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Synthesis and Characterization of a Novel Germanate Material Containing 16-Ring Channels and Templated by a Simple Primary Amine

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The new framework germanate $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ (tetragonal, *I*4*cm*, $a = 24.9728(6)$ Å, $c = 9.8957(2)$ Å, $Z = 4$) has been synthesized by solvothermal methods and the crystal structure determined using single-crystal X-ray diffraction data. The framework of this novel material contains a three-dimensional intersecting channel system, the two largest channels of which are encompassed by large circular 16-rings and elliptical 14-rings, respectively. The material is synthesized in the presence of the relatively small structure-directing agent isopropylamine. $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ is only the second material to be constructed from the secondary building unit $[Ge_9(O,OH)_{25}]$ cluster, and the frameworks of these two materials are shown to differ only by the number of chains of $[Ge_9(O,OH)_{25}]$ clusters that are used to construct the respective frameworks. Thermal stability studies indicate that the framework of the material is stable with respect to loss of the extraframework water molecules but is unstable with respect to the removal of the extraframework charge-compensating cations.

1. Introduction

Crystalline microporous inorganic oxides form an extremely important family of material with applications ranging from the traditional uses, such as ion exchange, separation, and catalysis, to numerous emerging applications, for example, use in membrane separation devices, as MRI contrast agents, and in fabrication of novel optoelectronic components.[1,2] One of the targets in this area is to prepare materials with large pores, typically with more than 12 polyhedra forming the pore opening to the internal volume of the material. The successful synthesis of such large-pore materials will enable a host of new shape-selective processes for the fine chemical, petrochemical, pharmaceutical, and other industries to be realized. The number of large-pore metallosilicate materials that have been synthesized is still rather limited, with 14-membered rings (14MRs) being found in UTD-1,[3] CIT-5,[4] IM-12,[5]OSB-1,[6] SSZ-53,[7] and SSZ-59[7] and 18MRs occurring in ECR[8] and ITQ-33.[9] A greater number of large-pore systems are found among metallophosphate frameworks, for example, AlPO-8 (14MR),[10] VPI-5 (18MR),[11] JDF-20 (20MR),[12]cloverite (20MR),[13] NTHU-1 (24MR),[14] ND-1 (24MR),[15] and VSB-1 and -5 (24MR).[16,17] More recently, work on germanate or silicon-substituted germanate framework materials has produced a wide range of structures including a variety of large-pore framework materials. The latter include the silicon-substituted germanate material SU-12 (24MR)[18]and the germanate materials ASU-12 (16MR),[19]ASU-16 (24MR),[20] FDU-4 (24MR),[21] and SU-M (30MR).[22] The latter is a remarkable

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crystalline nanoporous germanate material that has a pore structure similar to that of the mesoporous material MCM-48 and pores of free diameter 10 × 22.4 Å.

The two most common methods to prepare framework materials involve the use of organic cations that can either, through their shape, size, and charge, influence the structure of the framework directly in a space-filling or structure-directing capacity or aid the formation of frameworks from polynuclear anionic clusters. The latter are formed during the synthesis process and then interact via a "cluster condensation" mechanism to form the resulting solid.[23]The former method has found great success in synthesizing large-pore silicate materials.[4] The latter method has been found to be particularly useful in preparing novel metallophosphate frameworks in which a mixture of different coordination polyhedra may form the polynuclear anionic clusters. The "cluster condensation" mechanism has been shown to occur in the solvothermal synthesis of several metal phosphate systems by using a combination of in situ/ex situ diffraction and NMR techniques.[24]The mechanism through which germanate framework materials are formed remains uncertain, although it has been shown that two germanate frameworks, a GeO_2-BEC analogue and STAG-1,[25] both of which contain cubic double four-ring $[Ge_8(O,OH,F)_{21}]$ clusters, can be synthesized using a starting reagent containing isolated $[Ge_8(O,OH,F)_{21}]$ clusters.[25,26]

