# SU-12: A Silicon-Substituted ASU-16 with Circular 24-Rings and Templated by a Monoamine

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A new silicogermanate, SU-12, $|(CH_3CH_2CH_2NH_3)_3(H_2O)_{2.5}|[(Ge_{6.44}Si_{0.56})O_{14.5}F_2]$, with 24-ring channel systems was synthesized under hydro/solvothermal conditions, and its structure was determined by single-crystal X-ray diffraction. It is the first silicogermanate with extra-large 24-rings templated by a primary monoamine. Crystallographic data: tetragonal, space group $I\bar{4}2m$, unit cell parameters $a = 27.6460(22)$ Å and $c = 17.0885(14)$ Å, $V = 13060.8(17)$ Å$^3$, $Z = 16$, $\rho_{calcd} = 1.797$ g/cm$^3$, R1 = 0.0512 [5471 observed reflections with $I > 2\sigma(I)$], wR2 = 0.1487, $S$ (goodness-of-fit on $F^2$) = 1.08. SU-12 has a structure topology similar to that of the pure germanate ASU-16. However, the symmetry of SU-12 is higher than that of ASU-16, and the 24-rings become more circular than those in ASU-16. The interaction between the templates and framework is compared for ASU-16 and SU-12, and their thermal stabilities are studied. The orthorhombic ASU-16 is thermally less stable than the tetragonal SU-12 and transformed to SU-12 by heating. The ion-exchange property of SU-12 is also studied.

## 1. Introduction

Zeolites and other microporous materials are very important due to their catalytic, ion-exchange, and adsorption properties.[1] While zeolites with a tetrahedral framework remain the most common and well-studied class of microporous materials, synthetic efforts during the past decade have been directed toward preparations of non-silicate materials with large pore structures, unique framework topologies, and novel polyhedral connectivity. There are two well-defined approaches in preparation of open-framework materials with large channel systems and ample internal pore volumes. The first is to utilize various sizes, shapes, and charges of organic cations to direct the structures and pores of inorganic frameworks. The second is to build frameworks from polynuclear anionic clusters, defined as the "cluster condensation" mechanism.[2] The second approach is found to be particularly fruitful in making microporous materials with "record-breaking" pores and channel sizes.

Structures with large pores were mainly found in phosphates: aluminophosphates AlPO-8 (14-ring),[3] VPI-5 (18-ring),[4] and JDF-20 (20-ring),[5] gallophosphates cloverite (20-ring)[6] and NTHU-1 (24-ring),[7] zinc phosphate ND-1 (24-ring),[8] vanadium phosphate (24-ring),[9] and nickel phosphate VSB-5 (24-ring).[10] In other systems such as germanates,[11−21] new compounds with extra-large pores, FDU-4 (24-ring)[22] and ASU-16 (24-ring),[23] were also reported.

The organic templates used for synthesizing open framework compounds with extra-large pores were often di- or multiamines. The templates were usually highly disordered and/or localized near the walls (instead of at the centers) of the extra-large pores. The host frameworks often did not preserve the size and shape of the templates.

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Germanates and silicogermanates have been attracting frequent attention. Interest in using germanium as a framework-forming element is not only because it is the element chemically closest to silicon, but also because of its ability to form polyhedra different from those of silicon: tetrahedra, trigonal bipyramids, and octahedra. Silicogermanates are intriguing from both the structural and industrial application points of view. Partial replacement of tetrahedrally coordinated germanium in germanates with silicon could lead to economically attractive molecular sieves and catalysts. However, very few silicogermanates have been discovered so far.[24,25]

We have synthesized several germanates[14−16] and silicogermanates[26] with novel or known zeolite topologies. We are currently searching for possibilities of synthesizing novel silicogermanates with extra-large pores using primary monoamines as templates since primary monoamines might be removed or exchanged more easily than di- or multiamines.[11] Here, we report a new silicogermanate, $|(CH_3CH_2CH_2NH_3)_3(H_2O)_{2.5}|[(Ge_{6.44}Si_{0.56})O_{14.5}F_2]$ (denoted as SU-12; SU = Stockholm University) with 24-ring channels templated by 1-aminopropane.

## 2. Experimental Section

**2.1. Synthesis.** SU-12, $|(CH_3CH_2CH_2NH_3)_3(H_2O)_{2.5}|[(Ge_{6.44}Si_{0.56})O_{14.5}F_2]$, was prepared under hydro/solvothermal conditions in the presence of the structure-directing agent 1-aminopropane (AP; 98%, Sigma-Aldrich). A typical synthesis procedure is as follows: A 0.13 g sample of $GeO_2$ (99.998%, Sigma-Aldrich) was added to a solution formed by a mixture of 1.0 mL of $H_2O$ and 12.0 mL of 1-aminopropane under continuous stirring. Then 0.20 mL of tetraethyl orthosilicate ($Si(OC_2H_5)_4$; 99.999%, Sigma-Aldrich) was dropped slowly into the solution, and a gel was formed. Finally, 0.2 mL of HF (40 wt %, Fluka) was added to the gel. All reagents were used without further purification. The typical molar ratio was $GeO_2$:$Si(OC_2H_5)_4$:AP:$H_2O$:HF = 1:0.72:116:51:3.7. The final mixture (pH 13) was sealed in a 33 mL Teflon-lined autoclave and heated at 170 °C for 6 days under autogenous pressure. Tetragonal prismatic crystals with typical sizes of $15 \times 15 \times 60$ $\mu m^3$ were obtained. They were washed first with water and then with acetone, and finally dried at 70 °C for 2 h. The maximum yield of SU-12 was 30 wt % based on $GeO_2$.

