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Complex Open-Framework Germanate Built by 8-Coordinated Ge_{10} Clusters

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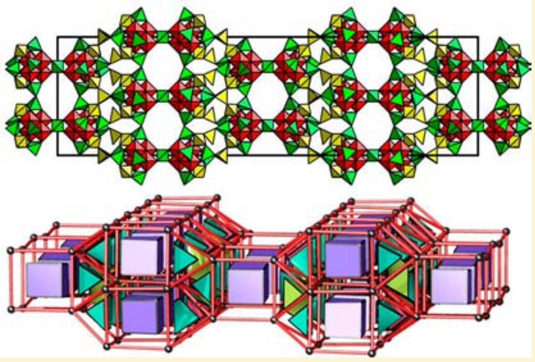
Supporting Information

ABSTRACT: A novel open-framework germanate $|(C_5H_{14}N_2)_2(C_5H_{12}N_2)_{0.5}(H_2O)_{2.5}|[Ge_{12.5}O_{26}(OH)_2]$ with three-dimensional 10- and 11-ring channels, denoted as SU-67, has been synthesized under hydrothermal conditions using 2-methylpiperazine (MPP) as the structure-directing agent (SDA). The synthesis is intimately related to that of JLG-5, a tubular germanate built from Ge_7 clusters. The influences of synthesis parameters are discussed. A strong influence of the hydrofluoric acid quantity on the resulting cluster building units can be concluded. The framework of SU-67 is based on an elaborate topological pattern of connected Ge_{10} clusters forming intersecting 10- and 11-ring channels and has a low framework density (12.4 Ge atoms per 1000 Å^3). We have discovered that the topology of SU-67 is a new 8-connected **nce-8-*I*4$_1$/*acd*** net. Strong hydrogen bonding among the organic SDAs, water molecules, and Ge_{10} clusters resulted in helical networks in SU-67.



■ INTRODUCTION

Porous materials with ever-increasing pore sizes and low framework densities are interesting for applications in catalysis, sorption, and separation. The design of such materials has been challenging in materials chemistry.[1] The concept of the design of solids from molecular building units by Férey et al.[2] has found a solid basis in modern materials science and pointed in new directions for materials designers. The concept has proven to be particularly fruitful for the design of new open-framework germanates, where germanium can be 4- (tetrahedral), 5- (trigonal-bipyramidal), and 6-coordinated (octahedral) to oxygen to form well-defined cluster building units consisting of GeO_n ($n = 4-6$) polyhedra.[3−6] Large building units can generate open-framework structures with large or extra-large pores.[1c,5d,e] One such example is the germanate SU-M,[1c] which is built from $Ge_{10}(O,OH)_{28}$ (Ge_{10}) clusters and contains 30-ring gyroidal channels with cavities larger than 2 nm. Germanates ICMM-7, ASU-21, and SU-61, also built from Ge_{10} cluster building units, feature 14-,[5b] 18-,[5e] and 26-ring channels,[5d] respectively. Thus, it is important to identify large structural fragments as possible building units and establish synthesis routes to produce such building units.

Much attention has been paid in our recent research to discerning the relationship between the formation of different building units and their packing into a crystalline material when the same structure-directing agent (SDA) is used. For instance, the same SDA, 2-methyl-1,5-pentanediamine, resulted in SU-M, SU-MB, and SU-44 containing Ge_{10}, $Ge_7(O,OH)_{19}$ (Ge_7) and $Ge_9(O,OH)_{26}$ (Ge_9), and Ge_7 and Ge_{10} clusters, respectively. A comparison of their synthesis conditions indicates that the addition of hydrofluoric acid (HF) in the synthesis of SU-M (Ge_{10}) leads to the formation of Ge_7 clusters, as found in SU-MB and SU-44. Our recent investigation in the system GeO_2−pyridine−1,6-diaminohexane−water−HF, which leads to the germanates SU-63 (Ge_7), SU-64 (Ge_7 and Ge_9), and ASU-21 (Ge_{10}), shows a strong influence of the HF quantity on the resulting cluster building units.[3l] The Ge_{10} clusters were found in the final structures with zero or a low HF content,[5] whereas Ge_7 requires a high concentration of HF in batch composition.[3] In our attempts to investigate the role of HF in the formation of other germanate structures, we chose 2-methylpiperazine (MPP) as the SDA, which was previously used in the synthesis of a tubular germanate JLG-5.[3i] JLG-5 is built from Ge_7 clusters and was synthesized in the presence of HF. In this work, we discovered a novel open-framework germanate SU-67 constructed from Ge_{10} clusters with a low framework density, synthesized in the absence of HF.