Unlike aluminosilicate zeolite framework materials that contain tetrahedral primary building units only, germanate-based frameworks are found to contain a variety of Ge-centered coordination polyhedra within the framework that include Ge-centered tetrahedra, trigonal bipyramids, square-based pyramids, and octahedra.[19−22] This rich variety of Ge-centered polyhedra has the potential to connect to form a plethora of structures. Within these structures certain secondary building units (SBUs) are being found that, through direct linkage or via other primary building units, for instance, GeO_4 tetrahedra or other SBUs, form a variety of framework structures. A relatively simple SBU that has been found in numerous microporous materials and a variety of germanate-based framework materials is the aforementioned cubic double four-ring $[(Ge,Si)_8(O,OH,F)_{20/21}]$ unit. This unit is one of the constituent SBUs in the framework ASU-7-type materials,[27−29] ASU-9,[27] FOS-5,[30] a GeO_2-BEC analogue, and STAG-1.[25] A more complicated SBU that has been found in several germanate-based materials is the $[(Ge,Si)_7(O,OH,F)_{19}]$ cluster that forms the basis of the chain-containing $[Ni(dien)_2]_2[Ge_7O_{13}(OH)_2F_3][Cl]$ FJ-6 material,[31] the layered ASU-19 and ASU-20 materials,[32]the small-pore framework material $[Ge_{10}O_{21}(OH)][N_4C_6H_{21}]$,[33] and the large-pore framework materials ASU-12, ASU-16, and SU-12[18−20] and fills some of the void volume of SU-M to form the chiral derivative SU-MB material.[22]

We present here the synthesis, structural characterization, and properties of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$, a novel germanate framework with a three-dimensional intersecting channel system, the largest channel of which is encompassed by a 16MR. The material is synthesised in the presence of the relatively small structure-directing agent isopropylamine. The title compound is the second framework structure to be constructed from the large $[Ge_9(O,OH)_{25}]$ cluster and exemplifies the potential for this SBU to form open-framework materials.

2. Materials and Methods

2.1. Synthesis. The reagents used to synthesize $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ were GeO_2 (Aldrich), isopropylamine (Aldrich), and deionized water. All the reagents were used without further purification. $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ was synthesized by mixing together GeO_2 (0.956 mmol), deionized water (56 mmol), and isopropylamine (93 mmol) to form a synthesis gel of molar ratio 1:58.6:97.3. The reagent mixture was loaded in a 23 mL Teflon-lined steel autoclave and heated for 7 days at 160 °C. The resultant crystalline product was washed with distilled water, separated by suction filtration, and dried under ambient conditions to reveal colorless crystals. The powder X-ray diffraction pattern of this product is provided in the Supporting Information and was judged to be monophasic from the excellent agreement between the experimental powder X-ray diffraction pattern and that calculated using the crystal structure obtained from the single-crystal analysis of the compound.

2.2. Characterization. Thermogravimetric analysis (TGA) data were collected using a Universal V4.2E TA Instrument Thermal Analysis Q5000 system. The sample was contained in a platinum crucible and heated under a flow of air from room temperature to 700 °C at a heating rate of 5 °C min^{-1}.

Thermodiffraction patterns were collected using a Phillips X'Pert Pro diffractometer, employing Cu $K\alpha_{1+2}$ radiation and an RTMS X'Celerator detector, fitted with an Anton Paar XRK 900 high-temperature furnace stage. The sample was heated, under vacuum, from room temperature to 700 °C at a heating rate of 10 °C min^{-1}, with patterns being collected at intervals of 40, 30, or 20 °C. The X-ray diffraction patterns were all collected in the $2\theta = 3-50°$ range with a scan time of 15 min per scan.

2.3. Single-Crystal Structure Determination. A suitable crystal of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ was mounted on a Nonius Kappa CCD area detector diffractometer, and data were collected from it. The intensity data analysis was performed using the Nonius software packages, and the absorption correction was applied to the data using the SORTAV program.[34,35] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs, as incorporated into the WINGX suite of programs.[36,37] Atomic

