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Synthesis and Characterization of an Aluminogermanate SU-46 with a Zeolite Structure

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A new three-dimensional open-framework aluminogermanate (denoted as SU-46) was synthesized solvothermally in a quasi nonaqueous media using diethylenetriamine (DETA) as the structure-directing agent. SU-46 was characterized by in situ X-ray powder diffraction (XRPD), infrared spectroscopy (FTIR), energy dispersive spectroscopy (EDS) on scanning and transmission electron microscopes, elemental analysis, and thermogravimetric analysis (TGA). The structure of SU-46 was determined by single-crystal X-ray diffraction. SU-46 is isostructural to the gallogermanate UCSB-9GaGe, having a new zeolite-framework structure built up by the secondary building unit 4=1. The structure is formed by vertex-sharing AlO_4 and GeO_4 tetrahedra and contains intersecting 8-ring channels in three different directions. The framework density of SU-46 is very low, 13.8 T atom/1000 Å^3. SU-46 is built from layers containing 3- and 9-rings. The building layer is compared to similar layers found in several pure germanates, borogermanates, and the gallogermanate UCSB-9GaGe. The structure refinement shows that aluminum and germanium share the same tetrahedral (T) positions. Both long-range ordering and short-range ordering of Al and Ge are present in SU-46. SU-46 was thermally stable up to 300 °C. Crystal data: $|C_4N_3H_{15}|[Al_2Ge_3O_{10}]$, hexagonal $P\bar{6}2c$ (No. 190), $a = 7.524(1)$ Å, $c = 14.746(3)$ Å, $Z = 2$, $R_1 = 0.0251$ ($F^2 > 2\sigma(F^2)$), and $wR_2 = 0.0647$ (all data).

Introduction

Zeolites with tetrahedrally coordinated frameworks and other microporous materials are very important because of their applications in catalysis, selective sorption, molecule recognition, and ion exchange.[1,2] Over the past decades, large efforts have been made to prepare zeolitic materials with new framework topologies or chemical compositions. Recently, open-framework germanates have attracted considerable interest because several new zeolite topologies have been discovered in germanates[3] and silicogermanates.[4,5] The germanate structures are built up by different building units, such as double 4-rings (D4Rs), and $Ge_7O_{17}F_2$ and $Ge_9O_{22}(OH)_4$ clusters. More recently, we have successfully synthesized a novel germanate SU-M formed by $Ge_{10}O_{24}(OH)_3$ clusters. SU-M contains 30-ring channels and has pores extending to the mesoporous range (>20 Å).[6] The main advantage of incorporating germanium into zeolite structures is that the T–O–T angles can be much smaller for germanates (~ 130°) than for silicates (~145°). The smaller T–O–T angles are favored for framework structures with 3- and 4-rings.

The properties of a porous material depend both on the pore structure and on the chemistry of the framework. Many efforts have also been made to incorporate other elements such as B, Al, Si, and Ga into germanate frameworks. For example, Corma and co-workers have synthesized several silicogermanates and Al-substituted silicogermanates with new zeolite frameworks.[7] We have successfully incorporated boron into germanates and obtained the first three-dimensional open-framework borogermanate SU-16 with a novel zeolite topology SOS.[8]

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A number of aluminogermanate analogues with zeolite framework topologies, such as JBW,[9] NAT,[10] CAN,[11] ABW,[12] MON,[13] ANA,[13] RHO,[14] GIS,[15] and FAU[16] have been reported. These compounds, except for the FAU analogue, were synthesized under hydrothermal conditions and in the presence of alkali metal cations. Stucky and coworkers extended the synthesis methodology developed for phosphate-based zeolite-type structures with high framework charge densities to germanate systems and obtained two aluminogermanates (UCSB-7 and UCSB-15) and one gallogermanate UCSB-9GaGe exhibiting novel zeolite frameworks.[17–20] To our knowledge, no other aluminogermanates with new zeolite topologies have been reported since then.

Here we present a new three-dimensional (3D) open-framework aluminogermanate (denoted as SU-46) synthesized in quasi nonaqueous media. The structure of SU-46 resembles that of the gallogermanate UCSB-9GaGe.[19] It is formed by AlO_4 and GeO_4 tetrahedra and has a zeolite framework built up from layers containing 3- and 9-rings.

