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$(C_4N_3H_{15})[(BO_2)_2(GeO_2)_4]$: The First Organically Templated 3D Borogermanate Showing 1D 12-Rings, Large Channels, and a Novel Zeolite-type Framework Topology Constructed from Ge_8O_{24} and B_2O_7 Cluster Units

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The first organically templated 3D borogermanate with a novel zeolite-type topology, $(C_4N_3H_{15})[(BO_2)_2(GeO_2)_4]$ **FJ-17**, has been solvothermally synthesized and characterized by IR spectroscopy, powder X-ray diffraction (PXRD), TGA, and single-crystal X-ray diffraction. The compound crystallized in the monoclinic space group *P*2(1)/*c* with $a = 6.967(1)$ Å, $b = 10.500(1)$ Å, $c = 20.501(1)$ Å, $\beta = 90.500(3)°$, $V = 1499.68(8)$ Å^3, and $Z = 4$. The framework topology of this compound is the previously unknown topology with the vertex symbols $3{\cdot}4{\cdot}3{\cdot}9{\cdot}3{\cdot}8_2$ (vertex 1), $3{\cdot}8{\cdot}3{\cdot}4{\cdot}6_2{\cdot}9_2$ (vertex 2), $3{\cdot}8_2{\cdot}4{\cdot}6_2{\cdot}6_2{\cdot}8$ (vertex 3), $4{\cdot}8{\cdot}4{\cdot}8{\cdot}8_3{\cdot}12$ (vertex 4), $4{\cdot}8{\cdot}4{\cdot}8{\cdot}8_2{\cdot}12$ (vertex 5), and $3{\cdot}8{\cdot}4{\cdot}6_2{\cdot}6{\cdot}8_2$ (vertex 6). The structure is constructed from Ge_8O_{24} and B_2O_7 clusters. The Ge_8O_{24} cluster contains eight GeO_4 tetrahedra that share vertices; the B_2O_7 unit is composed of two BO_4 tetrahedra sharing a vertex. The cyclic Ge_8O_{24} clusters connect to each other through vertices to form a 2D layer with 8,12-nets. The adjacent layers are further linked by the dimeric B_2O_7 cluster units, resulting in a 3D framework with 12- and 8-ring channels along the *a* and *b* axes, respectively. In addition, there is a unique B_2GeO_9 3-ring in the structure.

The search for large-pore open-framework structures with new topologies has been extremely intensive because of the widespread applications of these materials in catalysts, ion exchangers, and sorbents.[1] The construction of inorganic frameworks with novel topological structures offers great challenges and opportunities in terms of framework-forming elements.[1] Thus far, more than 25 chemical elements have been introduced into frameworks, and many new zeotype topologies have been unearthed.[1a] Since the discovery of 2D borogermanate in 2000,[2a] no systematic investigation across the B−Ge−O system has been carried out.[2b−2e] Because of the flexible coordination geometries for Ge and B atoms and their ability to form Ge−O[1c,1d,3−6] and B−O frameworks[7] under rational conditions as well as their unique 3-ring structures,[6b,7,8] the B−Ge−O system is likely to provide new structures with new topological frameworks. Herein, we report a novel borogermanate of $(C_4N_3H_{15})[(BO_2)_2(GeO_2)_4]$, **FJ-17**, that not only is the first organically templated 3D borogermanate constructed from Ge_8O_{24} and B_2O_7 clusters but also exhibits a distinct zeolite-type framework topology containing new B_2GeO_9 3-rings.

Colorless crystals of **FJ-17** were obtained by the solvothermal reaction of GeO_2, H_3BO_3, pyridine (py), diethylenetriamine (DETA), H_2O, and hydrofluoric acid (HF, 40 wt %) under basic conditions. In a typical synthesis of **FJ-17**, GeO_2 (0.104 g) was added to a stirring colorless solution of pyridine (3.0 mL) and H_2O (1.0 mL) in the presence of DETA (2.0 mL). After a few minutes, H_3BO_3 (0.217 g) and HF (0.1 mL) were added, and the stirring was continued for 4 h. The final mixture with pH = 8.0 was heated in a Teflon-lined stainless steel autoclave at 170 °C for 11 days under autogenous pressure and then cooled to room temperature.