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Table 1. Crystallographic Data and Structure Refinement Parameters for $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$

chemical formula	$(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$
cryst syst	tetragonal
space group	*I*4*cm*
a (Å)	24.9728(6)
c (Å)	9.8957(2)
V (Å^3)	6171.4(2)
Z	4
crystal dimens (mm)	0.25 × 0.05 × 0.05
calcd density (g cm^{-3})	2.528
$2\theta_{max}$ (deg)	55
radiation, wavelength (Å)	Mo Kα, 0.71073
μ (mm^{-1})	8.727
T_{min}/T_{max}	0.215/0.648
scan mode	ϕ and ω scans
temp (K)	200
no. of measured reflns/no. of independent reflns/R(int)	3425/1804/0.0289
no. of independent reflns ($I > 2\sigma(I)$)	1578
no. of params/restraints	217/6
R1, wR2 ($I > 2\sigma(I)$)	0.0269, 0.0577
R1, wR2 (all data)	0.0347, 0.0598
residual electron density, max/min (e Å^{-3})	1.026/−0.807

scattering factors for neutral atoms were used throughout the refinement. The Ge and framework O atoms were found from the direct methods solution, and the remaining extraframework atoms were located from difference Fourier maps. One of the extraframework oxygen atoms [O(15)] and the nitrogen atom [N(2)] of one of the isopropylammonium cations were found to partially occupy the same crystallographic site. The occupancy of the two species was then refined under the constraint that the total occupancy of the site should be unity. The refined value of the occupancy of the O(15)/N(2) site was close to 1/2, so the occupancies of the extraframework O(15) atom and the isopropylammonium cation [N(2)C(4)C(5)] were fixed at half the crystallographic site occupancy for the remainder of the refinement. The atomic coordinates and atomic displacement parameters of O(15) and N(2) were also fixed to have the same values during the refinement. The occupancy of the two extraframework species O(13) and O(14) were fixed at half the crystallographic occupancy of the sites they occupy to avoid unreasonably close contacts with other extraframework atoms being made. The atomic displacement parameters of all the non-hydrogen atoms were refined anisotropically, with the anisotropic displacement components of the atoms in the isopropylammonium cation [N(2)C(4)C(5)] restrained to be equal along the lines joining them together. The N−C and C−C distances in the isopropylammonium cation [N(2)C(4)C(5)] were also restrained at chemically reasonable values during the refinement. All the hydrogen atoms in the structure were geometrically placed and refined in riding mode with their isotropic atomic displacement factors fixed at values of 1.2 and 1.5 × U_{eq} of the carbon or nitrogen/oxygen atoms, respectively, to which they were directly connected. The hydrogen atoms attached to the oxygen atoms of water molecules were not located or placed in the structure. The crystallographic data and structure refinement parameters are summarized in Table 1, and the asymmetric unit of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$ is shown in the Supporting Information. Elemental analysis (wt %) of single crystals of the title compound gave values of 8.5 (calculated 7.6), 2.7 (calculated 2.8), and 3.3 (calculated 3.0) for C, H, and N, respectively, which is in reasonable agreement with the chemical formula obtained by crystallography.

3. Results and Discussion

3.1. Structure Description. The primary building units of the framework of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$ are tetrahedral $Ge(5)O_4$ and $Ge(3)O_3(OH)$ units, trigonal bipyramidal $Ge(2/4)O_5$ units, and square-based pyramidal $Ge(1)O_4(OH)$ moieties. Two of the Ge(2/3/4/5)-centered polyhedra and one Ge(1)-centered polyhedron combine to form the single type of secondary building unit $[Ge_9O_{22}(OH)_3]$ found in this framework and shown in Figure 1. The polyhedra within one SBU are connected to each other through corner-sharing of two coordinated oxygen atoms except for the connection of the trigonal bipyramidal Ge-