Experimental Section

Synthesis. Single crystals of SU-46 were prepared solvothermally in a quasi nonaqueous media from a mixture containing germanium dioxide, aluminum triisopropoxide $Al(i\text{-}PrO)_3$, diethylenetriamine (DETA), pyridine, and hydrofluoric acid (40 wt %) in a molar ratio of $GeO_2/Al(i\text{-}PrO)_3/DETA/pyridine/HF/H_2O = 1:0.8–2.4:12:28–59:96:2.5:4.2$. Except for that present in the hydrofluoric acid, no additional water was added in the mixture. The mixtures were stirred until they were homogeneous, subsequently sealed in 22 mL Teflon lined autoclaves, and heated at 170 °C for 7 days. The autoclaves were left to cool to room temperature. The products, hexagonal colorless plate-like crystals, were washed with deionized water and acetone and then dried at room temperature. The experimental and simulated X-ray powder diffraction (XRPD) patterns of SU-46 (Supporting Information, Figure S1) show that the as-synthesized sample contains no other crystalline phases.

Many synthesis parameters were found to affect the formation of SU-46, as shown in Table 1. First of all, the type of solvents was crucial. SU-46 could only be synthesized using pyridine as a solvent. When pyridine was replaced by ethylene glycol or 2-butanol, only amorphous material was formed. When a small quantity of additional deionized water was introduced into the initial gels with pyridine as the solvent (the molar ratio of water/pyridine was 6:96), a different aluminogermanate, UCSB-7AlGe, was obtained.[20] The molar ratio of Al/Ge was also important. While other parameters were kept unchanged, SU-46 was only obtained within the molar ratio range of Al/Ge between 0.8 and 2.4. Energy dispersive spectroscopy (EDS) showed that the Al/Ge molar ratio of the SU-46 crystals was kept at 2:3, independent of the initial Al/Ge molar ratios of the synthesis batches. However, when the initial Al/Ge molar ratio was below 0.6, only a layered germanate that is isostructural to ASU-20[21] was formed. When the initial Al/Ge molar ratio was higher than 2.6, only amorphous samples were obtained. If the molar ratio of pyridine/DETA was 50:50 instead of 39:96, a mixture of SU-46 and UCSB-7AlGe was obtained. Finally, when other organic amines were used instead of DETA, for example, methylamine (used for the synthesis of gallogermanate UCSB-9GaGe),[19] 1,3-diaminepropane, 2-aminopyridine, *N,N,N′,N′*-tetramethylethylenediamine and triethylenetetraamine, only amorphous samples were formed. Hydrofluoric acid was also found to be essential for the crystallization of SU-46, although it was not incorporated in the final product.

Table 1. Molar Ratios of the Batch Syntheses and the Resulting Products[a]

sample	GeO_2	$Al(i\text{-}PrO)_3$	DETA	pyridine	HF	H_2O	products
1	1.0	0.80–2.4	28–59	96	2.5	4.2	SU-46
2	1.0	1.12	39	96	2.5	4.2	large SU-46 crystals
3	1.0	1.12	39	96	2.5	10.2	UCSB-7AlGe
4	1.0	<0.60	39	96	2.5	4.2	germanate ASU-20
5	1.0	>2.60	39	96	2.5	4.2	amorphous
6	1.0	1.12	50	50	2.5	4.2	SU-46 and UCSB-7AlGe

[a] The reaction was at 170 °C for 7 days.

Characterization. XRPD of as-synthesized SU-46 was performed on a Huber Guinier camera 670 equipped with an imaging plate, using synchrotron radiation ($\lambda = 1.1542$ Å) at the Beam Line I711, Max-laboratory, Lund University, Sweden. SU-46 was heated in air from 20 to 500 °C at 50 °C/step with an average heating rate of 5 °C/min. XRPD patterns were collected at each step. In situ XRPD experiments showed that SU-46 was stable up to 300 °C and turned amorphous at higher temperature (Supporting Information, Figure S2). Thermogravimetric (TG) analysis was carried out in N_2 gas in the temperature range 20–700 °C and with a heating rate of 5 °C/min, using a high-resolution thermogravimetric analyzer (Perkin Elmer TGA 7). The TG curve of SU-46 (Supporting Information, Figure S3) shows an obvious weight loss starting from 160 °C up to 700 °C. The total weight loss was 18.0 wt %, corresponding to the decomposition of the DETA molecules (calcd, 17.6 wt %). There is a large weight loss (5 wt %) between 320 and 390 °C, corresponding to the removal of more DETA molecules and a subsequent structure decomposition of SU-46 (Supporting Information, Figure S3). The morphology of the as-synthesized samples was investigated by scanning electron microscopy (SEM, JEOL JSM 820). The Al/Ge molar ratio was determined by EDS on both SEM and transmission electron microscopy (TEM, JEOL JEM 2000FX), both equipped with EDS analysis (LINK system AN1000). Different points, from different areas of the same crystal, as well as from different crystals, were analyzed. The elemental analysis of C, H, and N was performed with a FISON 1108 elemental analyzer by Mikro Kemi AB, Sweden. IR spectroscopy was carried out on a Bruker FTIR IFS-55 spectrometer in the range