Different synthesis conditions were applied to increase the yield of SU-12 and the Si:Ge ratio in the framework. The Si:Ge molar ratio was varied during the synthesis, whereas the other conditions were kept the same. SU-12 was only obtained when the ratio of Si to Ge was in the range of 0.72−2.00. The Si:Ge ratio of SU-12 was not very much affected by the Si:Ge ratio of the starting gel for the synthesis, as indicated by electron probe microanalysis. When the Si:Ge ratio was below 0.72, no SU-12 was obtained. When the Si:Ge ratio was kept at 2.00, SU-12 could be obtained in the AP:$H_2O$ molar ratio range from 127:28 to 116:51. The presence of HF acid was also essential for the synthesis of SU-12.

**2.2. Characterizations.** X-ray powder diffraction (XRPD) was performed on a Huber Guinier camera 670 equipped with an imaging plate, using synchrotron radiation ($\lambda$ = 1.3051 Å) at Beamline I711, Max-lab, Lund University, Sweden. The reflection positions were calibrated using Si powder as a standard. SU-12 was manually heated from 60 to 240 °C with 20 °C/step and an average heating rate of 7 °C/min. X-ray powder diffraction data were collected at each step. Electron probe microanalysis (EPMA) was performed on a Cameca electron microprobe SX100 to analyze germanium, silicon, and fluorine contents. Different points were selected, both from different areas of the same crystal and from different crystals. Carbon, nitrogen, and hydrogen contents were determined by CNH analysis (Mikro Kemi AB, Sweden). Thermogravimetric analysis was carried out in air in the temperature range of 20−500 °C with a heating rate of 5 °C/min, using a high-resolution TGA 7 thermogravimetric analyzer (Perkin-Elmer).

FTIR spectroscopy was carried out on a Bruker FTIR IFS-55 spectrometer in the range of 400−4000 $cm^{-1}$ using a KBr pellet. The absorption peak at 3440 $cm^{-1}$ corresponds to the vibrations of O−H bonds. The strong absorption peaks at 1633, 1515, and 1478 $cm^{-1}$ may correspond to the asymmetric and symmetric bond-bending frequencies of the C−H and N−H bonds. Absorption peaks, due to the asymmetric and symmetric stretching vibrations of Si−O and Ge−O, are in the range of 530−1000 $cm^{-1}$.

**2.3. Structure Determination.** Single-crystal X-ray diffraction was performed on two different as-synthesized crystals. One data collection was performed at 170 K, on a STOE IPDS diffractometer, equipped with an imaging plate system, using graphite-monochromatic Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) from a rotating anode generator. Two data sets were collected by using different distances (120 and 70 mm) between the imaging plate and the crystal to collect both low- and high-angle diffraction data. Data integration was carried out by the STOE IPDS software package, and numerical absorption was performed by X-RED and X-SHAPE.[27] Another data collection was performed at 100 K on a Bruker SMART 1000 CCD with synchrotron radiation ($\lambda$ = 0.87934 Å) at Beamline I711, Max-lab, Lund University, Sweden. The intensity data analysis was carried out by the Bruker software package, and the absorption correction was applied by SADABS.[28]

Structure solution and refinement were carried out with the SHELX97 software package, using atomic scattering factors for neutral atoms. All non-hydrogen atom positions were refined anisotropically. All germanium or silicon atoms were coordinated with either oxygen atoms or fluorine atoms. The 5- and 6-coordinated T-atoms were refined as pure germanium since Si is seldom 5- and 6-coordinated to oxygen in microporous materials. All tetrahedrally coordinated T-atoms were refined as mixed occupancy; no significant difference of the Si:Ge ratios was observed for the four tetrahedrally coordinated positions. The average Si:Ge ratio for these four positions was 0.16. Two terminal atoms were assigned as fluorine atoms in the refinement since they gave more reasonable thermal displacement parameters than oxygen. Three unique 1-aminopropanes were found from the difference Fourier maps, corresponding to 1.5 1-aminopropanes in the formula. 1-Aminopropane is a primary monoamine; only the amino group of the molecule was hydrogen bonded to the framework and stable in the refinement. The carbon chains were refined with restraints, by fixing the C−C or N−C distances. Four more peaks were found from the difference Fourier maps, and they were assigned as water oxygen atoms. OW1 was at the special position 4d, and OW4 had an occupancy of 0.25. However, the rather short distance of OW2−OW3 (1.567 Å) may indicate that they belong to the fragment of