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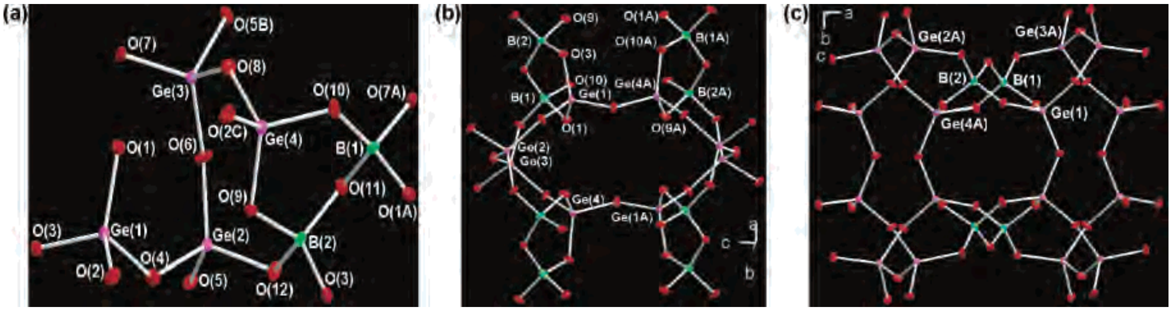

Figure 1. (a) View of the coordination environments of the Ge and B atoms in **FJ-17**. Atoms having A, B, or C in their labels are symmetry-generated. (b,c) Views of the linkages of Ge_8O_{24} and B_2O_7 clusters, showing that each Ge_8O_{24} (B_2O_7) unit is bridged by four B_2O_7 (two Ge_2O_7) groups to other Ge_8O_{24} (B_2O_7) units.

Pure, colorless, prism-like crystals of **FJ-17** were obtained by filtration; washed with water, alcohol, and acetone; and dried in air (51.2% yield based on Ge). It is noteworthy that the HF used in the synthetic process not only adjusts the pH of reaction system but also apparently plays a key role in the formation of **FJ-17** as attempts to make **FJ-17** without HF 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, Supporting Information). The elemental analysis is consistent with the stoichiometry. Anal. Calcd: C, 7.89; H, 2.48; N, 6.90%. Found: C, 7.85; H, 2.08; N, 6.76%. IR (KBr pellet): 825 cm^{-1} (GeO_4), 1027 cm^{-1} (BO_4), 1514 and 1603 cm^{-1} (DETA), 3265 cm^{-1} (H_2O) (Figure S2).

FJ-17 crystallizes in the monoclinic space group $P2(1)/c$[9] and consists of Ge_8O_{24} and B_2O_7 cluster units. Figure 1 illustrates the coordination environments of the central B and Ge atoms and the connectivity of the Ge_8O_{24} and B_2O_7 clusters. In the structure, all of the Ge and B centers are tetrahedrally bound to four oxygens, and all of the oxygen atoms are μ_2-bridging. Two BO_4 groups share a vertex to form a dimeric B_2O_7 cluster unit and are further connected to Ge(1) and Ge(4) atoms by μ_2-O atoms to form unique 3-rings containing one GeO_4 and two BO_4 tetrahadra (Figures 1a,b and S3). The B−O distances vary from 1.460(6) to 1.511(5) Å. The O−B−O angles are between 106.3(3)° and 111.7(3)°. Eight GeO_4 tetrahedra share vertices to give a cyclic Ge_8O_{24} cluster in which the Ge−O distances range from 1.726(3) to 1.762(3) Å and the O−Ge−O bond angles are 99.2(1)−114.9 (1)°. The Ge−O−Ge, B−O−Ge, and B−O−B angles observed in **FJ-17** are ca. 135°, 117°, and 122°, respectively, and are smaller than those of in porous silicates for Si−O−Si (ca. 145°). Each Ge_8O_{24} cluster is connected to two adjacent clusters through four bridging B_2O_7 clusters (Figure 1b), and each B_2O_7 cluster bridges adjacent Ge_8O_{24} clusters (Figure 1c). Furthermore, the cyclic Ge_8O_{24} clusters are connected to four adjacent Ge_8O_{24} clusters through four μ_2-O(5) atoms, resulting in a 2D $\{Ge_8O_{24}\}_n$ layer containing 8,12-nets (Figure S4). The alternate connectivity between the $\{Ge_8O_{24}\}_n$ layers and the pillared dimeric B_2O_7 clusters through the sharing of μ_2-O atoms with cyclic Ge_8O_{24} clusters gives rise to a 3D macroanionic $[(BO_2)_4(GeO_2)_8]_n^{4n-}$ framework with 12- and 8-ring channels in the *bc* and *ac* planes, respectively (Figures 2, 3, and S5). The widest and narrowest diameters of the 12-ring channels are 12.4 and 6.6 Å, respectively (Figure S6). The charge of the macroanionic $[(BO_2)_4(GeO_2)_8]_n^{4n-}$ framework is balanced by protonation of two terminal NH_2 groups in each DETA molecule. In the structure, there are strong hydrogen bonds between the H atoms of the protonated DETA molecules located in the 12-ring channels and the O atoms from the framework, with N···O distances in the range of 2.762(5)−2.974(5) Å (Table S1). The extensive interactions between the templates and the framework appear to play an important role in stabilizing the structure, because attempts to ion exchange the protonated templates with Na^+ ions resulted in the collapse of the structure and the appearance of an unknown phase.