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Table 2. Crystallographic Data and Refinement Details for SU-46

chemical formula	$\|C_4N_3H_{15}\|[Al_2Ge_3O_{10}]$
space group	$P\bar{6}2c$
a (Å)	7.524(1)
c (Å)	14.746(3)
V (Å^3)	722.9(2)
Z	2
crystal dimensions (mm)	0.06 × 0.03 × 0.03
temperature (K)	100(2)
radiation λ (Mo Kα) (Å)	0.71073
ρ_{calcd} (g/cm^3)	2.467
μ (Mo Kα) (mm^{-1})	6.373
min, max θ (°)	4.14, 40.97
total, unique data, R(int)	24646, 1625, 0.0406
observed data [$F^2 > 2\sigma(F^2)$]	1407
N_{ref}, N_{par}	1652, 39
GOF on F^2	1.062
$R(F)^a$	0.0251
$wR(F^2)^b$	0.0647
T_{min}, T_{max}	0.701, 0.832
min, max residual density (e/Å^3)	−1.202, 0.711

[a] $R(F) = \sum \| |F_o| - |F_c| \| / \sum |F_o|$. [b] $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for SU-46[a]

T(1)^b–O(1)	1.7241(16)	T(1)–O(2)–T(1)#3	130.00(12)
T(1)–O(2)	1.7427(18)	T(1)–O(1)–T(2)	137.29(11)
T(1)–O(2)#1	1.7526(18)	T(2)#4–O(3)–T(2)	180.0(0)
T(2)^c–O(1)#2	1.7376(15)		
T(2)–O(3)	1.7047(5)		

[a] Symmetry codes: #1, $-x + y - 1$; $-x + 1$, z; #2, $x - y + 1$, $-y + 2$, $z + 1/2$; #3, $-x + y$, $-x - 1$, $-z - 3/2$; #4, $y + 1$, $x - 1$, $-z - 1$. [b] T(1): Al/Ge = 1:2. [c] T(2): Al/Ge = 1:1.

of 400–4000 cm^{-1} using KBr pellets (Supporting Information, Figure S4). The absorption peak at 3440 cm^{-1} corresponds to the vibrations of N–H bonds.[22] The strong peaks at 1648, 1545, and 1380 cm^{-1} may correspond to the asymmetric and symmetric bond-bending frequencies of C–H and N–H bonds. Absorption peaks due to the asymmetric and symmetric stretching vibrations of Al–O and Ge–O are in the range of 570–900 cm^{-1}.[23]

Structure Determination. Single crystal X-ray diffraction data of SU-46 (0.06 × 0.03 × 0.03 mm^3) were collected at 100 K on an Xcalibur3 diffractometer equipped with a CCD camera using Mo Kα radiation (λ = 0.71073 Å) from an enhanced optic X-ray tube. Data integration and numerical absorption corrections were carried out by the Crysalis software package from Oxford Diffraction with a linear absorption coefficient of 6.373 mm^{-1}. A total of 24 646 reflections, of which 1625 were unique (R(int) = 0.0406), were collected in the region 4.17°< θ < 41.02°. The structure solution and refinement were carried out using the SHELX-97 software package.[24] The framework atoms were refined anisotropically, and the C and N atoms of the guest DETA cations were refined isotropically by a full-matrix least-squares technique. The DETA cations were found to be disordered in the structure and have three different orientations. Hydrogen atoms in the DETA molecules were therefore not added. The crystallographic data and details of data collection and structure refinement are given in Table 2. Selected bond distances and angles are listed in Table 3.