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**Table 1. Crystallographic Data and Refinement Details of SU-12**

| | |
|---|---|
| chemical formula | $\|(CH_3CH_2CH_2NH_3)_3(H_2O)_{2.5}\|$-$[(Ge_{6.44}Si_{0.56})O_{14.5}F_2]$ |
| cryst syst | tetragonal |
| space group | $I\bar{4}2m$ (No. 121) |
| unit cell params (Å) | $a = 27.6460(22)$, $c = 17.0885(14)$ |
| $V$ (Å$^3$) | 13060.8(17) |
| Z | 16 |
| $D$(calcd) (g/cm$^3$) | 1.797 |
| radiation, $\lambda$ (Å) | Mo Kα, 0.71073 |
| $F$(000) | 6724 |
| cryst size (mm) | 0.15 × 0.15 × 0.60 |
| temp (K) | 170 |
| $\theta$ min, max (deg) | 2.0, 25.0 |
| dataset | −32, +32; −31, +32; −19, +20 |
| total no. of data, no. of unique data, $R$(int) | 47555, 5977, 0.103 |
| no. of obsd reflns with $I > 2.0\sigma$ | 5471 |
| $N_{ref}$, $N_{par}$ | 5977, 327 |
| R1, wR2, $S$ | 0.0512, 0.1487, 1.08 |
| max, av shift per error | 0.17, 0.00 |
| min, max residual density (e/Å$^3$) | −0.85, +1.58 |

a disordered 1-aminopropane. Hydrogen atoms in the *n*-propylammonium cations were introduced at the ideal positions as riding on their bonded atoms and assigned isotropic thermal parameters 1.2 and 1.5 times those of the bonded C and N atoms, respectively. SU-12 can be formulated as $|(CH_3CH_2CH_2NH_3)_3(H_2O)_{2.5}|[(Ge_{6.44}Si_{0.56})O_{14.5}F_2]$. The Ge, Si, and water contents were obtained from the structure refinement, and the template content was estimated from the CNH analysis. The Ge and Si molar ratios agree with those obtained by electron probe microanalysis (observed Ge:Si:F = 1:0.089(6):0.24(3), calculated Ge:Si:F = 1:0.087:0.31). The observed F content is slightly lower than the calculated one, which may be due to some of the terminal positions being occupied by $OH^-$ groups. The elemental analysis of C, N, and H (wt %) was C, 11.1 (calcd 10.6), N, 4.3 (calcd 4.5), and H, 3.5 (calcd 3.5). The crystallographic data and the results of structure refinement for SU-12 are listed in Table 1. Structure solution from synchrotron radiation gave similar results on both the framework and the templates.

## 3. Results and Discussion

**3.1. Structure Description.** SU-12 is a three-dimensional framework containing intersecting 24-, 12-, 10-, and 8-ring channel systems. The framework is built up from one unique heptameric cluster, $(Ge,Si)_7O_{17}F_2$ (defined as $(Ge,Si)_7$ from here), consisting of one $[GeO_{4/2}O_{1/3}F]$ octahedron, two trigonal bipyramids, $[GeO_{4/2}O_{1/3}]$ and $[GeO_{3/2}O_{1/3}F]$, and four $[(Ge,Si)O_{4/2}]$ tetrahedra (Figure 1). Eight such $(Ge,Si)_7$ clusters are condensed through vertex-sharing to form a 24-ring (Figure 2a). The 24-rings are translated along the *a* and *b* axes and further connected to each other by corner-sharing to form a layer with 8- and 24-rings. The layers are then packed along the *c*-axis through a $\bar{4}$ operation to form a three-dimensional framework. Within the layer, the $(Ge,Si)_7$ clusters are connected by corner-sharing between the (Ge7)-$O_4$ tetrahedra and between the $(Ge2)O_5$ trigonal bipyramid and $(Ge5)O_4$ tetrahedron. The layers are connected through corner-sharing of the $(Ge4)O_4$ and $(Ge6)O_4$ tetrahedra. Two of the seven polyhedra in the $(Ge,Si)_7$ cluster, the $(Ge1)O_5F$ octahedra and the $(Ge3)O_4F$ trigonal bipyramid, are not connected to the other $(Ge,Si)_7$ clusters, and both of them have a terminal $F^-$. The total charge of the $(Ge,Si)_7$ cluster is −3, and the framework charge density is 0.43 electron per (Ge,Si).

