Zeolites

SU-16: A Three-Dimensional Open-Framework Borogermanate with a Novel Zeolite Topology**

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Microporous materials with tetrahedrally coordinated frameworks, such as zeolites, are important from both industrial and academic points of view due to their shape-selective catalytic properties and ion-exchange behaviors.[1,2] Great efforts have been made to synthesize open frameworks with extra-large pores, and thus very low framework densities. Such compounds often consist of secondary building units (SBUs) of small rings formed by three or four tetrahedrally coordinated T atoms (TO_4).[3] Owing to the large T-O-T angles ($\approx$145°), silicon seldom forms 3-rings alone with oxygen, but sometimes together with Zn[4] and Be,[5] and in a few cases with Al[6] and Li.[7] Recently, germanates have been receiving attention since a number of new zeolite topologies were discovered in germanates and silicogermanates (ASV, BEC, IWR, IWW, UOZ).[8] The major advantage of incorporating germanium into zeolite structures is that the T-O-T angles can be much smaller ($\approx$130°), which is needed to form framework structures with 3- and 4-rings. In fact, germanium can form both 3-rings and 4-rings, and has a tendency to form double 4-rings with oxygen.[8–10] Germanium can also adopt other coordination geometries than tetrahedral with oxygen, and several open frameworks with extra-large pores (24-rings) have been reported.[11]

Attempts have also been made to incorporate elements from the third main group (B, Al, Ga) into the silicate zeolite frameworks to adjust the acid strength of zeolite-based catalysts. Although aluminum and gallium have been introduced into germanate zeolite frameworks,[12] no borogermanates with zeolite topologies have been reported so far. We have successfully incorporated boron into germanates and obtained the first two-dimensional templated borogermanates,[13] where both germanium and boron are tetrahedrally coordinated with oxygen. The 3-rings formed by the GeO_4 tetrahedra are also present in the framework. Now we present the first three-dimensional open-framework borogermanate $[NH_3(CH_2)_2NH(CH_2)_2NH_3]\cdot[(GeO_2)_4(BO_2)_2]$ (SU-16). It has a novel zeolite topology with intersecting 12- and 8-ring channels.

Treatment of a mixture of GeO_2, diethylenetriamine (DETA), H_3BO_3, H_2O, and pyridine under mild hydrothermal conditions provides SU-16 as colorless needlelike crystals. The crystal structure analysis shows that there are four unique Ge and two unique B atoms in the asymmetric unit, all of them tetrahedrally coordinated by oxygen. The framework of SU-16 can be described by using a secondary building unit (SBU) consisting of two edge-sharing 3-rings (B_2Ge) connected to two GeO_4 tetrahedra, one on each side of the 3-rings (Figure 1a and b). The SBUs are connected in the [100] direction to form a ladder, with alternating 3-ring (B_2Ge) and 4-ring (BGe_3) pairs (Figure 1c). All the ladders are parallel, running along the [100] direction in the framework. Six such ladders are connected, producing a three-dimensional framework with 12-ring channels along the [100] direction (Figure 1d). The openings of the 12-rings are built by pure GeO_4

