DOI: 10.1002/chem.200701796

$GeB_4O_9 \cdot H_2en$: An Organically Templated Borogermanate with Large 12-Ring Channels Built by B_4O_9 Polyanions and GeO_4 Units: Host–Guest Symmetry and Charge Matching in Triangular-Tetrahedral Frameworks

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Abstract: A new borogermanate open-framework, **FJ-18**, with intersecting 12-/8-, 9-, and 9-ring channels in multi-dimensions was synthesized by using an organic diamine as structure-directing agent (SDA). X-ray diffraction showed that its structure is constructed by flexible connection of strictly alternate B_4O_9 clusters (with fictitious tetrahedral geometry) and GeO_4 tetrahedra to form a zeotype framework with the CrB_4 topology. The topology and structural relations between **FJ-18** and **FJ-16**, a known borogermanate based on the linkage of B_4O_9 clusters and GeO_4 units, are described in detail. Different guest SDAs can, by means of their shape, size, and charge, directly influence the structure of the host framework, and the origin of these phenomena can be attributed to fundamental parameters such as host–guest symmetry and charge matching through H-bonding interactions, the concept of which has for the first time been extended to tetrahedral-triangular frameworks. This result is a part of our ongoing work aimed at making new large-pore materials constructed from B–O polyanions and Ge–O cluster units.

Keywords: borogermanates · boron · germanium · host–guest systems · porous materials

Introduction

Porous compounds with open frameworks have been intensively investigated because of their widespread applications in catalysis, absorption, and ion exchange.[1–4] Construction of inorganic frameworks with novel topological structures and unique functions offers great challenges and opportunities due to the diversity of available framework-forming elements. Aluminosilicates, aluminophosphates, and their isomorphically substituted forms are still among the largest classes of these materials, which are usually constructed by alternate linkage of various framework polyhedra. So far, more than 25 chemical elements have been introduced into the frameworks of these materials, and many new zeotype topologies have been discovered.[2] However, compared to mathematically possible topologies, the number of topologies for existing zeotype materials is limited because of bonding requirements between framework polyhedra. An alternative strategy for rational design of new porous materials is to replace the nodes of a simple underlying net by polyatomic structure-building units (SBUs) such as clusters, which was termed “decoration” by Férey[5] in the concept of scale chemistry.

Since the discovery of the first open-framework germanates by Xu and Cheng in the early 1990s,[6,7] great efforts have been made in this domain.[8,9] In contrast to aluminosilicate zeolites and microporous phosphates, porous germanates have new structural features. Of fundamental importance is that germanium has flexible coordination geometries and the ability to form 3-rings and Ge–O cluster aggregates. On the basis of different arrangements of these cluster units, a number of germanates with extra-large pores and very low framework density has been made.[9] An notable example is the crystalline germanate SU-M,[9f] with 30-ring extra-large channels and pores extending to the mesoporous range (>20 Å), which is constructed from a unique Ge_{10} cluster and has the lowest framework density of any inorganic material. Another remarkable feature is that most germanate materials consist of pure GeO_2 frameworks, and only a small number of germanate frameworks incorporat-

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ing heteroatoms such as In,[10a,b] Ga,[10c–e] Al,[10e–g] Zr,[10h–j] Nb,[10k,l] Zn,[10m] Sb,[10n] Si,[10o] and B[11] have been documented.

We focus on the synthesis of porous materials constructed from Ge–O clusters[9e,12,13,14] and investigating the effect of introducing heteroatoms on their framework structures.[10b,11c–f] Notably, incorporation of boron leads to a new class of porous borogermanates.[11b–f] Our interest in borogermanates is based on the following considerations: 1) The combination of the flexible coordination behavior of germanium (GeO_4 tetrahedron, GeO_5 square pyramid or trigonal bipyramid, and GeO_6 octahedron) with that of boron (BO_3 triangle and BO_4 tetrahedron) is expected to enhance the structural diversity of porous materials. 2) The potential ability of germanium and boron to form Ge–O clusters and B–O polyanions offers great opportunities for rational design of open frameworks with even larger channels based on the concept of scale chemistry and molecular building blocks. 3) The large fraction of crystalline borates with noncentrosymmetric structures increases the likelihood of producing new borogermanates with efficient nonlinear optical (NLO) effects, such as **FJ-16**.[11d]

We herein report the synthesis, crystal structure, and properties of the new organically templated borogermanate $GeB_4O_9{\cdot}H_2en$ (**FJ-18**, en = ethylenediamine). Its structure is constructed by alternating linkage of B_4O_9 polyanions and GeO_4 units to form a 3D framework with an intersecting channel system in three dimensions, the largest channel of which is encompassed by a 12-membered ring (12-MR). Notably, **FJ-18** is the first open-framework borogermanate containing triangular BO_3 units templated by an organic template, and the first in which host–guest symmetry and charge matching were observed.