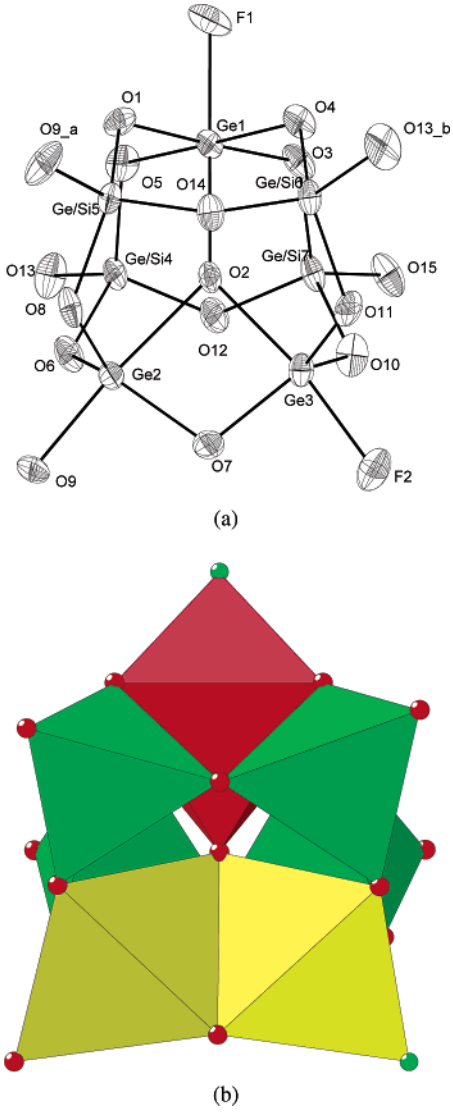


**Figure 1.** $(Ge,Si)_7O_{17}F_2$ cluster in SU-12 shown (a) as a thermal ellipsoid plot and (b) in polyhedral presentation. Symmetry codes: a, $-y, 1-x, z$; b, $y, 1-x, 1-z$. Different polyhedra are in different colors: tetrahedra, green; trigonal bipyramids, yellow; octahedra, red.

SU-12 can be considered as a silicon-substituted form of ASU-16.[22] The structures of both SU-12 and ASU-16 are built up from the same $(Ge,Si)_7$ clusters, and the connections between the clusters are very similar. The 4-fold rotation axis is lost from SU-12 to ASU-16. Consequently, the space group is reduced from $I\bar{4}2m$ for SU-12 to the subgroup $I222$ for ASU-16. The unit cell parameters *a* and *b* are changed from 27.646 to 30.210 and 24.267 Å, respectively. The *c* parameters of SU-12 and ASU-16 differ by only 1% (17.089 and 16.911 Å, respectively). The total volumes of the unit cells are reduced by 5%, from 13060.8 Å$^3$ for SU-12 to 12397.5 Å$^3$ for ASU-16.

Compared with the 24-rings in SU-12, the 24-rings in ASU-16 are squeezed in the [0,1,0] direction (Figure 2). The shapes of the 24-rings are changed from more circular (15.2 × 14.0 Å) for SU-12 to more elliptical (17.2 × 11.1 Å) for ASU-16. The T−O−T angles between the $(Ge,Si)_7$ clusters in the 24-rings for ASU-16 are only slightly larger (146.8° and 132.6°) than those for SU-12 (145.0° and 131.2°), except

**Table 2. Bond-Valence Calculation of Selected Atoms in SU-12**

| | Ge1 | Ge2 | Ge3 | Ge4 | Si4 | Ge5 | Si5 | Ge6 | Si6 | Ge7 | Si7 | sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| F1 | 0.699 | | | | | | | | | | | 0.699 |
| F2 | | | 0.682 | | | | | | | | | 0.682 |
| O1 | 0.669 | | | | | 1.050 | 0.784 | | | | | 1.690 |
| O2 | 0.553 | 0.402 | 0.586 | | | | | | | | | 1.541 |
| O3 | 0.672 | | | | | | | | | 1.014 | 0.769 | 1.647 |
| O4 | 0.715 | | | | | | | 1.139 | 0.850 | | | 1.818 |
| O5 | 0.715 | | | 1.067 | 0.797 | | | | | | | 1.745 |
| O6 | | 0.917 | | 1.019 | 0.761 | | | | | | | 1.901 |
| O7 | | 0.893 | 0.905 | | | | | | | | | 1.798 |
| O8 | | 0.900 | | | | 1.019 | 0.761 | | | | | 1.891 |
| O9 | | 0.839 | | | | 1.170 | 0.874 | | | | | 1.977 |
| O10 | | | 0.940 | | | | | | | 1.039 | 0.790 | 1.939 |
| O11 | | | 1.011 | | | | | 0.960 | 0.717 | | | 1.932 |
| O12 | | | | 1.014 | 0.757 | | | | | 1.025 | 0.778 | 1.965 |
| O13 | | | | 1.090 | 0.814 | | | 1.176 | 0.878 | | | 2.181 |
| O14 | | | | | | 0.997 | 0.745 | 0.971 | 0.725 | | | 1.902 |
| O15 | | | | | | | | | | 1.030 | 0.768 | 1.798 |
| sum | 4.023 | 3.951 | 4.124 | 4.190 | 3.129 | 4.236 | 3.164 | 4.246 | 3.170 | 4.108 | 3.105 | |
| sum(Ge/Si) | 4.023 | 3.951 | 4.124 | 4.046[a] | | 4.120[a] | | 4.075[a] | | 3.949[a] | | |

[a] The bond-valence sum for the mixed Ge/Si at each position in the last row was estimated from the occupancy of Ge and Si determined from the structure refinement by interpolation of the bond-valence sum of pure Ge and Si. Sum $= \sum V_i O_i$ ($V_i$ = bond-valence value, $O_i$ = occupancy for the corresponding atom).