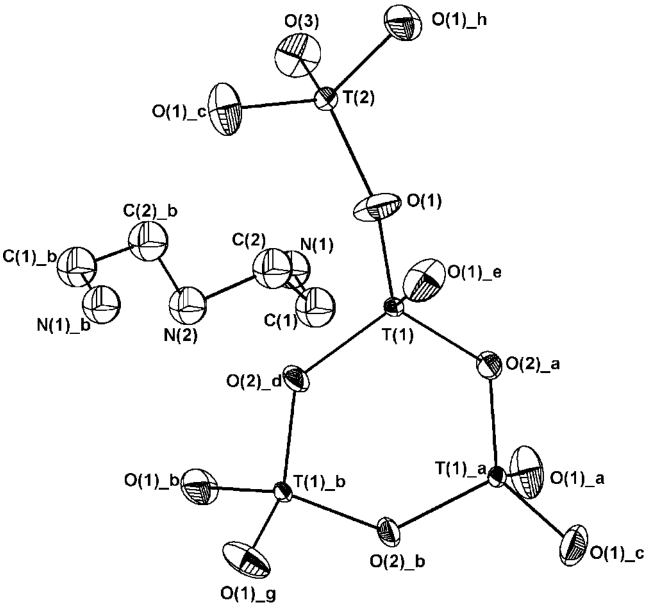

Figure 1. An ORTEP plot of the atoms in SU-46, shown at 50% probability. Symmetry codes: a, y, x, z; b, $x - y$, y, z; c, y, x, $1/2 + z$; d, x, $x - y$, z; e, x, $x - y$, $1/2 + z$; f, $x - y$, x, $1/2 + z$; g, $x - y$, y, $1/2 + z$; h, $x - y$, $-y$, $1/2 + z$.

Results and Discussion

Structure Description. The structure of SU-46 contains two crystallographically distinct T sites (T = Ge, Al) and three crystallographically distinct O atoms (Figure 1). Both T sites are shared by Al and Ge atoms that are tetrahedrally coordinated by four oxygen atoms. The structure of SU-46 is built from the secondary building unit (SBU) 4=1, containing three T(1)O$_4$ and two T(2)O$_4$ tetrahedra. There are two such 4=1 SBUs in each unit cell, located at (0, 0, ±1/4), respectively (Figure 2). The three T(1)O$_4$ tetrahedra in each 4=1 SBU are on the equatorial *ab* plane and connected to the two axial T(2)O$_4$ tetrahedra, one above and one below the equatorial *ab* plane. The 4=1 SBUs are arranged in a hexagonal manner; each 4=1 SBU is connected to six other 4=1 SBUs through their three equatorial T(1)O$_4$ tetrahedra to form a layer (Figures 2a and 3a). Each layer contains 3- and 9-rings. The layers are stacked along the *c*-axis and connected through the T(2)O$_4$ tetrahedra (Figure 2b) to form a 3D framework. Adjacent layers are related to each other by a 2-fold rotation along the *a*(*b*)-axis so that the 3-rings in one layer superimpose with the 9-rings in the adjacent layers (Figure 2a). The final framework of SU-46 contains intersecting 8-ring channels along the [100], [010], and [110] directions, respectively. No 9-ring channels are present in the *c* direction (Figure 2a).

The structure refinement shows that the molar ratios of Al/Ge for the two T positions differ significantly. The Al/Ge molar ratio is approximately 1:2 (refined values 0.312(7): 0.688(7)) for the T(1) site forming the 3-rings and 1:1 for the T(2) site connecting the 3-rings (refined values 0.539(6): 0.461(6)). Taking into account the Lowenstein's rule that Al–O–Al bonds do not exist in zeolites, we can build a structure model of SU-46 consisting of ordering of Al and Ge, as shown in Figure 3. Each 3-ring is formed by one AlO$_4$ tetrahedron and two GeO$_4$ tetrahedra (T(1) sites), resulting in the Al/Ge molar ratio of 1:2. Three AlO$_4$

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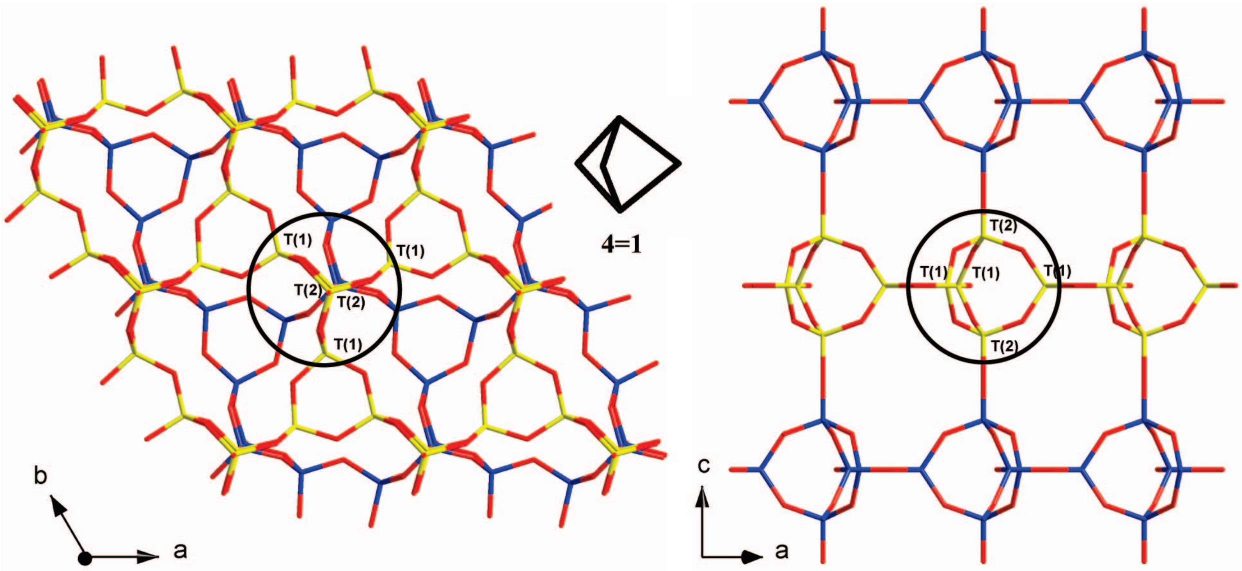