Results and Discussion

Structure description: X-ray structure analysis revealed that **FJ-18** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Table 1), and the 3D framework is constructed by alternating linkage of B_4O_9 polyanions and a GeO_4 tetrahedra unit via shared corners (Figure 1 a). The asymmetric unit of **FJ-18** contains one unique Ge center, four unique B centers, and nine unique O atoms (Figure 1 a). The Ge atom is tetrahedrally coordinated with a $Ge{-}O_{av}$ distance of 1.738 Å. Of the four independent B atoms, B1 and B4 are triangularly coordinated with a $B{-}O_{av}$ bond length of 1.364 Å, and B2 and B3 are tetrahedrally coordinated with a $B{-}O_{av}$ bond length of 1.470 Å. The B-O-Ge and B-O-B bond angles of 122.8–130.3 and 112.5–126.6°, respectively, are similar to those observed in reported borogermanates.[11] All oxygen atoms are two-coordinate and bonded to B or Ge centers. The four B–O polyhedra form two approximately perpendicular edge-sharing 3-MR, each of which is constructed from two BO_4 units and one BO_3 unit by sharing oxygen atoms to produce B_4O_9 polyanion with four potential linking oxygen atoms that correspond to four corners of a fictitious $(B_4O_5)O_4$ tetrahedron (Figure 1 b). Such an arrangement of B centers is commonly observed in the isolated $[B_4O_5(OH)_4]^{2-}$ anion,[15] in which four terminal hydroxyl ligands prevent further connection of $[B_4O_5(OH)_4]^{2-}$. In contrast, GeO_4 units link the B_4O_9 anions to form an extended 3D framework in **FJ-18**.

Table 1. Crystal data and structure refinement for **FJ-18**.

empirical formula	$C_2H_{10}B_4GeN_2O_9$
formula weight	321.94
T	293(2) K
crystal system	monoclinic
space group	$P2_1/n$
a	6.9779(6) Å
b	11.6710(11) Å
c	12.0454(10) Å
β	90.133(6)°
V	980.96(15) Å^3
Z	4
ρ_{calcd}	2.140 g cm^{-3}
absorption coefficient	7.595 mm^{-1}
$F(000)$	590
crystal size	0.2 × 0.2 × 0.18 mm
θ for data collection	3.37–27.49°
index ranges	$-9 \leq h \leq 9$, $-15 \leq k \leq 12$, $-15 \leq l \leq 15$
reflections collected/unique	7158/2199 [R(int) = 0.0373]
refinement	full-matrix least-squares on F^2
GOF on F^2	1.237
R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0930$, $wR_2 = 0.1967$
R indices (all data)[a]	$R_1 = 0.0962$, $wR_2 = 0.1983$
largest difference peak/hole	1.422/−1.484 e A^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

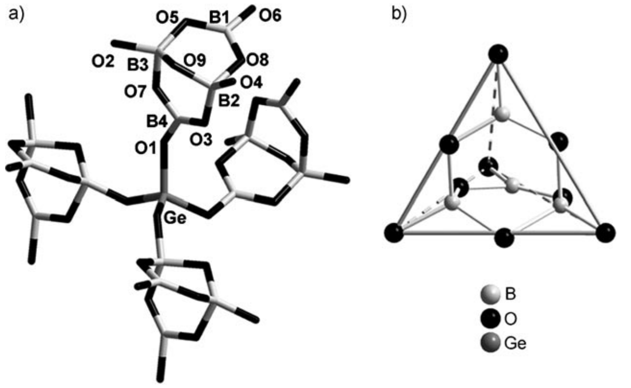

Figure 1. a) Structural fragment of **FJ-18** with unique atoms labeled. b) B_4O_9 polyanion with fictitious tetrahedral geometry.