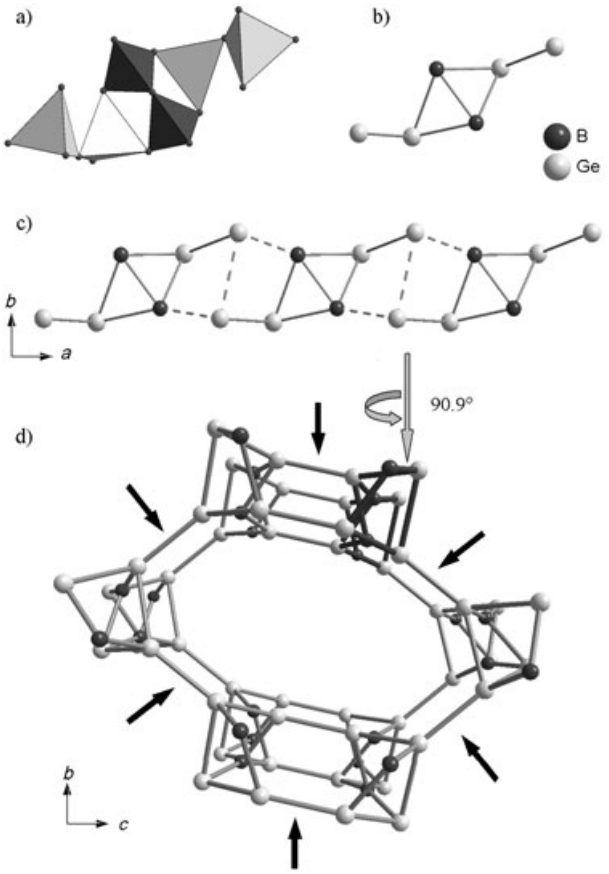

Figure 1. The secondary building unit (SBU) of SU-16 shown a) as tetrahedra (BO_4: dark gray, GeO_4: light gray) and b) in terms of T—T connections. c) The SBUs are connected in the [100] direction to form a ladder. The dashed lines show the T—T connections of different SBUs. d) All the ladders in SU-16 are parallel, running in the [100] directions. Here the structure is shown along these ladders, rotated by 90.9° with respect to the representation in (c); one of the ladders is marked in black. Six such ladders are connected, forming a 12-ring channel. There are six 8-ring windows perpendicular to the 12-ring channel, running in the $\pm$[010], $\pm$[0$\bar{1}$1], and $\pm$[011] directions (indicated by dark arrows). Each 8-ring window connects the 12-channel to the neighboring 12-ring channel.

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tetrahedra, and no BO_4 tetrahedra are involved (Figure 2a). The 12-ring channels are elliptical (with a free diameter of 4.7×9.0 Å), which is very unusual in zeolite framework structures. There are six 8-ring windows perpendicular to each

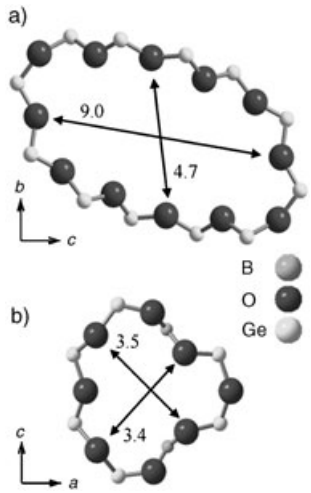

Figure 2. a) The elliptical 12-ring opening with a free diameter of 4.7×9.0 Å and b) the 8-ring opening with a free diameter of 3.4×3.5 Å. The van der Waals diameter of oxygen atoms is assumed to be 2.7 Å.

12-ring channel; each connects the 12-ring channel to a neighboring 12-ring channel (Figure 1d). Although they run along different directions, the atomic arrangements and shape of all the 8-ring windows are the same, built by two BO_4 and six GeO_4 tetrahedra (Figure 2b). The free diameter of the 8-ring openings is 3.4×3.5 Å.

The structure of SU-16 is very open, containing three-dimensional intersecting channel systems. Three 8-ring channels are perpendicular to the 12-ring channels, all intersecting with each other and running along three different directions: [010], [01$\bar{1}$], and [011] (Figure 3).

The B-O-B connection found in SU-16 violates Löwenstein's rule. The Ge–O distances range from 1.72 to 1.76 Å and the B–O distances from 1.45 to 1.51 Å, similar to those reported earlier.[13] The Ge-O-Ge and B-O-B bond angles are 130.0–141.5° and 122.0(3)°, respectively, and thus close to those reported.[13,14] Interestingly, the Ge-O-B angles (115.5–117.8°) are significantly smaller than those in other borogermanates with tetrahedral coordination (121.6–127.8°).[13] The diprotonated DETA cations are located in the 12-ring channels, balancing the charges of the framework (Figure 4). Furthermore, they are strongly hydrogen-bonded to the framework; each DETA cation is hydrogen-bonded to three SBUs (Figure 4). The N–H···O distances are between 2.76 and 3.22 Å.

The borogermanate SU-16 has a novel zeolite framework topology, with coordination sequences different from any existing zeolite frameworks (see the Supporting Information).[15] It is one of the very few zeolite framework structures which contain 3-rings. The two edge-sharing 3-rings of SU-16 have not been observed in other zeolite structures. As a result, two novel configurations of the T atoms are formed (see the