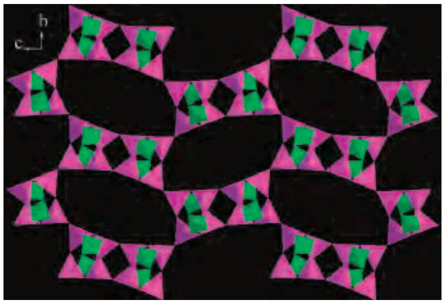

Figure 2. View of the 12-ring channels of **FJ-17** along the *a* axis. GeO_4 and BO_4 are represented by purple and blue tetrahedra, respectively.

Another unique structural feature of **FJ-17** is that it contains 1D helical channels in the [010] direction (Figure 3). Along the [010] direction, the channel seems to have an 8-ring aperture (Figure 3a,b). In fact, there is no closed 8-ring present in the structure. The unclosed −B2−O−B1−O−Ge3−O−Ge2−O−B2−O−B1−O−Ge3−O−Ge2−O− linkage gives rise to two types of helices with opposite chirality presented alternately along the [001] direction (Figures 3a−c and S7). The left- and right-handed helices are coupled to each other though Ge_2O_7 dimeric units containing Ge(1) and

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(9) Structure determination: colorless prism-like crystal with dimensions of 0.30 × 0.20 × 0.15 mm was determined on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα radiation at 298 K in the range of 2.18° ≤ θ ≤ 25.02° using ω scan. The structure was solved by direct methods and refined using SHELXL 97 software. Crystal data for **FJ-17**: monoclinic, $P2(1)/c$ (No.14), $a = 6.967(1)$ Å, $b = 10.500(1$ Å), $c = 20.501(1)$ Å, $\beta = 90.500(3)°$, $V = 1499.68(8)$ Å^3, $Z = 4$, $\mu = 8.012$ mm^{-1}, $\rho_{calcd} = 2.698$ $g\cdot cm^{-3}$, GOF = 1.067, R1 (wR2) = 0.0276 (0.0730). 7082 reflections measured, 2641 unique (R_{int} =0.0394). The C3 atom statistically occupies two positions with an occupancies of 0.3 and 0.7. All the non-hydrogen atoms were refined anisotropycally.

