which are linked to form two planar B_3O_3 rings that are almost perpendicular to each other. Different from the $[B_5O_6(OH)_4]^-$ group commonly found in isolated pentaborates,[2a] each B_5O_{10} unit here is connected to four AlO_4 tetrahedra through four terminal bridging oxygen atoms. Similarly, each AlO_4 tetrahedron is also connected by four B_5O_{10} groups. So, there is no Al−O−Al connection in the structure. The B−O distances are in the range of 1.313(9)−1.416(9) Å (av 1.362 Å) and 1.436(9)−1.490(8) Å (av 1.468 Å), and the O−B−O bond angles span from 116.4(6) to 123.1(6)° and from 107.6(5) to 111.2(5)° for BO_3 and BO_4 units, respectively. The Al−O distances are in the range of 1.706(6)−1.758(5) Å (av 1.727 Å), and the O−Al−O bond angles are in the range of 106.1(2)−115.1(2)°, in agreement with other related mateials.[3]

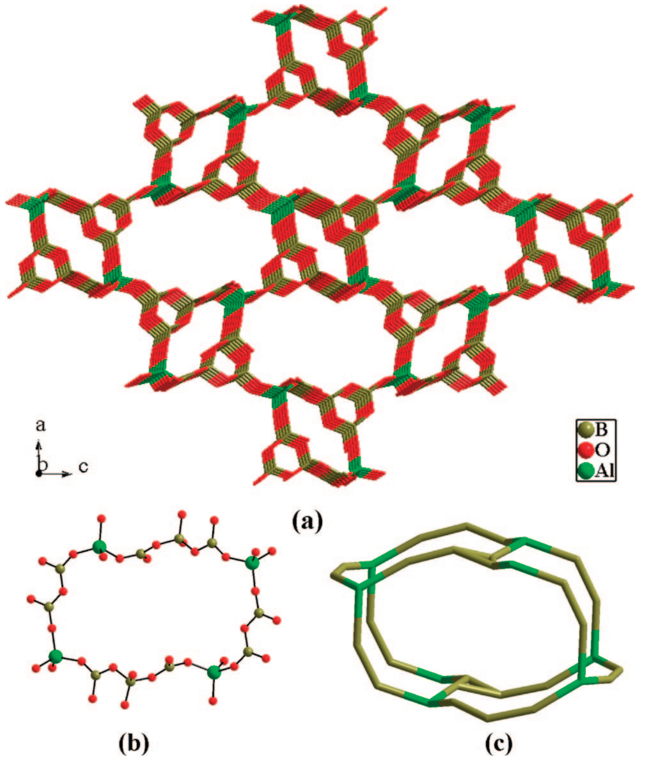

Figure 2. (a) View of a three-dimensional structure of **QD-3** along the *b* axis. (b) Elliptical 14-ring opening. (c) Four windows of the 14-ring opening.

The open framework of **QD-3** is constructed from strictly alternating B_5O_{10} clusters and AlO_4 tetrahedra, which are arranged in parallel 14- and 8-ring channels extending along the crystallographic *b* axis (Figure 2a). The openings of the 14-ring channels are elliptical in shape and delimited by 10 BO_4 and BO_3 units and 4 AlO_4 tetrahedra with an approximate free-pore diameter of 12.8 × 7.5 $Å^2$ (Figure 2b). Each pore wall of the 14-ring channels is built from two 12-ring windows with the $AlO_4-2(BO_3)-AlO_4-2(BO_3)-AlO_4-2(BO_3)-AlO_4-2(BO_3)$ sequence along the [001] direction and two 11-ring windows with the $AlO_4-BO_3-BO_4-BO_3-AlO_4-2(BO_3)-AlO_4-BO_3-BO_4-BO_3$ sequence along the [100] direction (Figure 2c), which results in the formation of an unprecedented three-dimensional intersecting-channel framework. It is worth noting that the odd rings are rare among the known zeolite topologies, with the exception of the 5-ring channel.[8b] **QD-3** represents the first example of aluminoborate materials with the largest odd

---

[9] Crystal data for **QD-3**: orthorhombic, *Pna*2(1), $a = 25.9174(2)$ Å, $b = 7.4028(5)$ Å, $c = 17.013(4)$ Å, $V = 3264.2(2)$ $Å^3$, $Z = 4$, $\rho = 1.592$ $mg\cdot cm^{-3}$, $\lambda = 0.710\,73$ Å, μ(Mo Kα) = 0.184 mm^{-1}, $F(000) = 1624$. A total of 24 055 reflections were collected in the range of 1.57° ≤ θ ≤ 26.00°, of which 3289 were unique reflections and 478 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 R1 = 0.0580 and wR2 = 0.1430 with GOF = 1.036. CCDC 666026 .

11-ring channel that was only present in ICMM6[10] and XA-1.[7c] The charge of the macroanionic $[Al_2B_{10}O_{20}]_n^{4n-}$ framework is balanced by protonation of two terminal NH_2 groups in each TETA molecule. Moreover, there also exist extensive hydrogen bonds between the NH_3^+ groups of TETA molecules that are located in the 14-ring channels and the framework oxygen atoms, with N···O distances in the range of 2.753(6)−3.134(7) Å.

It is of interest to compare the structural features of **QD-3** and other aluminoborate analogues. In PKU-1[3b] and PKU-5,[3c] for example, the aluminum atoms are all octahedrally coordinated to form purely octahedral frameworks by sharing edges; in PKU-6,[3d] the aluminum atoms adopt a relatively rare square-pyramidal geometry in the formation of an extended structure. In the present **QD-3** structure, however, aluminum atoms adopt typically tetrahedral coordination modes and the B_5O_{10} groups also connect with four neighboring AlO_4 units as mentioned above. Thus, the overall framework topology is four-connected and is just like the ABW type of zeolites.[11] To the best of our knowledge, such a zeolite topology was first observed in the B−O−Al system. The thermogravimetric analysis (TGA) of **QD-3** (in N_2) shows a minor weight loss from 30 to ~80 °C corresponding to the removal of the water molecules per formula unit. Then, a gradual weight loss occurs in the range of 240−920 °C, which is assigned to the decomposition of the template TETA (found, 36.76%; calcd, 37.36%). The structure collapsed and converted to an amorphous phase, suggesting that the framework of **QD-3** was not stable to the thermal removal of the template.

In summary, a novel aluminoborate of the composition $(TETA)_2[Al_2B_{10}O_{20}]\cdot 0.25H_2O$ (**QD-3**) has been synthesized under mild hydrothermal conditions. Besides providing the first example of an organically templated aluminoborate, **QD-3** also possesses a novel three-dimensional open framework with large 11-, 12-, and 14-ring intersecting channels. The successful synthesis of **QD-3** not only enriches the existing field of microporous materials but also opens possibilities for synthesizing other novel aluminoborates using different templates, as well as the combination of versatile B−O groups with Al−O units under desirable conditions. Further investigation on this work is in progress.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant 50602028).

Supporting Information Available: IR spectrum, XRD patterns, and a TGA plot. This material is available free of charge via the Internet at http://pubs.acs.org.

IC702448G

---

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

(11) www.iza-online.org.