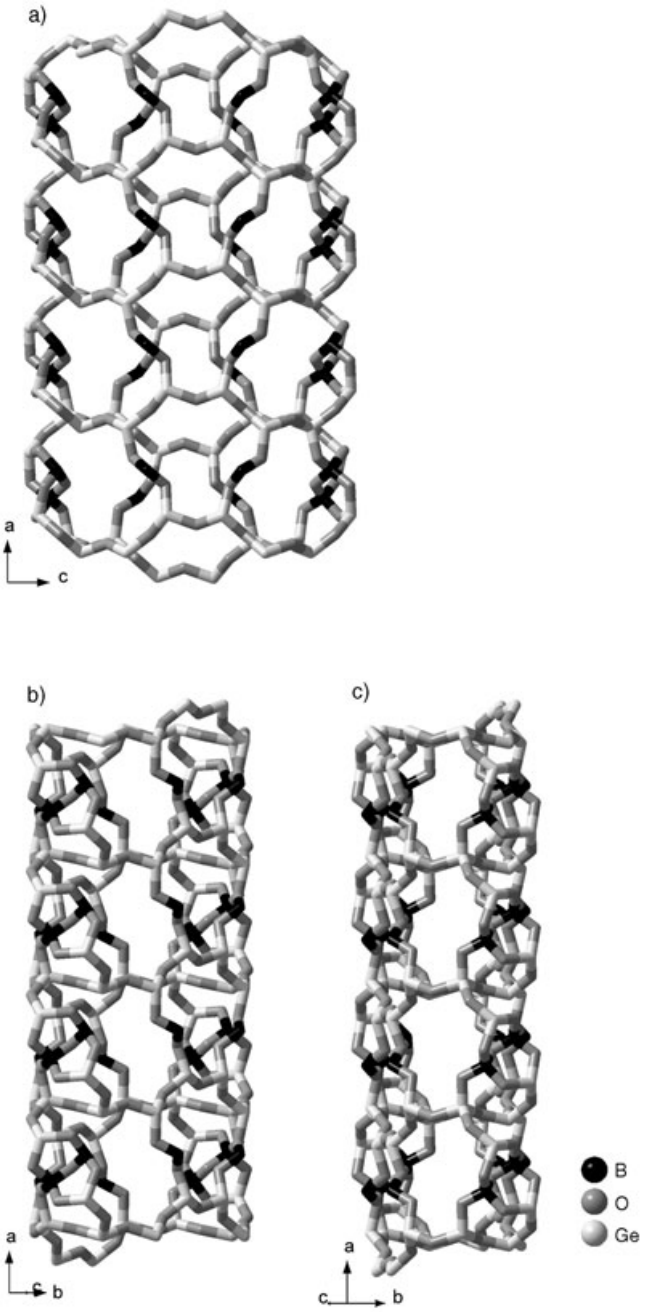

Figure 3. The three-dimensional channel systems in the SU-16 zeolite structure. The 12-ring channel is vertical, along the [100] direction. There are three different 8-ring channels perpendicular to the 12-ring channels, all of them intersecting with each other and with the 12-ring channel. a) The 8-ring channels running along the [010] direction. Here two columns of 8-ring channels (left and right) are shown. b) The 8-ring channels running along the [01$\bar{1}$] direction. c) The 8-ring channels along the [011] direction.

Supporting Information). The framework density of SU-16 is 16.1 T atoms per 1000 Å^3.

The thermogravimetric analysis of SU-16 (in N_2) shows a large weight loss from 370 °C to 465 °C and then a gradual loss from 465 °C to 800 °C. The total weight loss is 16.6%, corresponding to decomposition of the template DETA (calcd 17.2%). The elemental analysis also agrees well with

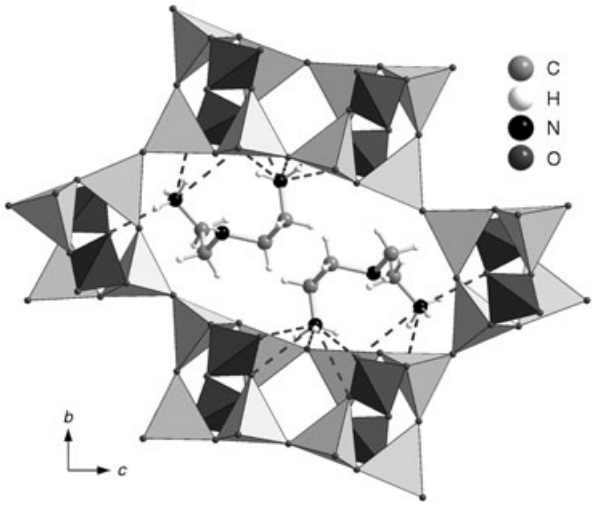

Figure 4. The 12-ring channel of SU-16 running along the [100] direction shown as polyhedra (BO_4: dark gray, GeO_4: light gray). The template cations DETA are located in the 12-ring channels; each is hydrogen bonded to three SBUs of the framework.

that obtained from single crystal X-ray diffraction (found: C 7.9, H 2.5, N 6.8; calcd: C 7.9, H 2.5, N 6.9%). The in situ X-ray powder diffraction in air showed that the crystallinity of SU-16 starts to decrease at 290°C. Attempts to exchange DETA with inorganic cations such as Na^+, K^+, and Ca^{2+} failed, maybe due to the strong interaction resulting from hydrogen bonding between the framework and the DETA cations.