The connectivity between the fictitious $(B_4O_5)O_4$ tetrahedra and GeO_4 tetrahedra in **FJ-18** is very similar to that in most zeolitic aluminosilicates or microporous aluminophosphates, in which strictly alternate cation–oxygen tetrahedra share corners to produce (4,2)-connected nets (4-coordinate cations 2-coordinate oxygen centers).[1] Four distinct channels with different apertures are observed in the resulting 3D open framework of **FJ-18**. Along the [100] direction, there are two kinds of channels with 12- and 8-MR, arrayed such that each 12-ring channel is surrounded by four 12-ring channels and four 8-ring channels, and vice versa (Figure 2 a). The large 12-ring windows are elliptical and consist

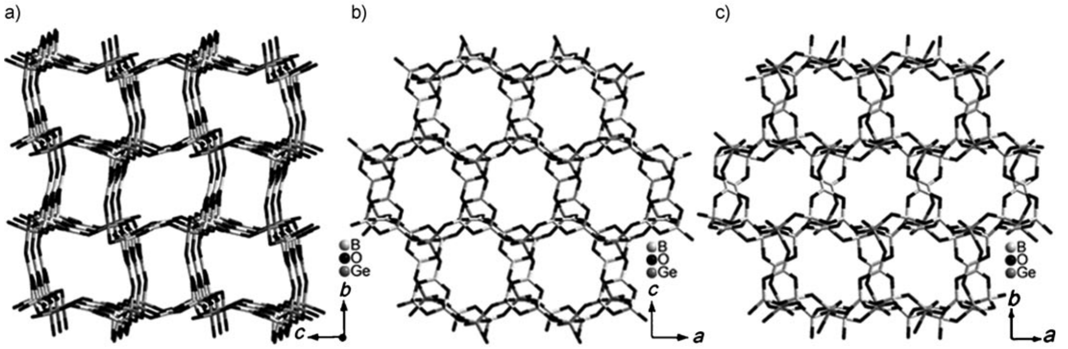

Figure 2. View of the 3D framework in **FJ-18** showing 12- and 8-ring channels along the [100] direction (a) and 9-ring channels along the [010] (b) and [001] (c) directions.

of four GeO_4, four BO_4, and four BO_3 groups. The openings of the 12-rings are built from GeO_4 and BO_4 tetrahedra and BO_3 triangular units and contain two repeating GeO_4-B1O_3-B2O_4-GeO_4-B4O_3-B3O_4 linkages. The free dimensions of the 12-ring channels are 8.5×10.2 Å (see Figure S1a in the Supporting Information). The small 8-ring openings parallel to the 12-ring channels along the [100] direction contain two GeO_4, two BO_4, and four BO_3 groups and are made of two repeating GeO_4-B1O_3-B2O_4(B3O_4)-B4O_3 linkages with free dimensions of 4.6×6.1 Å (see Figure S1a in the Supporting Information).

Two 9-ring channels running along the [010] and [001] directions (Figure 2b and c) intersect with the 12-/8-ring channels along the [100] direction to form four 9-ring windows perpendicular to each 12- and 8-ring channel (Figure 3a). Because the four 9-ring channels run along [010] and [001] directions, the atomic arrangements and sizes of the 9-ring windows are different. They are built from three GeO_4, four BO_4, and two BO_3 groups in GeO_4-B2O_4-B1O_3-GeO_4-B3O_4-B2O_3-GeO_4-B1O_3-B3O_4 and GeO_4-B2O_4-B4O_3-GeO_4-B2O_4-B3O_4-GeO_4-B4O_3-B3O_4 linkages with free dimensions of 5.6×6.7 Å and 6.6×6.8 Å, respectively (see Figures S1c and S1d in the Supporting Information). Thus, the open structure of **FJ-18** contains a 3D intersecting channel system (Figure 3b). Two 9-ring channels running along [010] and [001] directions intersect with each other. Although the 8- and 12-ring channels are parallel to one another, they can indirectly communicate through 9-ring channels. While the 9-ring channels communicate with each other not only directly through 12-ring channels but also indirectly via 8-ring channels. Therefore, all types of channels can directly or indirectly communicate in the structure of **FJ-18**.