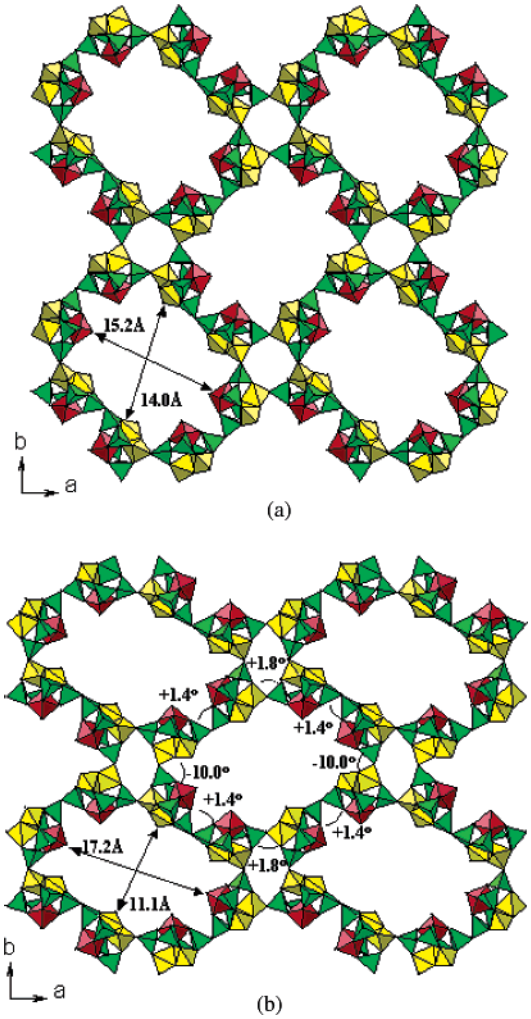


**Figure 2.** Polyhedral presentation of the 24-ring layer viewed along the *c*-axis in (a) SU-12 and (b) ASU-16. Tetrahedra are in green, trigonal bipyramids in yellow, and octahedra in red. Templates and water molecules are removed for clarity. The respective changes (+, increasing; −, decreasing) of the T−O−T angles between the $(Ge,Si)_7$ clusters from SU-12 to ASU-16 are indicated in (b).

for one pair (all the T−O−T angle changes are marked in Figure 2b). This pair of T−O−T angles, which are between one tetrahedron and one trigonal bipyramid, are reduced by 10° from 145.0° in SU-12 to 135.0° in ASU-16. This is due to the deformation of the 24-rings in the [0,1,0] direction from SU-12 to ASU-16. This deformation further affects the connection between the adjacent layers. The angle between two tetrahedra connecting the adjacent layers in SU-12 is significantly larger (147.5°), compared to those (135.4° and 142.0°) in ASU-16.

Within the $(Ge, Si)_7$ clusters all T−O−T angles except those between the tetrahedra are similar for SU-12 and ASU-16. The average T−O−T angles between the tetrahedra are 120.32° for SU-12 and 118.37° and 119.06° (from two different unique clusters) for ASU-16. The slightly larger T−O−T angles between the tetrahedra within the $(Ge, Si)_7$ cluster in SU-12 may be due to the incorporation of Si, since Si prefers larger T−O−T angles than Ge. However, the T−O−T angles between the tetrahedra within the $(Ge,Si)_7$ clusters (about 120°) are much smaller than the typical Si−O−Si angles (145°), but close to the typical Ge−O−Ge angles (130°). This might be the reason no more Si could be incorporated into the framework of SU-12.

Bond-valence calculations show that the bond valances (Table 2) for the mixed (Ge,Si) positions are quite close to 4.00 with a maximum deviation of 0.12 (3%), in good agreement with the structure refinement.

The refined templates were located close to the framework wall, always between the $(Ge, Si)_7$ clusters (Figure 3a). No complete templates were found at the centers of the 8- and 24-ring channels in the [0,0,1] direction and the 12-ring channels in the [1,0,0] direction. Due to the high symmetry of SU-12, most atoms of the *n*-propylammoniums were located on the symmetry elements (2-fold axes, mirror planes). Those that were away from the symmetry elements (C2, C3, and C8 and most of the H-atoms) were located in two positions with half-occupancy each, resulting in disordered *n*-propylammonium cations. Attempts were made to reduce the symmetry of SU-12 in the refinement to see if more templates could be better defined. However, no improvement was observed. Interestingly enough, although