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EXPERIMENTAL SECTION

Synthesis. SU-67 was prepared under mild hydrothermal conditions. The starting materials include germanium dioxide (GeO_2; 99.99%, Nanjing Chemical Reagent Co.), 2-methylpiperazine (MPP; 95%, Sigma-Aldrich), and deionized water.

In a typical synthesis of SU-67, 0.10 g of GeO_2, 0.50 g of MPP, and 0.30 mL of water were mixed and stirred until the mixture was homogenized, resulting in a molar ratio of GeO_2:MPP:H_2O = 1:5.25:17.6. The mixture was sealed in a 22 mL Teflon-lined autoclave and heated at 160 °C for 7 days. The final product was colorless square-plate-like crystal aggregates, which were filtered, washed with deionized water and acetone, and finally dried in air at room temperature. The experimental and simulated powder X-ray diffraction (PXRD) patterns of SU-67 (Supporting Information, Figure S1a) show that the as-synthesized sample contains no other crystalline phases.

Characterization. Thermogravimetric analysis (TGA) of SU-67 was conducted using a Perkin-Elmer TGA7 thermogravimetric analyzer under a nitrogen atmosphere from 30 and 750 °C at a heating rate of 2 $°C \cdot min^{-1}$.

In situ PXRD on SU-67 was performed on a PANalytical X'Pert PRO diffractometer equipped with an Anton-Parr XRK900 reaction chamber using Cu Kα radiation (λ = 1.5418 Å) and variable slits (Supporting Information, Figure S1b). The sample was heated under vacuum from room temperature to 350 °C with a heating rate of 5 $°C \cdot min^{-1}$. The temperature was equilibrated for 2 min prior to each measurement. PXRD patterns were first recorded at 30 and 75 °C, then up to 250 °C with an increment of 25 °C, and finally to 350 °C with measurements every 50 °C. In situ PXRD experiments showed that SU-67 was stable up to 300 °C before decomposing into an amorphous phase.

Elemental analysis of C, H, and N was performed on a Fisons Instruments 1108 analyzer at the University of Santiago de Compostela, Coruña, Spain.

Structure Determination. Single-crystal X-ray diffraction data were collected on a MarCCD at 100 K using synchrotron radiation (λ = 0.907 Å) at the Beamline I911: 5, Max IV Laboratory, Lund University, Lund, Sweden. Data reduction and numerical absorption correction were applied with the program *TwinSolve*[7] with a linear absorption coefficient of 9.279 mm^{-1}. Crystal data for SU-67: tetragonal, space group $I4_1/acd$ (No. 142), a = 20.894(3) Å, c = 73.811(15) Å, V = 32224(9) $Å^3$. A total of 50189 reflections, of which 7165 are unique, were collected in the region 5.24° < θ < 32.93°. Numerical absorption correction was applied. R_{int} = 0.1751, R1 = 0.0828 for reflections with $I > 2\sigma(I)$ and 0.1502 for all reflections, wR2 = 0.1578. The structure solution by direct methods and the refinement were carried out using the *SHELX-97* software package.[8a] The Ge atoms were refined anisotropically, and the O, C, and N atoms were refined isotropically by a full-matrix least-squares technique. Two GeO_4 tetrahedra were disordered in two positions. Three independent H_2MPP cations were found. The methyl groups that belong to the H_2MPP cations at the special positions could not be located because of disorder. Some H atoms were added based on the geometry. *SQUEEZE* was applied using *PLATON* to manage solvent-accessible voids.[8b] The crystallographic data and refinement details are given in Table 1. The atomic coordinates and selected bond lengths and angles are listed in Tables S1 and S2 in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis. Various synthesis parameters were found to affect the formation of SU-67, as shown in Table 2. First of all, the absence of HF was crucial. When a small amount of HF was added, the product became JLG-5 (Ge_7).[3i] The type of the solvent was also important. When water was replaced by dimethylformamide (DMF), only dense quartz-like GeO_2 was formed. When DMF and pyridine were introduced into the initial gel as the solvents, the product was a mixture of SU-67 and GeO_2. When both DMF and HF were used, ASU-7[9a] and ASU-12[3a] were formed. ASU-7 and ASU-12 contain double 4-rings (D4Rs) and Ge_7 clusters, respectively. Earlier investigations showed that HF promotes the formation of D4Rs[9] and Ge_7 clusters.[3] Finally, the water content also plays a key role for obtaining a pure SU-67 phase. When the water to GeO_2 ratio increased from 18 to 30, SU-67 was formed together with ASU-14 (Ge_9).[4b] A further increase of the water content resulted in only the GeO_2 phase.