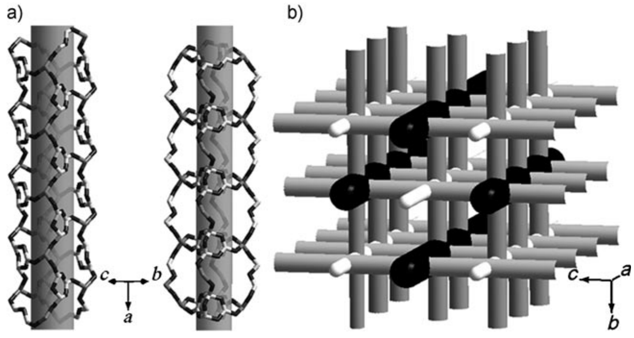

Figure 3. a) 12-Ring (left) and 8-ring (right) channels in **FJ-18** along the [100] direction. Two different 9-ring channels running along the [010] and [001] directions are perpendicular to the 12- and 8-ring channels; they all intersect with each other and with the 12- and 8-ring channels. Color codes: B light gray, Ge dark gray, O black. b) The 3D intersecting channel systems in the structure of **FJ-18**. Color codes: 12- and 8-ring channels along the [100] direction, black and white columns; two 9-ring channels along the [010] and [001] directions, dark gray and light gray columns, respectively.

Structure relations: Interestingly, the structure of **FJ-18** has no Ge-O-Ge linkages; this is a rather unusual structural feature, even for microporous germanates containing framework heteroatoms, in which Ge–O polyhedra usually exist as isolated clusters or chainlike or layered anions, which are further linked by heteroatom polyhedra to form 3D framework structures. Some examples are several structures based on gallium and aluminum germanates[10c–g] with strictly alternate tetrahedral frameworks, but no borogermanate analogues have been found, which is attributed to the fact that the radius of B, in contrast to that of Al and Ga, is much small than that of Ge, and the cation-to-anion radius ratio for both B and Ge is somewhat outside the commonly observed range for tetrahedral oxygen environments.[11a] Thus, polymerization of Ge polyhedra or B polyhedra is commonly observed in borogermanate systems. For example, **FJ-7** is a 3D chiral framework containing helical chains formed by condensation of GeO_4 tetrahedra through common vertices,[11e] **FJ-17/SU-16** is constructed from Ge–O layers pillared by B_2O_7 dimers.[11b,c] In addition, several layered borogermanates $[H_2\text{diamine}][Ge_3B_2O_9(OH)_2]$, where diamine = en, *trans*-1,4-diaminocyclohexane (DACH), or *trans*-1,4-bis(3-aminopropyl)piperazine (BAPPZ), are constructed by alternate connection of the 3-ring of GeO_4 and pairs of isolated BO_4 tetrahedra.[11f] Borogermanate **FJ-16** with the composition $K_2[Ge(B_4O_9)]\cdot 2H_2O$,[11d] which is built by the linkage of GeO_4 tetrahedra and B_4O_9 polyanions to form a 3D framework with 10-, 9-, and 9-ring channels along the [100], [010], and [001] directions, respectively, is the only instance of a borogermanate without Ge-O-Ge linkages. In **FJ-16**, each B_4O_9 unit is linked to 11 others by four bridging

GeO_4 groups. Like the B_4O_9 unit (Figure 4a), each GeO_4 group also links 11 others by four bridging B_4O_9 units (Figure 4b). Such linkage modes differ from that of **FJ-16**, in which each B_4O_9/GeO_4 unit links 12 others by four bridging GeO_4/B_4O_9 groups (Figure 4c and d). In **FJ-18**, one exterior GeO_4/B_4O_9 group is linked by two B_4O_9/GeO_4 units (Figure 4a and b), so that only 11, and not 12, B_4O_9/GeO_4 groups are bonded to the central GeO_4/B_4O_9 unit via four bridging GeO_4/B_4O_9 groups, whereas no such linking modes exist for any exterior GeO_4/B_4O_9 unit in **FJ-16** (Figure 4c and d). Compounds **FJ-18** and **FJ-16** have the same building blocks (B_4O_9 and GeO_4 groups) but different structures: centrosymmetric in **FJ-18** and noncentrosymmetric in **FJ-16**, governed by different structure-directing agents: centrosymmetric $[H_2en]^{2+}$ ions for **FJ-18** and noncentrosymmetric $[K_2(H_2O)_2]^{2+}$ complex cations for **FJ-16**. In addition, a layered borogermanate of formula $K_4[B_8Ge_2O_{17}(OH)_2]$ with Ge_2O_7 and $B_4O_8(OH)$ groups as building blocks was recently reported.[11g] In $K_4[B_8Ge_2O_{17}(OH)_2]$, one GeO_4 group is linked to another GeO_4 unit and three $B_4O_8(OH)$ clusters, whereas one $B_4O_8(OH)$ cluster only links three GeO_4 units. One B atom of $B_4O_8(OH)$ groups is bonded by one OH^- group, which prohibits further connection with GeO_4 groups and thus results in the layered structure of $K_4[B_8Ge_2O_{17}(OH)_2]$. The formation of **FJ-16**, **FJ-18**, and $K_4[B_8Ge_2O_{17}(OH)_2]$ shows that it is possible to make different framework structures from the same or similar structural building units by using different structure-directing agents.