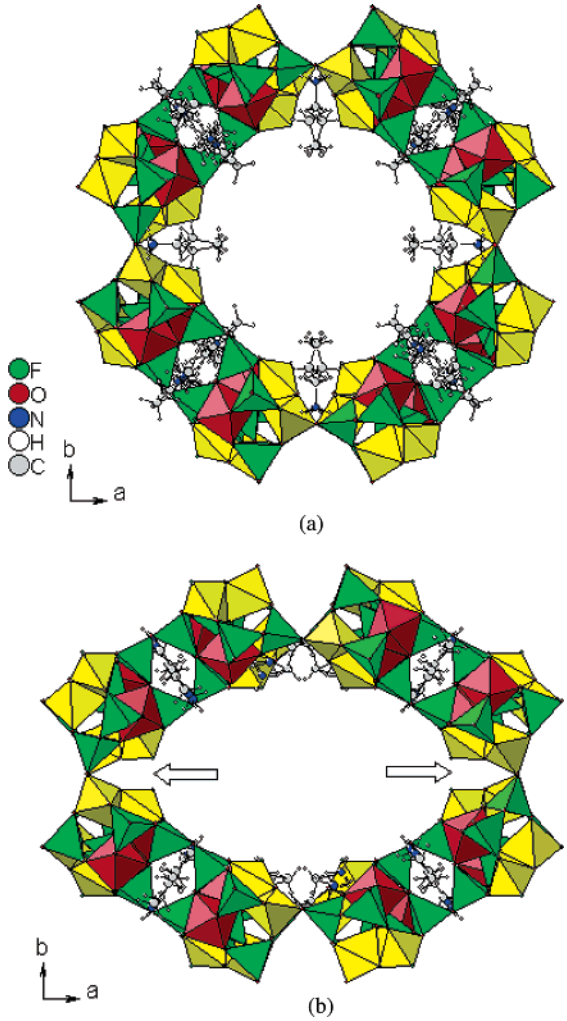


**Figure 3.** Location of the organic templates in the 24-ring channel for (a) SU-12 and (b) ASU-16. The templates (1-aminopropane in SU-12 and 1,4-diaminobutane in ASU-16) are located in similar positions for both structures, except for the positions marked by arrows in ASU-16, where no templates are found. Water molecules are removed for clarity.

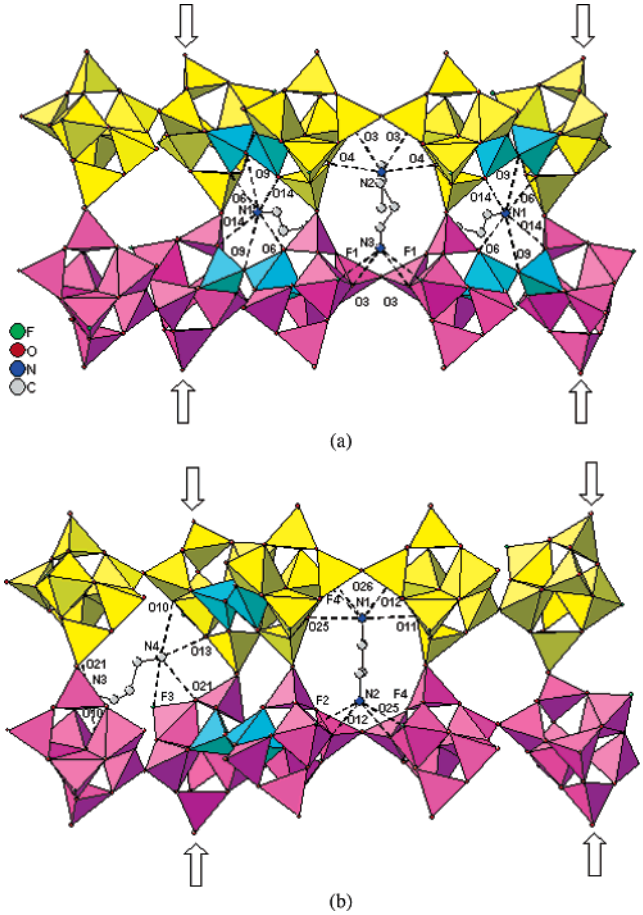


**Figure 4.** Comparison of H-bonding in (a) SU-12 and (b) ASU-16, viewed along the [1,−1,0] direction for SU-12. Polyhedra in the upper layer with 24-rings are drawn in yellow and those in the lower layer in purple. The polyhedral pairs with the largest difference of the T−O−T angels (∼10°) between SU-12 and ASU-16 are drawn in blue. H and water molecules are removed for clarity. The H-bonding in the 10-rings is very similar for SU-12 and ASU-16, but very different in the 8- and 12-rings. The orientations of the two $(Ge,Si)_7$ clusters shared by the 8- and 12-rings are very different in SU-12 and ASU-16 (marked by arrows).

different templates were present in SU-12 and ASU-16, the locations of the templates in SU-12 and ASU-16 were similar, except for the positions (marked by arrows in Figure 3b), where no template was found for ASU-16.