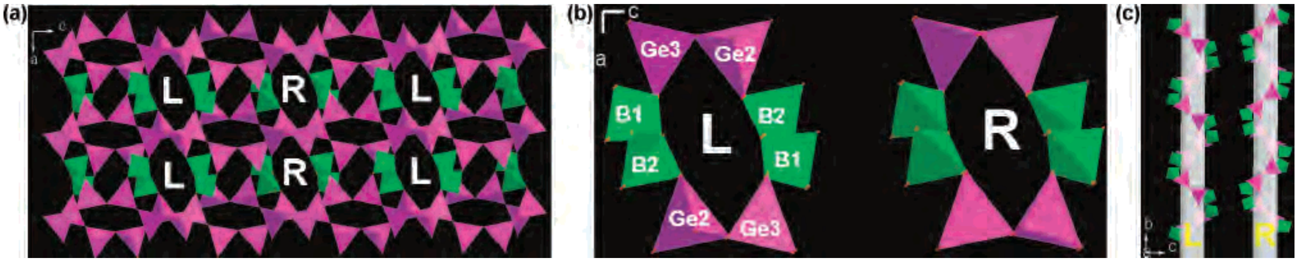

Figure 3. (a) View of the 8-ring channels in the structure of **FJ-17** along the *b* axis, showing the formation of the $\{(BO_2)_4(GeO_2)_8\}_n$ framework constructed from $\{Ge_8O_{24}\}_n$ layers and B_2O_7 dimeric cluster units along the *a* axis and alternate the left- and right-handed 8-ring helical channels along the *c* axis. (b) left- and right-handed helical channels with 8-rings along the *b* axis in the structure. (c) Side view of the 8-ring helical channels along the *b* axis in the structure. L and R indicate the left- and right-handed helical channels, respectively. GeO_4 and BO_4 are represented by purple and blue tetrahedra, respectively.

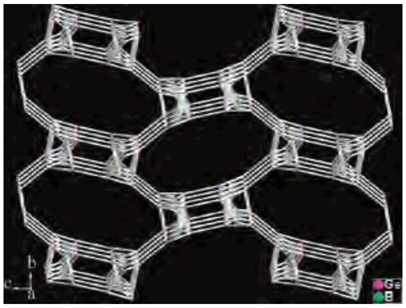

Figure 4. Framework topology of **FJ-17** along the [100] direction.

Ge(4) atoms to form the 3D framework with 8-ring helical channels along the *b* axis, where no water molecules and templates reside (Figure S7).

FJ-17 is the first organically templated borogermanate with 12-ring channels constructed from distinct Ge−O and B−O cluster units, and it has a previously unknown framework topology (Figure 4) having the vertex symbols $3\cdot4\cdot3\cdot9\cdot3\cdot8_2$ (vertex 1), $3\cdot8\cdot3\cdot4\cdot6_2\cdot9_2$ (vertex 2), $3\cdot8_2\cdot4\cdot6_2\cdot6_2\cdot8$ (vertex 3), $4\cdot8\cdot4\cdot8\cdot8_3\cdot12$ (vertex 4), $4\cdot8\cdot4\cdot8\cdot8_2\cdot12$ (vertex 5), and $3\cdot8\cdot4\cdot6_2\cdot6\cdot8_2$ (vertex 6).[10] The framework density is 16 T per 1000 Å^3 (T = tetrahedrally coordinated atoms, namely, Ge and B), which is the similar to those of known open-framework materials.[11]

Preliminary thermogravimetric and differential thermal analysis (TG-DTA) of **FJ-17** under a dry N_2 atmosphere shows that it is stable up to 380 °C and that the weight loss occurs in two steps accompanied by two endothermic energy changes between 380 and 1200 °C. The total loss of ca. 15% weight in the first step from 380 to 600 °C corresponds to the removal of DETA molecule, which results in the collapse of the framework. Above 600 °C, a gradual weight loss of 46% up to 1200 °C is observed and was assigned to the partial removal of the volatile germanium oxide phase.[3b,12]

In summary, we have successfully obtained the first organically templated 3D borogermanate with a previously unknown zeotype topology and large 12-ring channels constructed by two distinct B_2O_7 and Ge_8O_{24} cluster units. The successful synthesis of **FJ-17** shows that it is possible to synthesize other new borogermanates using Ge−O clusters in combination with B−O clusters or borogermanate materials for NLO devices using Ge−O clusters in combination with asymmetric B−O clusters.[2d] As a major research interest and aim, we are now using other B−O clusters and Ge−O clusters as building blocks to make new borogermanates with open frameworks. Further work in this direction is in progress.

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Supporting Information Available: Crystallographic data in CIF format and eight additional plots including IR, TGA, PXRD, etc., data. This material is available free charge via the Internet at http://pubs.acs.org.

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