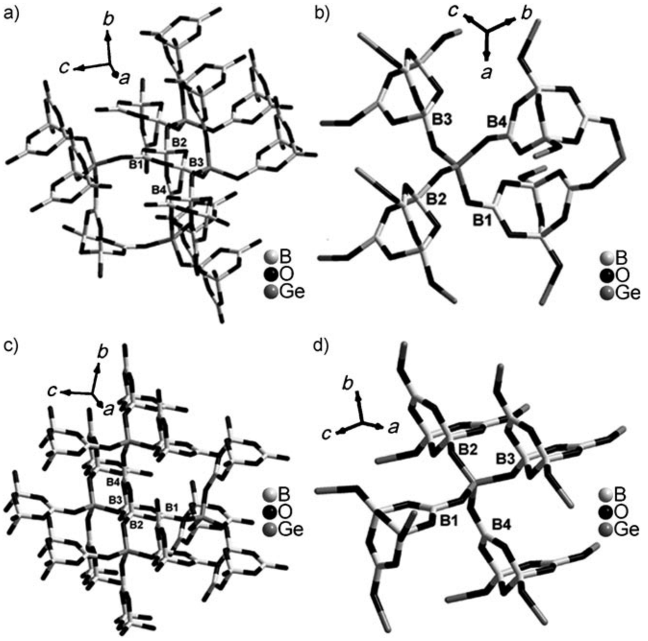

Figure 4. a, b) Topological view of the linkages of B_4O_9 and GeO_4 groups in **FJ-18**. Each B_4O_9/GeO_4 unit is bridged by four GeO_4/B_4O_9 groups to 11 other B_4O_9/GeO_4 units, in contrast to **FJ-16**, in which each B_4O_9/GeO_4 unit is bridged by four GeO_4/B_4O_9 groups to 12 other B_4O_9/GeO_4 units (c, d). The oxygen atoms coordinated to the exterior Ge atoms of GeO_4 tetrahedra are omitted for clarity in b) and d).

From the topological point of view, the 3D framework of **FJ-18** has the same topology as CrB_4[16] if B_4O_9 clusters act as four-connected nodes (Figure 5a). Compounds **FJ-18** and **FJ-16** have some obvious differences in structure: 1) Different topological types: **FJ-18** has CrB_4 topology with vertex symbols $4{\cdot}6_2{\cdot}6{\cdot}6{\cdot}6{\cdot}6$ (Figure 5a), whereas **FJ-16** has a diamond topology (Figure 5b) with vertex symbols $6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2$. 2) Different space groups and sizes and shapes of channels: **FJ-18** crystallizes in space group $P2_1/n$ and has large 12-ring elliptical channels templated by chain-like H_2en^{2+} cations (Figure 6a), whereas **FJ-16** crystallizes in space group *Cc* and has medium double 10-ring interweaving circular helical channels templated by $[K_2(H_2O)_2]^{2+}$ complex cations containing ball-like K^+ ions and water molecules (see below).

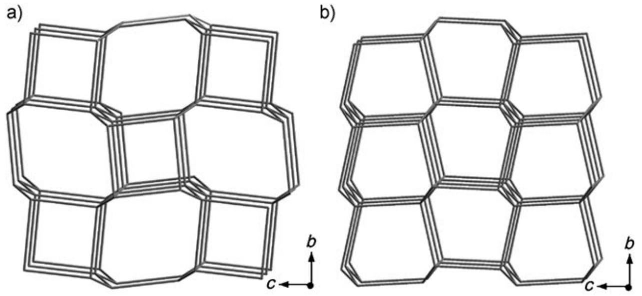

Figure 5. a) Topology of **FJ-18** is the same as that of CrB_4 with vertex symbols $4{\cdot}6_2{\cdot}6{\cdot}6{\cdot}6{\cdot}6$. b) Topology of FJ-16 with vertex symbols $6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2$.