Table 1. Crystallographic Data and Refinement Details for SU-67

identification code	SU-67
empirical formula[a]	$Ge_{12.5}O_{26}(OH)_2[C_5H_{14}N_2]_2(H_2O)_2$
fw	3195.57
temperature (K)	100(2)
wavelength (Å)	0.90770
cryst syst	tetragonal
space group	$I4_1/acd$
unit cell dimens	
a (Å)	20.894(3)
b (Å)	20.894(3)
c (Å)	73.811(15)
α (deg)	90
β (deg)	90
γ (deg)	90
volume ($Å^3$)	32224(9)
Z	16
calcd density ($g \cdot cm^{-3}$)	2.635
abs coeff (mm^{-1})	9.279
F(000)	24384
cryst size (mm^3)	0.03 × 0.02 × 0.01
θ range for data collection (deg)	5.24−32.93
index ranges	$-24 \leq h \leq 20$, $-22 \leq k \leq 24$, $-75 \leq l \leq 88$
reflns collcd	50189
indep reflns	7165 (R_{int} = 0.1751)
completeness to θ = 32.93 (%)	98.7
abs corrn	numerical
max and min transmn	0.9129 and 0.7682
refinement method	full-matrix least squares on F^2
data/restraints/param	7165/33/292
GOF on F^2	1.014
final R indices [$I > 2\sigma(I)$]	R1 = 0.0828, wR2 = 0.1458
R indices (all data)	R1 = 0.1502, wR2 = 0.1578
largest diff peak and hole ($e \cdot Å^{-3}$)	2.392 and −2.552

[a] The formula here is based on the structure refinement. Additional 0.5 water and 0.5 MPP molecules could not be allocated by the structural refinement and were deduced from CHN analysis and the TGA curve.

Characterization. The chemical formula of SU-67 was deduced by combining the structure refinement, elemental CHN analysis, and TGA as $|(C_5H_{14}N_2)_2(C_5H_{12}N_2)_{0.5}(H_2O)_{2.5}|[Ge_{12.5}O_{26}(OH)_2]$. Elemental analysis of the as-synthesized compound shows the same molar ratio (C/N = 2.50) as that of the MPP molecules, indicating that the MPP molecules remained intact during the synthesis. The results of the CHN analysis are as follows: C, 9.07; H, 2.66; N, 4.25 (calcd: C, 9.03; H, 2.47; N, 4.21). Besides those guest molecules that were located by the structure refinement, there are additional 0.5 water and 0.5 MPP molecules that are probably disordered in the structure. The TGA curve shows a total weight loss of 19.4% (calcd 19.9%) from room temperature up to 600 °C. The first weight loss of 5.8% up to 175 °C corresponds to the removal of all water molecules and the disordered MPP

Table 2. List of Batch Compositions (Molar Ratio) and the Resulting Products in the Synthesis of SU-67[a]

no.	GeO_2	MPP	H_2O	DMF	pyridine	HF	H_2O (mol %)[b]	products
1	1.0	5.3−10.5	17.6−29.3	0	0	0	72−74	pure SU-67
2	1.0	5.3−10.5	29.3−58.5	0	0	0	82−84	SU-67 and ASU-14
3	1.0	5.3	58.5	0	0	0	90	GeO_2[c]
4	1.0	2.1	0	13.6	0	0	0	GeO_2[c]
5	1.0	10.5	58.5	0−13.6	26.1−39.2	0	84	SU-67 and GeO_2[c]
6	1.0	5.3−10.5	17.6	0	0−26.1	2.1	60−74	JLG-5/JLG-5 and amorphous
7	1.0	1.1−5.2	0−11.7	4.1−6.8	0	2.2−3.8	0−65	ASU-7
8	1.0	5.3−10.5	29.3−58.5	27.2	0	2.2−3.3	72−90	ASU-7 and ASU-12