Figure 2. (a) Structure of SU-46 viewed almost down to the *c* axis. Each layer contains 3- and 9-rings. (b) The 8-ring channels of SU-46 viewed along the *b* axis. Adjacent layers are shown with the T-atoms in blue and yellow, respectively. The secondary building unit 4=1 is marked by circles. The DETA molecules are omitted for clarity.

tetrahedra from three different 3-rings are connected by a pair of GeO$_4$ tetrahedra (T(2) sites), one on each side of the 3-rings. Similarly, three GeO$_4$ tetrahedra from three different 3-rings are connected by a pair of AlO$_4$ tetrahedra (Figure 3). The AlO$_4$ and GeO$_4$ tetrahedra at the T(2) sites are ordered along the *c*-axis in a sequence of –Al. . .Al–Ge. . .Ge–Al. . .Al–Ge. . .Ge– (Figure 3b), thus resulting in a strict Al/Ge molar ratio of 1:1 at the T(2) sites. However, the distribution of Al and Ge in the T(1) sites does not show a long-range order but only a local ordering within the 3-rings (Figure 3a); hence, no superstructure is expected in SU-46. The entire Al/Ge molar ratio of SU-46 is 2:3, which is in agreement with the ratio obtained from EDS, as discussed below.

The structure of SU-46 is closely related to those of UCSB-9, UCSB-11, UCSB-46,[25] and three natural zeolites (edingtonite, natrolite, and thomsonite), all built up from the same 4=1 SBU.[26] The building layer of SU-46 resembles those in the 3D gallogermanate UCSB-9GaGe[19,25] and several layered germanates[27,28] and borogermanates,[29] as shown in Figure 4. The differences are that the axial (Al, Ge)O$_4$ tetrahedral pair in SU-46 is replaced by a (Ga, Ge)O$_4$ tetrahedral pair in UCSB-9GaGe, a GeO$_6$ octahedral pair in the germanates[27,28] and a BO$_4$ tetrahedral pair in the borogermanates.[29] In all of the compounds, Ge atoms have participated in forming the 3-rings in the structures. We observe that the orientations of the TO$_4$ tetrahedra in the 3-rings are the same as those for layered germanates and borogermanates, as well as for the 3D gallogermanate UCSB-9GaGe. Despite the large size difference between Ga/Ge and B, the orientations of the (Ga, Ge)O$_4$ tetrahedral pairs in the 3D gallogermanate UCSB-9GaGe are the same as those of the BO$_4$ tetrahedral pairs in the layered borogermanates. Thus the shapes of the 9-rings in both structures are similar (Figure 4b,d). However, as a result of the higher symmetry of the aluminogermanate SU-46, the orientations of the three (Al, Ge)O$_4$ tetrahedra forming the 3-ring are related by a $\bar{6}$ symmetry and different from those in the other three structures (Figure 4). Consequently, the (Al, Ge)O$_4$ tetrahedral pairs connecting the 3-rings in SU-46 are rotated so that the two tetrahedra superimpose to each other and are related by a mirror symmetry perpendicular to the *c*-axis. The 9-rings in SU-46 have different shapes than those in the other three structures. The size of the 9-ring is significantly larger in SU-46 than those in the other structures, with the O–O distances 6.19 × 6.94 Å for SU-46, 5.39 × 5.69 Å for UCSB-9GaGe, 5.01 × 5.32 Å for SU-1, and 5.07 × 5.27 Å for SU-6. It is interesting that elements with different sizes such as B, Al, and Ga can be incorporated into the same layer that further forms both layered compounds and 3D frameworks. Although Al lies between B and Ga in the same group of the periodic table, the aluminogermanate layer in SU-46 differs much more from the borogermanate and gallogermanate layers in SU-6 and UCSB-9GaGe. The nature of the organic templates may play important roles for these.