In SU-12, all nitrogen atoms from the three *n*-propylammonium cations (N1, N2, N3) are H-bonded to the framework oxygen or fluorine atoms, with the N−H···O(F) distances between 2.867 and 3.319 Å. Two *n*-propylammonium cations (N2, N3) are located inside the 10-rings (Figure 4a); each is H-bonded simultaneously to two different $(Ge,Si)_7$ clusters within the same layer. N2 is bonded to the upper layer (in yellow) and N3 to the lower layer (in purple). Very similar H-bonding is also found in the corresponding 10-rings in ASU-16 (Figure 4b), although the templates are very different in SU-12 (1-aminopropane) and ASU-16 (1,4-diaminobutane). The only difference is that the H-bonds are from two different templates in SU-12, but the same template in ASU-16. Consequently, the arrangement and orientation of the four $(Ge,Si)_7$ clusters forming the 10-rings are very similar in SU-12 and ASU-16 (Figure 4).

Although the H-bonding inside the 10-rings is very similar in SU-12 and ASU-16, it is rather different in the 8- and 12-rings (Figure 4). The nitrogen atom of the third *n*-propylammonium cation (N1) in SU-12 is located at the center of the 8-rings and H-bonded simultaneously to four different $(Ge,Si)_7$ clusters, two from the upper (in yellow) and two from the lower (in purple) layers (Figure 4a), while no templates are found in the corresponding 8-rings in ASU-16. On the other hand, there is a 1,4-diaminobutane cation inside the 12-ring of ASU-16 (Figure 4b), while no templates are found in the corresponding 12-ring in SU-12. Due to different H-bonding, the orientations of the two $(Ge,Si)_7$ clusters shared by the 8- and 12-rings are very different in SU-12 and ASU-16 (marked by arrows). The T−O−T angles that differ mostly (∼10°) between SU-12 and ASU-16 are from the polyhedra (colored in blue in Figure 4) forming the 8-rings. The presence of the monoamine 1-aminopropane in the small 8-rings in SU-12 probably plays an important role for the higher symmetry and higher stability of SU-12 compared to ASU-16. Due to its larger size, 1,4-diaminobutane could not be present in the 8-rings and instead goes into the 12-rings.

The different hydrogen-bonding schemes in SU-12 and ASU-16, especially the lack of H-bonding in the 8-rings in ASU-16, may cause the framework structure of ASU-16 to be more flexible and easily distorted than SU-12. This can

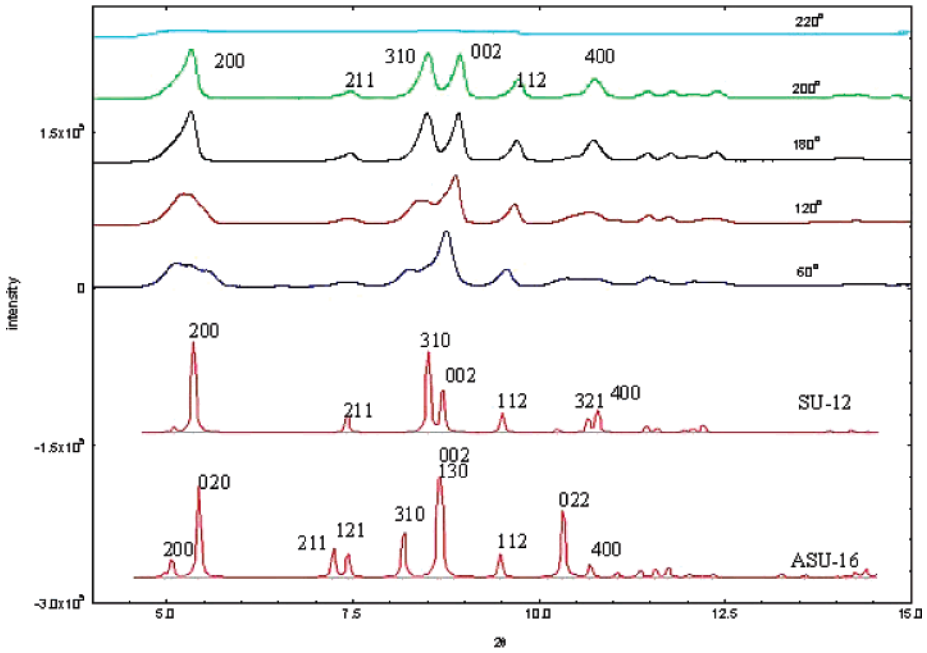


**Figure 5.** In situ XRPD patterns of the as-synthesized mixture of ASU-16 and SU-12 at different temperatures. Calculated XRPD patterns of SU-12 and ASU-16 are inserted for comparison. The XRPD pattern of ASU-16 is calculated from the coordinates given by Plevert et al.,[19] with the modified unit cell parameters $a = 28.75$ Å, $b = 26.90$ Å, and $c = 17.03$ Å.

also be seen in Figure 3 along the 24-ring channels. The lack of templates (thus H-bonding) at the position (marked by arrow) in ASU-16 makes the framework readily distorted in the [0,1,0] direction, and thus lowers the symmetry of the framework. The presence of the *n*-propylammonium cations (thus H-bonding) at the corresponding position prevents the framework from being distorted. This is probably the reason no big changes in unit cell dimensions were observed in SU-12.