[a] The synthesis temperature was 170 °C, and the time was 7 days. [b] Molar percentage of water added in the synthesis batch. [c] GeO_2 in the final product is hexagonal, a β-quartz analogue according to PXRD.

molecules (calcd 5.7%); the second weight loss (13.6%) started around 300 °C, which corresponds to the loss of the rest of the MPP molecules trapped in the channels (calcd 14.2%). In situ PXRD (Supporting Information, Figure S1b) shows that the peak intensities started to decrease between 150 and 175 °C and the structure of SU-67 collapsed above 300 °C when the MPP molecules were released. A nitrogen adsorption isotherm of SU-67 was measured at 77 K on a Micromeritics ASAP 2020 system. The as-synthesized sample was degassed at 433 K for 10 h. SU-67 did not show significant N_2 gas uptake. The reason might be due to decomposition of the structure after the MPP molecules have been removed.

Structure Description. SU-67 crystallizes in a tetragonal space group $I4_1/acd$ (No. 142) with a = 20.894(3) Å and b = 73.811(15) Å. The asymmetric unit of SU-67, as obtained from the structure refinement, consists of 12.5 Ge atoms, 28 O atoms, 2 water molecules, and 3 H_2MPP cations. Two of H_2MPP cations are at special positions with an occupancy of 0.5 for each. The framework of SU-67 is built of Ge_{10} clusters consisting of a central tetramer Ge_4O_{16} encapsulated by six GeO_4 tetrahedra. The tetramer unit is formed by four edge-sharing octahedra. The tetramers are connected to the six GeO_4 tetrahedra via their 12 O atoms by vertex-sharing. Five of these six GeO_4 tetrahedra further connect three additional GeO_4 tetrahedra, which are 1-, 2-, or 3-coordinated to the inner Ge_{10} cluster, respectively (Figure 1a).

In the reported germanates built from Ge_{10} clusters, the linkages between the clusters are established by either sharing a common tetrahedron or corner-sharing via their tetrahedra or even being bridged via one or two additional tetrahedra.[5,6,10] In the framework of SU-67, all three sorts of connections of Ge_{10} clusters are realized (Supporting Information, Figure S2). In the equatorial ab plane, each Ge_{10} cluster links to four neighboring Ge_{10} clusters by vertex-sharing their tetrahedra similar to that in $Na_4Ge_9O_{20}$.[5a] Three additional tetrahedra further connect the vertex-sharing tetrahedral pair along the a or b direction, forming a 5-ring. Therefore, a layer containing 11- and 5-rings is formed in the ab plane (Figure 1b). The layer is further bound to an adjacent layer in the c direction to form a bilayer by sharing the common tetrahedra in a manner similar to that in germanium pharmacosiderite.[6] The two layers are related by a center of symmetry. The bilayer further connects other bilayers in the c direction by vertex-sharing the GeO_4 tetrahedra. The neighboring bilayers are rotated to one another by 90° around the c axis (Figure 1c) and further bound into a framework by additional tetrahedra. There are totally four bilayers per unit cell that are symmetry-related by the 4_1 screw axis. The three-dimensional framework contains 10-ring channels along the a and b axes and 11-ring channels along the c axis that intersect one another, with free diameters of 4.8 × 6.0 and 5.1 × 5.8 Å, respectively.