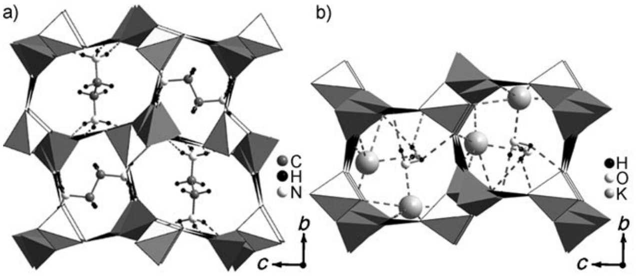

Figure 6. a) The 8- and 12-ring channels of **FJ-18** running along [100] direction shown as polyhedra (BO_3 black, BO_4 gray, GeO_4 white). Two different H_2en cations as templates are located in the 12- and 8-ring channels. b) The $[K_2(H_2O)_2]^{2+}$ complex cation as a larger template, located in the 10-ring channels of **FJ-16** along the [100] direction. The K–O bond lengths are in the range 2.704(8)–3.269(8) Å.

Framework condensation: It appears that the formation of the B_4O_9 and GeO_4 unit is independent of the different SDAs, the function of which rather to direct these building units in the reaction gel/solution to form the resultant framework structures during condensation. In fact, numerous polyborate anions can coexist in relatively concentrated borate solutions, for example, the $[B_5O_6(OH)_4]^-$, $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, and $[B_3O_3(OH)_5]^{2-}$ ions, arranged according to increasing basicity of their associated solutions.[17] This type of process seems to be a plausible mechanism for formation of open-framework materials, but so far in situ experimental measurements to clarify the mechanistic aspects of the synthesis of these materials have not been reported.

Alternatively, from the viewpoint of structure, host–guest symmetry and charge matching through hydrogen-bonding interactions are fundamental parameters for the formation of the different frameworks of **FJ-16** and **FJ-18**. First, host–guest hydrogen-bonding interactions influence the formation of the different channel systems in the two compounds. Note that the anionic frameworks of **FJ-18** and **FJ-16** have uniform formal charges of −2, which necessitate two crystallographically unique diprotonated en molecules situated on the special sites (the center of symmetry) in **FJ-18** or two crystallographically distinct K^+ ions occupying the general sites in **FJ-16** to neutralize the negative charges of the frameworks. In **FJ-18**, the two H_2en cations are located in the 8- and 12-ring channels, respectively, and they form strong hydrogen bonds to the inorganic framework with N−H···O distances in the range of 2.77 and 3.36 Å (Figure 6a). The hydrogen-bonding interactions inside the 12-ring channels shorten the 12-ring and extend the 8-ring along the *b* axis, whereas the hydrogen-bonding interactions inside the 8-ring channels extend the 12-ring and shorten the 8-ring along the *c* axis. Hence, the shapes of both the 12- and 8-ring channels are elliptical, not circular. However, in **FJ-16**, two K^+ cations and two water molecules are incorporated into one channel and form a larger template $[K_2(H_2O)_2]^{2+}$ (a hydrated inorganic cation complex, see Figure S2 in the Supporting Information) with two two-center hydrogen bonds. The electrostatic interactions between the K^+ ions and the framework, as well as the hydrogen-bonding interactions between water and the framework (Figure 6b), result in 10-ring channels with almost circular shape.

Second, the molecular symmetry element of the SDAs coincides with that of the anionic framework. Thus the inorganic framework symmetry is dictated by a point-group symmetry element of the SDAs through the host–guest interactions. In the 10-ring channel of **FJ-16**, the template $[K_2(H_2O)_2]^{2+}$, without any symmetry, interacts with the framework through four two-center hydrogen bonds (Figure 6b, and Figure S2 in the Supporting Information), resulting in a noncentrosymmetric framework (space group: *Cc*), while in **FJ-18**, the H_2en cations as strong SDAs are ordered at the middle of two interconnected channels with elliptical 12- and 8-ring openings (Figure 6a). Note that the H_2en cations possess different orientations in the 12- and 8-ring channels. The guest–framework interaction involved in the structure-directing effect appears to consist of six two-center H-bonds for the 12- and 8-ring channels, respectively (Figure 6a, and Figure S2 in the Supporting Information). It is the centrosymmetric nature of the H_2en cations that leads to the centrosymmetric structure of **FJ-18** (space group: $P2_1/n$). Therefore, symmetry matching between the template and the framework lattice is a very important feature of **FJ-18** and **FJ-16**. In **FJ-18**, the symmetry element of H_2en as guest is only one of the crystallographic symmetries of the inorganic framework. It is further confirmed that the inorganic lattice need not necessarily adopt the full symmetry of the template molecules.[18]