In contrast to the synthesis of most germanates and borogermanates, in which the addition of F^- ions as mineralizers was essential, SU-16 could only be synthesized in the absence of F^-. In the presence of hydrofluoric acid, boron could not be incorporated into the framework. Instead, a layered germanate (SU-17) with the same framework structure as ASU-20[16] was formed.

We have shown for the first time that the two kinds of tetrahedra BO_4 and GeO_4, which differ very much in size (T–O 1.48 and 1.74 Å, respectively), can be connected to form an open framework with three-dimensional intersecting 12- and 8-ring channels. SU-16 is built from a new secondary building unit formed by 3-rings, which has not been reported before. This opens possibilities of designing new zeolite structures with more open frameworks than the existing zeolite structures and novel structure topologies.

Experimental Section

SU-16 was synthesized from a mixture containing GeO_2, H_2O, $[NH_2(CH_2)_2NH(CH_2)_2NH_2]$ (DETA), pyridine, and H_3BO_3 in a molar ratio of 1:20:8:40:2. Typically GeO_2 (0.25 g) was added to H_2O (0.85 mL) under stirring, and then DETA (2.04 mL) was added dropwise to the mixture until the GeO_2 was completely dissolved. Finally, pyridine (7.59 mL) and H_3BO_3 (0.29 g) were added. The reaction mixture ($pH \approx 14$) was stirred for 3 h, sealed in a 38-mL Teflon-lined autoclave and heated at 165°C for eight days. The autoclave was slowly cooled to room temperature, and then the product was filtered, washed with distilled water and acetone, and dried at room temperature. Large colorless needlelike single crystals of SU-16 were obtained in yields up to 70% (based on GeO_2). The X-ray powder diffraction indicated that the product was a single phase and a new structure (see the Supporting Information). The synthesis conditions of SU-16 were not very critical: Crystals of SU-16 could be obtained with molar ratios of GeO_2/DETA ranging from 1:4 to 1:12, GeO_2/H_2O from 1:20 to 1:40, GeO_2/pyridine from 1:20 to 1:60, and GeO_2/H_3BO_3 from 1:1 to 1:2. However, when other polyamines, such as 1,6-diaminohexane, 1,7-diaminoheptane, tetraethylenepentamine (TEPA), and bis(3-aminopropyl)amine were used instead of DETA, no SU-16 was formed.

The in situ X-ray powder diffraction (XRPD) of as-synthesized SU-16 was performed on a Huber Guinier camera 670 equipped with an imaging plate, using synchrotron radiation ($\lambda = 1.2768$ Å) at the Beam line I711, Max-lab, Lund University, Sweden. SU-16 was heated in air from 30°C to 650°C at 20°C/step and an average heating rate of 7°C min^{-1}. Powder diffraction patterns were collected at each step.

Elemental analysis of C, H, and N was performed on a FISON 1108 elemental analyser by Mikro Kemi AB, Uppsala University, Stockholm, Sweden. Thermogravimetric analysis (TGA) was carried out in N_2 gas in the temperature range 20–800°C with a heating rate of 5°C min^{-1}, using a high-resolution TGA 7 thermogravimetric analyzer (PERKIN ELMER).

X-ray diffraction data were collected at 293 K from a single crystal ($0.60 \times 0.10 \times 0.10$ mm^3) on a STOE IPDS diffractometer equipped with an image plate and graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a rotating anode. A total of 9062 reflections, of which 2760 are unique ($R(\text{int}) = 0.0445$), were collected in the region $2.78° < \theta < 26.03°$. The crystal was monoclinic with space group $P2_1/c$ (no. 14) and unit cell dimensions $a = 6.9365(14)$, $b = 10.493(2)$, $c = 20.448(4)$ Å, $\beta = 90.09(3)°$, and $V = 1488.3(5)$ Å^3, $\rho_{calcd} = 2.719$ g cm^{-3}. The structure was solved by the direct-method routine of SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. Numerical absorption correction was applied with a linear absorption coefficient 8.073 mm^{-1}, using X-red and X-shape;[18] $T_{max}/T_{min} = 0.6202/0.1405$. $R_1 = 0.0337$ for 2483 reflections with $F_0 > 2\sigma(F_0)$ and 0.0377 for all 2760 reflections, $wR_2(F^2) = 0.0990$, GOF = 1.188. Max/min residual electron densities are 0.726/−1.182 e Å^{-3}, respectively. The C atoms bonded to N2 and C4 (C3 and C3′) are disordered, with occupancies of 0.675 and 0.325, respectively. The hydrogen atoms were geometrically idealized and allowed to ride on their parent atoms.

CCDC-243002 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. The FTIR spectroscopy data, the TGA curve, calculated and experimental XRPD patterns, the loop configurations and the coordination sequences of SU-16 are presented in the supporting information.

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