The framework of SU-12/ASU-16 could be obtained by using 1-aminopropane (SU-12), 1,4-diaminobutane (ASU-16),[23] and 2-methyl-1,5-pentanediamine (SU-30).[25] These three templates are very different in size, shape, and number of amino groups. Compounds with similar topologies can be synthesized using different amines. This means that the size and shape of the pores are not directly related to the size and shape of the templates. This may be why it is possible to synthesize framework structures with extra-large pores using small amines. During the synthesis, the $(Ge,Si)_7$ clusters may be first formed in the solution/gel, and the organic templates play important roles in directing the condensation of these clusters to form the 3D framework. Finally, these templates interact with the framework through extensive hydrogen bonding to stabilize the framework structure. The pure germanium form of the heptameric cluster was also found in some other germanates.[17,29,30]

The importance of 1-aminopropane in stabilizing the framework structure of SU-12 was determined by ion-exchange experiments on the as-synthesized sample. $NaNO_3$ was used as the main ion-exchange medium. Even at a very low concentration of $NaNO_3$ (0.005 M), crystals of SU-12 dissolved completely after 48 h. At a high concentration of $NaNO_3$ (5 M), the structure of SU-12 already collapsed after 45 min. Similar phenomena were observed when solutions of KCl or NaCl were used for ion-exchanging. These phenomena show that 1-aminopropane can very easily be ion-exchanged by other ions, maybe because it is a primary monoamine. After 1-aminopropane was exchanged, the framework collapsed because of the lack of interaction between the 1-aminopropane and framework, which is critical for the stability of the framework.

**3.2. Thermal Stability Study.** Three steps of weight loss were clearly observed from the TG curve. The first step was from room temperature up to 200 °C, which corresponds to the removal of crystal water (observed weight change 3.2 wt %, calculated 4.61 wt %). There was a dramatic weight loss (11.7 wt %) within a narrow temperature range, 200−240 °C. When the sample was continuously heated to 450 °C, a small weight change (5.0 wt %) was observed. The total weight loss from 200 °C was about 17 wt %, corresponding to the decomposition of the templates (calculated 18.44 wt %). A gray powder was obtained after the thermal measurement, indicating that the removal of carbon was not completed. X-ray powder diffraction showed that the final powder was amorphous.

In situ XRPD experiments at different temperatures showed that SU-12 is stable up to 200 °C. Sometimes we found that the orthorhombic phase ASU-16 was present together with the tetragonal phase SU-12, as indicated by the reflection splitting and peak broadening in the XRPD patterns at low temperature (Figure 5). The unit cell parameters of the silicogermanate ASU-16, calculated from the XRPD pattern at 60 °C, are $a = 28.75$ Å, $b = 26.90$ Å, and $c = 17.03$ Å. The ratio $a/b$ (=1.07) is significantly lower than that observed by Plevert et al. (=1.24).[22] An interesting phenomenon was observed when a mixture of ASU-16 and SU-12 was heated. With increasing temperatures, the diffraction peaks became sharper and reflection splitting dis-

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appeared. The *a* parameter of the orthorhombic phase ASU-16 became shorter, the *b* parameter became longer, and finally ASU-16 was transferred completely to the tetragonal phase SU-12. This indicates that the tetragonal phase SU-12 is more stable than ASU-16 at high temperatures. As a result, the elliptical 24-ring became more circular after heating. The higher stability of SU-12 may be due to the change of the hydrogen bonding. We are currently trying to improve the synthesis to obtain larger crystals of ASU-16 to study the hydrogen-bonding behaviors.

The in situ XRPD experiments also show that, during the heating, the *a* and *b* dimensions of SU-12 did not change very much, as indicated by the reflection positions 200, 310, and 400 (Figure 5). This means that the shape and size of the circular 24-rings are still kept up to 200 °C. The *c* parameter, on the other hand, decreased with the temperature by 2%, from 17.1 to 16.7 Å.

In conclusion, we have succeeded in partly substituting tetrahedrally coordinated germanium by silicon in the $Ge_7O_{17}F_2$ clusters to build up the first silicogermanate with extra-large 24-ring channels. The 24-ring channel of SU-12 is larger and more circular than that of ASU-16. Its higher symmetry and thermal stability compared with those of ASU-16 may result from the different hydrogen bonding between the templates and framework. The template, 1-aminopropane, plays an important role in stabilizing the framework structure of SU-12.

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**Note Added after ASAP Publication.** One of the references was incomplete and the space group was written incorrectly in the version published ASAP March 15, 2005; the corrected version was published ASAP April 19, 2005.

**Supporting Information Available:** Tables of atomic coordinates, equivalent isotropic displacement parameters, and selected bond lengths and angles for SU-12, an X-ray crystallographic file (CIF), and TG curve and FTIR spectrum from the as-synthesized sample and SEM image of SU-12 (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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