The structure of SU-46 is analogous to that of UCSB-9GaGe. SU-46 crystallizes in the space group $P\bar{6}2c$ (No. 190) with $a = 7.524(1)$ Å and $c = 14.746(3)$ Å, while UCSB-9GaGe crystallizes in the space group *Pnna* (No. 52) with $a = 12.4987(3)$ Å, $b = 14.3155(2)$ Å, and $c = 7.3751(2)$ Å.[19]

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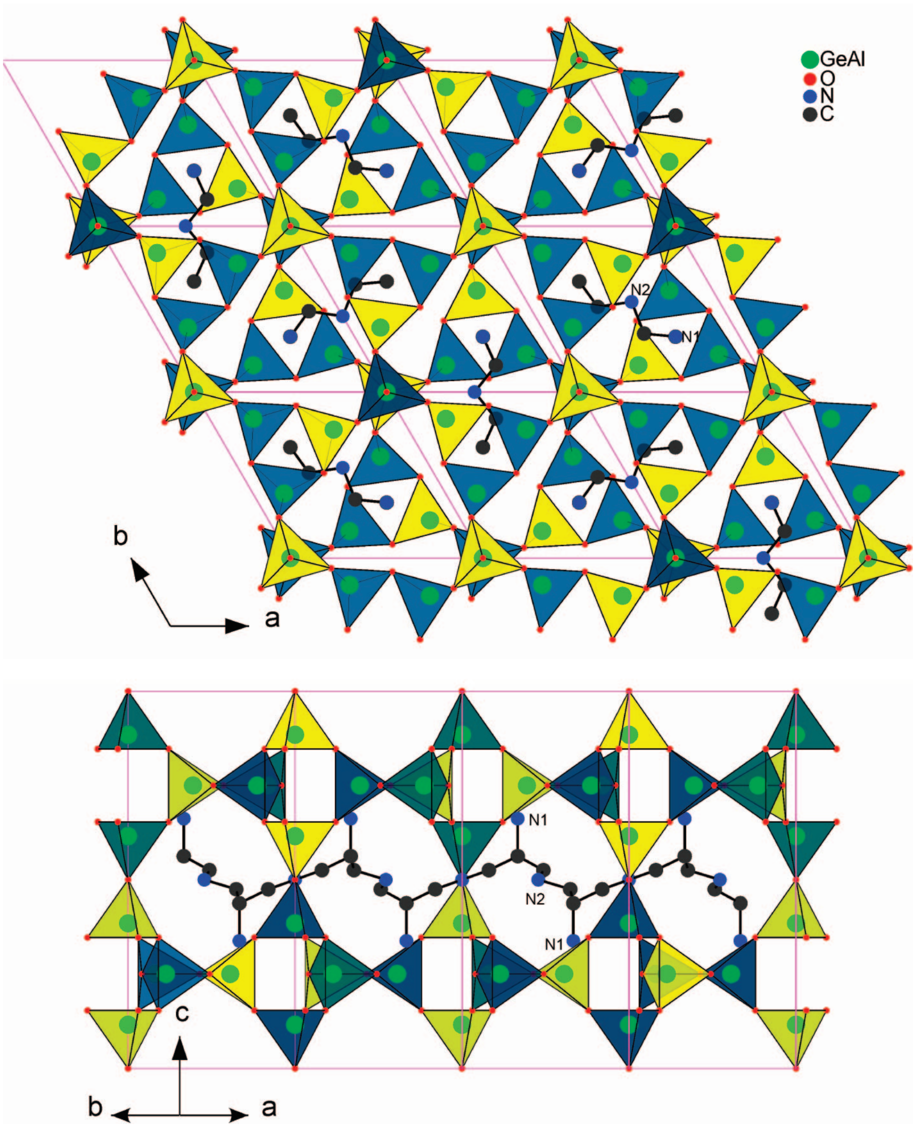

Figure 3. Polyhedral representation of SU-46 showing the possible ordering of Al and Ge in the structure viewed (a) along the *c* axis (3 × 3 × 1 super cell) and (b) along the [110] axis. AlO_4 and GeO_4 tetrahedra are in yellow and blue, respectively. Note that there are three possible orientations of the DETA molecules within the structure, as shown in part a.