Third, host–guest charge matching is another important characteristic of **FJ-18** and **FJ-16**. In the structure of **FJ-16**, the hydrated dimeric inorganic complex cation $[K_2(H_2O)_2]^{2+}$ is located on the side of the 10-ring channel without any symmetry, whereas in **FJ-18**, two diprotonated en molecules are located in the middle of two different 12- and 8-ring channels with an inversion center. Compared with **FJ-16**, therefore, the charge on the inorganic framework in **FJ-18** is adjusted to the charge of the H_2en template by restructuring or rearranging the framework assembly based on SBUs of B_4O_9 clusters and GeO_4 tetrahedra. Notably, this alteration in **FJ-18** is achieved solely by adjusting the curvature of the framework (based on rearrangement with different orientations of B_4O_9 clusters and GeO_4 tetrahedra) and the charge of the framework surrounding the template by creation of different 12- and 8-ring channels, not by appropriately changing the framework composition.[19] Thus, for **FJ-16** and **FJ-18** with different topological structures and templates, the negative charges on the frameworks are completely determined by framework topology. Such topology-determined charge density is balanced by the inclusion of hydrated inorganic complex cations $[K_2(H_2O)_2]^{2+}$ in **FJ-16** and H_2en^{2+} in **FJ-18**.

IR spectroscopy: The existence of GeO_4, BO_3, BO_4, and organic components is confirmed by the characteristic bands in the FTIR spectrum (see Figure S3 in the Supporting Information). The sharp peaks at 2935 and 2871 cm^{-1} are characteristic of stretching vibrations of CH_2 groups, the peak at 1639–1577 cm^{-1} is characteristic of NH bending, and peaks at 3205, 3112, and 3036 cm^{-1} correspond to NH stretching modes. The bands at about 1386 and 1325 cm^{-1} are attributed to trigonal boron (BO_3), and those at about 1047 and 983 cm^{-1} to tetrahedral boron (BO_4).[20] The peaks at 886 and 842 cm^{-1} can be assigned to asymmetric GeO stretching of the tetrahedral germanium. The bands at 580 cm^{-1} are due to symmetric GeO stretching.[21]

Thermal properties: Thermogravimetric analysis of **FJ-18** under a dry N_2 atmosphere (see Figure S4 in the Supporting Information) showed that **FJ-18** is stable up to 317 °C and then loses weight in two steps between 317 and 1000 °C. The weight loss of 20.8 % in the first step from 362 to 408 °C corresponds to removal of the en template and water (calcd 19.2 %), which results in collapse of the framework according to powder X-ray diffraction (PXRD). Above 635 °C, a gradual weight loss of 24.26 % up to 1000 °C is observed and assigned to partial removal of the volatile germanium oxide phase.[22]

Ion-exchange experiments: Attempts to exchange H_2en with inorganic cations such as NH_4^+, Na^+, and K^+ were unsuccessful, perhaps due to the strong hydrogen-bonding interaction between the H_2en guest cations and the host framework.[11b] However, a sample treated with $AgNO_3$ solution slowly darkens when exposed to light and the framework of **FJ-18** transforms to an unknown germanate, as demonstrated by PXRD, IR spectroscopy, and energy-dispersive spectroscopy (EDS). The IR spectrum of the Ag^+-treated sample showed that all bands of the B−O and H_2en groups had disappeared, and only Ge−O bands were present. An Ag/Ge ratio for the Ag^+-treated sample of 1:1.1 was obtained by EDS.