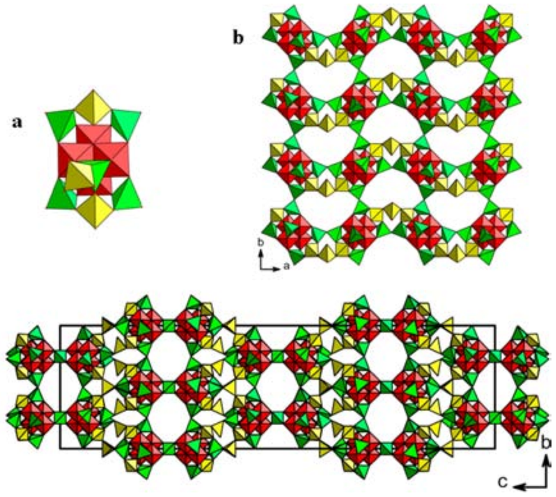

Figure 1. Polyhedral representation of the SU-67 structure: (a) Ge_{10} cluster (octahedra in red and tetrahedra in green) connected to three additional tetrahedra (in yellow); (b) building layer perpendicular to the c axis; (c) 3D framework exhibiting 10-ring channels along the a axis.

There are two unique water molecules and three unique diprotonated MPP cations in SU-67 (Figure 2). Two of the MPP cations are at special positions, and one is at a general position.[11] One MPP cation and one H_2O molecule (O2w) are located in a 10-ring channel along the a and b axes (Figure 2a), with a rather strong hydrogen bond (O2w···N15 = 2.495 Å) between them. O2w further interacts with Ge_{10} clusters through strong hydrogen bonding (O2w···O3 = 2.608 Å; Figure 2a). In a different 10-ring channel along the a and b axes (Figure 2b), another MPP molecule is strongly hydrogen bonded to a H_2O molecule (N8B···O1w = 2.363 Å). Each O1w molecule holds a Ge_{10} cluster with a strong hydrogen bond (O1w···O4 = 2.690 Å). The third MPP molecule is trapped in the 11-ring windows and has only weak hydrogen-bonding interactions with the framework (Figure 2c; N6···O5 = 3.196 Å and N6···O23 = 3.235 Å). Interestingly, the strong hydrogen bonding among the inorganic Ge_{10} clusters and the H_2MPP cations and water molecules in the 10-ring channels results in a helical network following the 2_1 screw axes along the a and b axes (Figure 2d). The hydrogen-bonding system plays an important role in stabilizing the framework, as confirmed by TGA of SU-67 (Figure 3). Such helical hydrogen bonding formed by guest molecules and inorganic hosts is particularly rare in microporous germanates and related materials.[12]

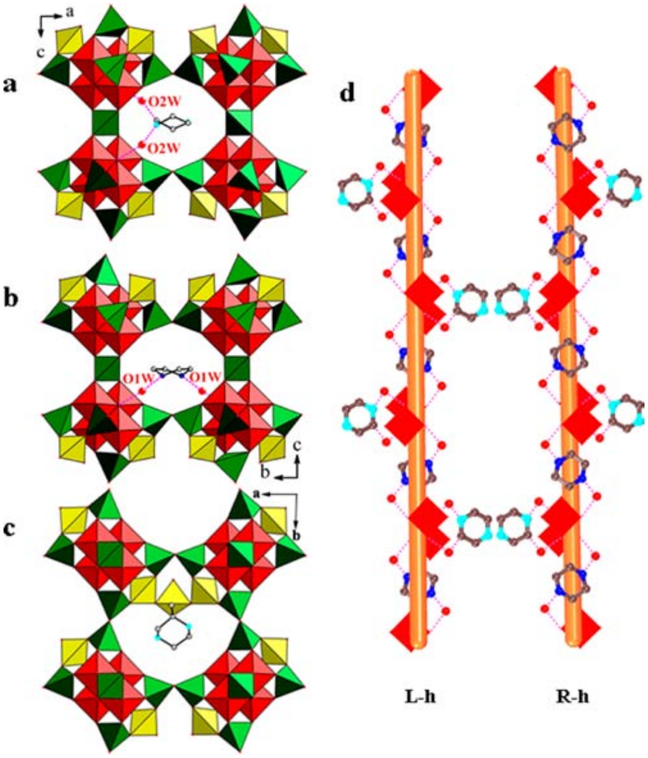

Figure 2. Representation of the guest species in SU-67: (a) MPP-1 and O2w residing in the 10-ring channels viewed along the *b* axis; (b) MPP-2 and O1w residing in the 10-ring channels viewed along the *a* axis; (c) MPP-3 located in the 11-ring window. (d) Helical hydrogen-bonding network in SU-67. Octahedra are shown in red, tetrahedra in green and three additional tetrahedra in yellow. The C atoms are in gray and N atoms in blue (b), and the positions shared by the C and N atoms are in cyan (a, c, and d). H atoms are omitted for clarity.