Selected bond distances and angles of SU-46 are shown in Table 3. The T–O distances are in the range of 1.7047(5)–1.7526(18) Å, similar to the typical Al–O or Ge–O distances reported in the literature.[30] The T(1)–O–T(1) angles (130.0(1)°) in the 3-rings are significantly smaller than the T(1)–O–T(2) and T(2)–O–T(2) angles (137.3(1)° and 180°, respectively) in the 4- and 8-rings. We have noticed that the T(2)–O(3) bond distance (1.7047(5) Å) is significantly shorter than the other T–O distances (1.7241(16)–1.7526(18) Å), and the 3-fold axis along the *c*-axis restricts the T(2)–O(3)–T(2) angle to be 180°. This indicates that the real O(3) position may be slightly displaced from the 3-fold axis so that the T(2)–O(3) distance increases and the T(2)–O(3)–T(2) angle decreases. This hypothesis is confirmed by the disk-like thermal ellipsoid of O(3), being perpendicular to the T(2)–O(3) bond (Supporting Information, Figure S5). The displacement of the O(3) atom may further cause the displacement of the other three O(1) atoms connected to the same T(2) atom to keep the tetrahedral coordination. This is also confirmed from the relatively large thermal ellipsoid of O(1). On the other hand, the thermal ellipsoid of O(2) is elongated and parallel to the *c*-axis (Supporting Information, Figure S5), indicating that the displacement of the O(2) atoms are mainly perpendicular to the 3-rings.

The average T–O distance in UCSB-9GaGe is 1.77 Å, which is between the ideal values for Ga–O (1.82 Å) and Ge–O (1.74 Å)[19] and larger than those in SU-46 (1.73 Å). The T–O–T angles (121.2 to 145.6°) in UCSB-9GaGe are smaller than those in SU-46. There are three crystallographically distinct T sites in UCSB-9GaGe. Although the entire Ga/Ge molar ratio in UCSB-9GaGe is 2:3, the same as the Al/Ge molar ratio in SU-46, it was not possible to determine the Ga/Ge molar ratio at each T site by the structure refinement from X-ray diffraction data due to the similar atomic scattering factors for Ga^{3+} and Ge^{4+}. A similar problem exists for aluminosilicate zeolites, where it is often not possible to distinguish between Al^{3+} and Si^{4+}.

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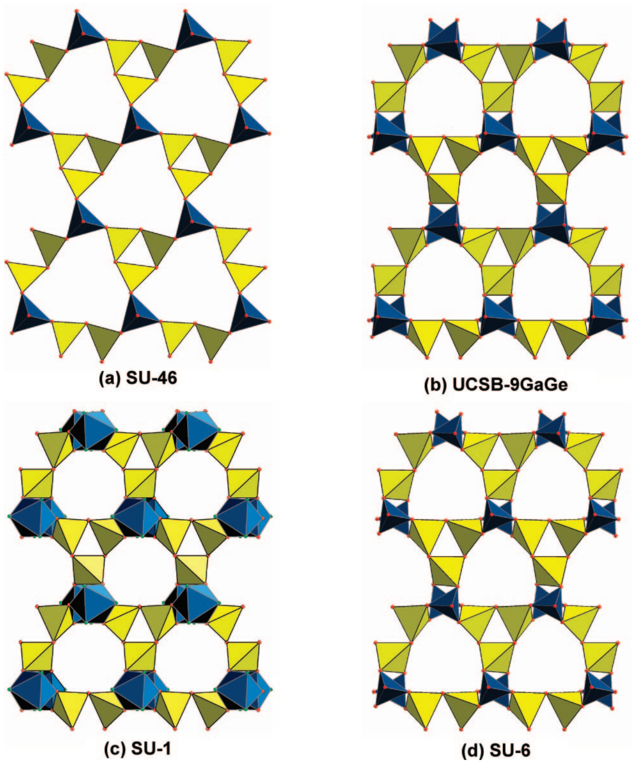

Figure 4. Polyhedral representation of the building layer within 3- and 9-rings in (a) aluminogermanate SU-46, (b) gallogermanateUCSB-9GaGe, (c) germanate $K_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot H_2O$[27] and $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]...0.67H_2O$ (SU-1),[28] and (d) borogermanate $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ (SU-6). The TO_4 tetrahedra forming the 3-rings are in yellow. The blue polyhedra represent (Al, Ge)O_4 in (a), (Ga, Ge)O_4 in (b), GeO_3F_3 in (c), and BO_4 in (d).