Conclusion

We have made the novel 3D open-framework borogermanate **FJ-18** with intersecting 12-/8-, 9-, and 9-ring channels in multidimensions by using an organic diamine as template. Compared with **FJ-16**, templated by inorganic cations, both structures have similar SBUs with the same negative framework charge, but their topologies are different because of the distinct shapes and symmetries of the templates. Although the concepts of host–guest symmetry[18] and charge matching[19,23,24] were put forward in tetrahedral phosphate-based zeolite-type materials,[18a] it has been extended to tetrahedral germanate zeolite-type materials, and octahedral vanadates[18b] and germanates,[24] that is, symmetry and charge matching between inorganic host and guest template are not limited to purely tetrahedral phosphate and germanate systems, but also suited to tetrahedral-octahedral vanadium phosphates[18b] and germanates.[24] Now we have further extended this concept to borogermanates with tetrahedral-triangular frameworks for the first time. In addition, for inorganic frameworks with similar SBUs and the same negative charge, such as **FJ-16** and **FJ-18**, the topology is only determined by rearrangement of the SBUs into different orientations that depend on the different shapes and symmetries of the SDAs. Symmetry and shape of the SDAs play a key role in forming and stabilizing the topological frameworks of **FJ-16** and **FJ-18**. We have also shown that B–O polyanions can be useful SBUs to construct borogermanate materials on the basis of flexible connection between B–O polyanions and Ge–O units, which exemplifies the great potential for the discovery of a wide array of open-framework materials, given the wide variety of B–O polyanions and Ge–O units that could be used in this synthetic regime. This result is a part of our ongoing work for new borogermanate materials with ever-increasing pore size and efficient NLO properties by combining B–O polyanions with Ge–O.

Experimental Section

Materials and physical measurements: All chemicals were purchased commercially and used without further purification. Elemental analysis (C, H, N) was performed on an Elemental Vario EL III analyzer. FTIR spectra were obtained from powder samples pelletized with KBr on an ABB Bomen MB 102 series IR spectrophotometer in the range 400–4000 cm^{-1}. Qualitative energy-dispersive spectroscopy (EDS) was performed on a JEOL JSM6700F field-emission scanning electron microscope equipped with an Oxford INCA system. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N_2 atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction patterns (PXRD) were collected with a PANalytical X'Pert Pro diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å).

FJ-18 was synthesized by boric acid flux reaction of GeO_2, water, and en. Typically, H_3BO_3 (1.00 g) and GeO_2 (0.10 g) were mixed in a 30 mL Teflon-lined bomb, and then water (0.40 mL) and en (0.20 mL) were added dropwise to the mixture. The sealed bomb was heated at 180 °C for 6 h and then slowly cooled to room temperature. White, blocklike single crystals were recovered in high yield (85 % based on GeO_2) by filtration, washed with distilled water, and dried in air. Elemental analysis (%) calcd for $C_2H_{10}B_4GeN_2O_9$: C 7.45, H 3.11, N 8.70; found: C 7.66, H 3.18, N 8.74. Good accordance of the experimental PXRD pattern with the simulated pattern indicated phase-purity (Figure 7).

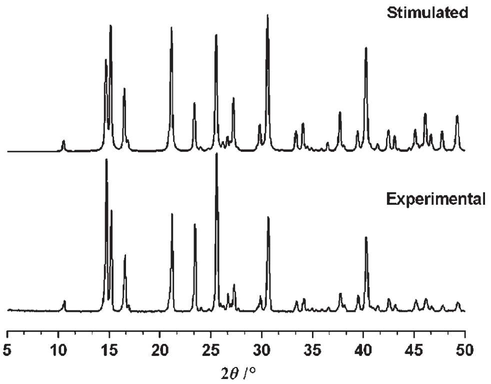

Figure 7. Simulated and experimental powder X-ray diffraction patterns of **FJ-18**.

Crystallographic studies: A single crystal of **FJ-18** with dimensions of 0.20 × 0.20 × 0.18 mm was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed with the multiscan program.[25] The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with the SHELXTL-97 program package.[26] All non-hydrogen atoms (except O1, O2, and O4) were refined anisotropically. Three unique atoms (O1, O2, and O4) statistically occupy two split positions (O1/O1′, O2/O2′, and O4/O4′) and have occupancies of 0.5. Crystal data and structure refinement parameters for **FJ-18** are listed in Table 1. CCDC 627142 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the National Natural Science Fund for Distinguished Young Scholars of China (no. 20725101), the 973 Program (no. 2006CB932904), The NSF of China (no. 20473093) and the NSF of Fujian Province (no. E0510030).

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Received: November 15, 2007