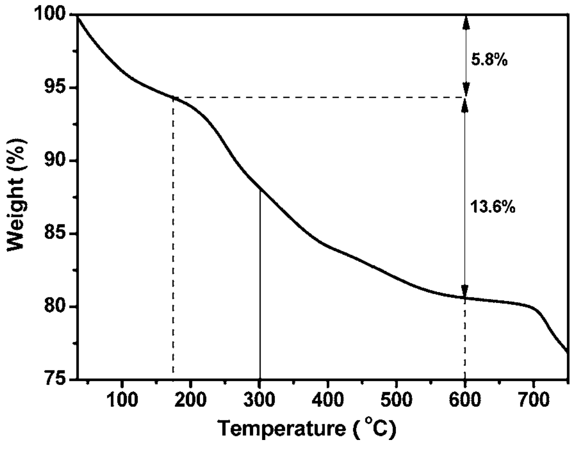

Figure 3. TGA trace of SU-67 in N_2 gas. TGA was performed on a high-resolution TGA7 thermogravimetric analyzer (Perkin-Elmer), with a heating rate of 2 °C·min^{-1}.

Topology Analysis. It is worth mentioning that the Ge_{10} clusters in SU-67 have the highest coordination numbers among all known germanates containing Ge_{10} clusters. Each Ge_{10} cluster connects eight other Ge_{10} clusters through complex linkages provided by tetrahedra (Figures 4 and S2 in the Supporting Information). It is important to analyze the underlying topology of SU-67, in order to have a better overview about the connectivity of the building units, as well as the running direction and intersection of the channels in this complex structure. The topology of the network of Ge_{10} clusters can be described by an **nce-8-*I*4$_1$/*acd*** net,[13,14] where each Ge_{10} cluster represents a vertex of the net and links to eight other Ge_{10} clusters (Figure 4). The **nce-8-*I*4$_1$/*acd*** net[13] has one kind of vertex and is genetically related to the uninodal 9-connected **nce** net.[14] The **nce-8-*I*4$_1$/*acd*** net was obtained from the **nce** net upon removal of one of the nine edges around a vertex (Supporting Information, Figure S3). SU-67 is the first example of the occurrence of the **nce-8-*I*4$_1$/*acd*** net in a real compound. To the best of our knowledge, SU-67 is the most complicated germanate among the published ones and the only one where the Ge_{10} clusters are 8-coordinated (Supporting Information, Figure S2). A topological study of the connectivity between Ge_{10} clusters provided by additional tetrahedra in the Ge_{10}-containing structures including SU-67 has been reported.[10]

SU-67 has a rather low framework density, 12.4 Ge atoms per 1000 Å^3. Only the 10-ring channels can be seen from the [100] or [010] projection, and the 11-ring channels are not visible from the [001] projection. This indicates that the structure has noncylindrical channels along [001] that are notoriously difficult to illustrate. A systematic investigation using the tiling approach shows the inner organization of the void space of the SU-67 structure. For clarity, we only consider framework Ge atoms and omit O atoms. This both keeps the resemblance to the original structure of SU-67 and considerably reduces the complexity of the topological analysis. The natural tiling[15] of the germanium framework is composed of six tile types of considerably different sizes (Supporting Information, Figure S4). The channel system is built by the three "largest" tiles: an A tile between the layers that encloses the largest cavity of the structure, a B tile that encloses a smaller volume and makes 10-ring channels in the bilayers, and interstitial C tiles formed by slightly distorted circle-shaped 11-rings, which act as channel articulations between four adjacent A tiles and have no common faces with the B tiles (Figure 4a). The natural tiling for SU-67 exhibits the 10-ring channel system in the structure as well as discloses noncylindrical 11-ring channels between the bilayers (Figure 5).