In contrast, the X-ray atomic scattering factors of Al^{3+} and Ge^{4+} are sufficiently different to allow a fairly accurate estimation of the Al/Ge molar ratio at each T site through refinement of the occupancy in SU-46. Although SU-46 and UCSB-9GaGe have the same framework structure and the Ga–O distances are even larger than the Al–O distances, the framework density of SU-46 (13.8 T-atom/1000 Å^3) is much lower than that for UCSB-9GaGe (15.2 T-atom/1000 Å^3). A search through the database of zeolite structures[31] gave only 15 zeolite structures with framework densities below 14.0 T-atom/1000 Å^3. This supports that zeolite structures with low framework densities may be built from small rings (3-, 4-rings) as proposed by Brunner and Meier.[32] SU-46 is the first reported aluminogermanate that contains 3-rings. The coordination sequences of T-atoms in SU-46 (Table S4 in Supporting Information) were calculated using the software Systre[33] and show that the structure is a new zeolite framework structure.

There is one diprotonated DETA cation per unit cell in SU-46. The DETA cations compensate for the charge resulted by incorporation of Al in the framework. There are two crystallographically distinct N sites and two crystallographically distinct C sites in SU-46 (Figure 1), three of them, N(1), N(2), and C(2), are partially occupied with occupancies of 1/2, 1/3, and 1/3, respectively. The DETA cations are statistically located at three different positions and with three different orientations (Figure 3 and Supporting Information, Figure S6). The centers of the DETA cations (N(2) sites) are located at the 2-fold rotation axes ((0, 0.456, 1/2), (0.4546, 0, 1/2), and (0.544, 0.544, 1/2), respectively), so one-half of the cation is related to the other half by a 2-fold rotation. The disorder of the DETA cations in SU-46 can be understood from symmetry considerations, because the N(1) sites of the DETA cations are located on the $\bar{6}$ axis.

The DETA cations in SU-46 are located between the layers (Supporting Information, Figure S7a). A pair of N(1) atoms is weakly H-bonded to three framework O(2) atoms (N(1)$\cdots$O(2) = 3.011 Å) from three different 3-rings in the same layer, one above and one below the center of a 9-ring. H-bonds are found not only within the layers but also between the layers. Each N(2) atom lies at the center of an 8-ring and between adjacent layers. It is H-bonded to two framework O(1) atoms from two adjacent layers (N(2)$\cdots$O(1) = 2.941 Å). In UCSB-9GaGe, the methylamine cations are located slightly above and below the center of the 9-rings. Each N atom in UCSB-9GaGe provides four H-bonds to the framework O atoms within the same layers (Supporting Information, Figure S7b), with the N–O distances in the range of 2.907–3.009 Å. No H-bonds exist between adjacent layers. In addition, the 8-rings in SU-46 are more circular (with the O-O distances of 6.77 × 7.20 Å) than those in UCSB-9GaGe (with the O–O distances of 6.17 × 7.27 Å).

Conclusions

We have presented a new aluminogermanate open-framework $|C_4N_3H_{15}|[Al_2Ge_3O_{10}]$ (SU-46) built up from the secondary building unit 4=1. SU-46 was synthesized solvothermally in a quasi nonaqueous medium using the organic amine DETA as the structure directing agent. Its structure is isostructual to that of UCSB-9GaGe, both built from vertex-sharing AlO_4 and GeO_4 tetrahedra, and contains intersecting 8-ring channels in three different directions. The Al/Ge molar ratio at each tetrahedral (T) site in SU-46 could be determined from the structure refinement using single crystal X-ray diffraction data. A model with the distribution of the AlO_4 and GeO_4 tetrahedra in SU-46 has been proposed.

Both SU-46 and UCSB-9GaGe are built from layers containing 3- and 9-rings. Different elements, such as B, Al, and Ga can be incorporated into such layers and form layered compounds as well as 3D frameworks. The orientations of the TO_4 tetrahedra within the layers of SU-46 are different from those in UCSB-9GaGe and other layered germanates and borogermanates. SU-46 is the first reported aluminogermanate that contains 3-rings.

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Supporting Information Available: Experimental and calculated XRPD patterns, in situ XRPD patterns at different temperatures, TG curve, FTIR spectroscopy data, thermal ellipsoids for T (T = Al, Ge) and oxygen atoms, SEM and TEM photographs, and the coordination sequence of SU-46 (PDF) and crystallographic data for SU-46 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-652600 contains the supplementary crystallographic data for SU-46 and can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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