Topological study shows that the solvent-accessible channels in SU-67 follow a 3-nodal net with a novel topology, where every unique vertex of the net symbolizes a unique cavity of the structure (Figure 5b and Table S4 in the Supporting Information), and each edge indicates an "open" window between two cavities. The net is carried out by two interlinked 4^4 layers. One of the layers contains two topologically distinctive vertices corresponding to the centers of the A and C tiles, where eight and four channels meet, respectively. The second layer includes only one type of vertex, corresponding to the centers of the intersection of six channels (Supporting Information, Table S4).

■ CONCLUSIONS

In summary, a novel open-framework germanate constructed from Ge_{10} clusters with a low framework density has been synthesized in the absence of HF, which favors formation of the Ge_{10} clusters. The solvent and water contents play important roles in the formation of SU-67. The framework contains intersecting 10- and 11-ring channels running in three directions. SU-67 is the most complex germanate reported so far, where the Ge_{10} building unit has the highest coordination number among all known germanates. The formation of SU-67

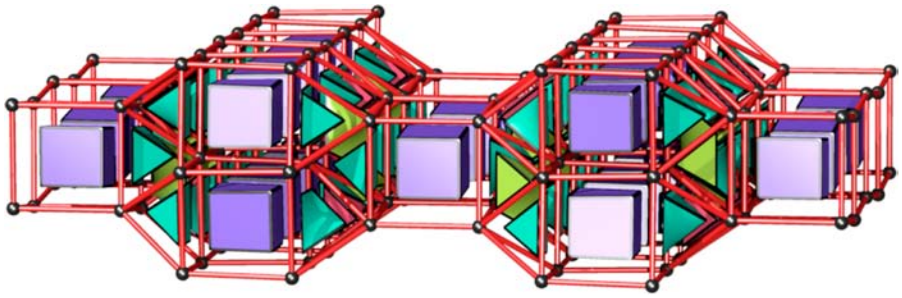

Figure 4. Topological description of the SU-67 structure as a net of Ge_{10} clusters, where edges show the connectivity between Ge_{10} clusters. The net has **nce-8-*I*4$_1$/*acd*** topology. The natural tiling for the net is shown.

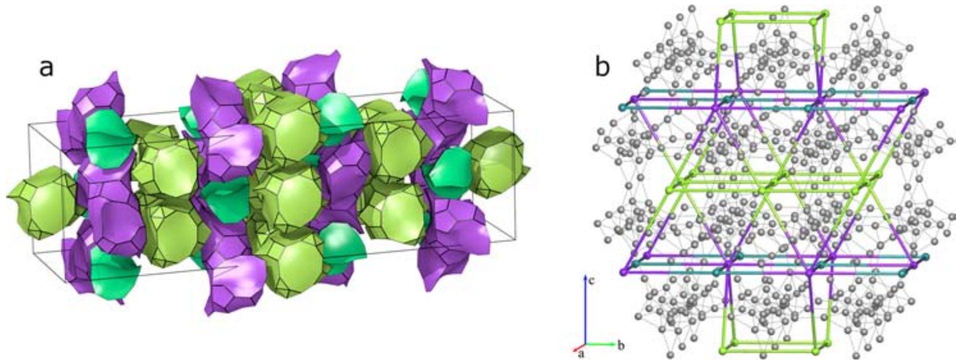

Figure 5. (a) Channel system in SU-67 constructed of the three largest tiles. Two cavities are connected if the corresponding tiles share a 10- or 11-ring face. The tile type is indicated by a color: purple for the A tile, green-yellow for the B tile, and green for the C tile. (b) Net of channels in the SU-67 framework (O atoms are not shown). Each vertex of the channel net corresponds to a cavity in the structure, and an edge indicates that the two cavities are connected. The 11-ring channels are noncylindrical but run zigzag along the *c* axis.

may be directed by the strong hydrogen-bonding interaction between the guest species and Ge_{10} clusters. Strong hydrogen-bonded helical networks were formed among the MPP cations and water molecules in the channels and Ge_{10} clusters. Studying the interactions between the SDAs and frameworks may be helpful for the design of future synthesis routes to obtain germanate compounds with large pores. The natural tiling study provides a valuable tool for discerning the organization of the channel system and its mathematical description in complex frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full synthesis procedure, crystallographic data, PXRD patterns, thermogravimetric analysis, topology analysis, and the CIF of SU-67. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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