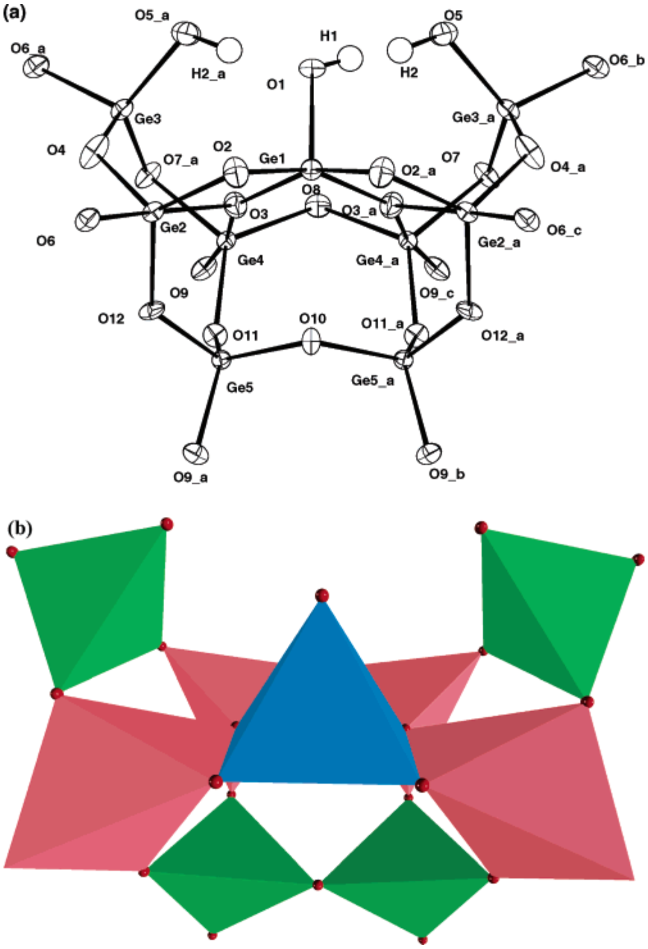

Figure 1. $Ge_9O_{22}(OH)_3$ cluster found in $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$ shown as (a) a displacement ellipsoid plot and (b) a polyhedral representation. Displacement ellipsoids are shown at the 50% probability level. The colors of the polyhedra are green, red, and blue for the tetrahedra, trigonal bipyramids, and square-based pyramid, respectively.

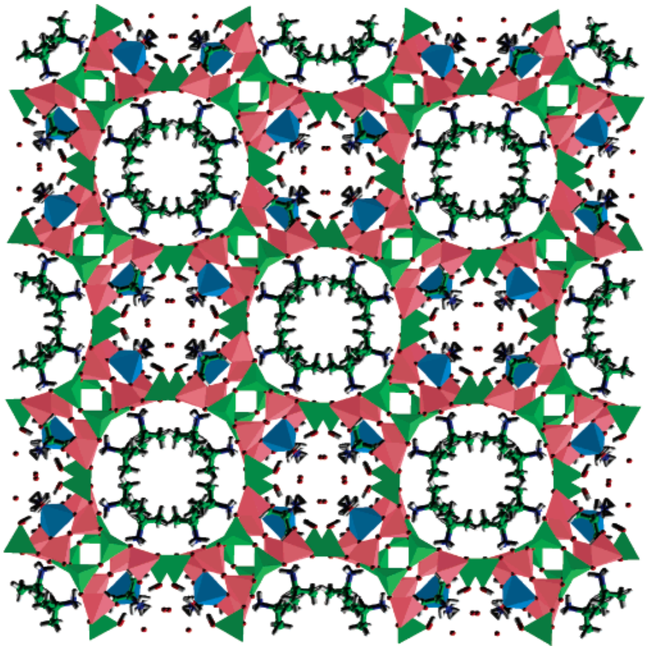

Figure 2. A polyhedral/ball and stick representation of the crystal structure of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ viewed along the *c* axis. The colors of the polyhedra are green, red, and blue for the tetrahedra, trigonal bipyramids, and square-based pyramids, respectively. The colors of the balls are gray, green, blue, and red for the H,C, N, and O atoms, respectively.

(2)O_5 and square-based pyramidal Ge(1)O_4(OH) units that share an edge in which one oxygen atom, O(2), is bicoordinated and one oxygen atom, O(3), is tricoordinated. The SBU found in $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ is similar to that found in the 24MR germanate material FDU-4,$[Ge_9O_{17}(OH)_4][N(CH_2CH_2NH_3)_3]_{2/3}[HCON(CH_3)_2]_{1/6}(H_2O)_{11/3}$.[21] The SBU in both materials possesses the same arrangement of the Ge-centered polyhedra and chemical connectivity. All the Ge–O bonds in the Ge-centered tetrahedra (mean 1.748 Å) and five coordinated Ge-centered polyhedra (range 1.751(6)−2.212(5) Å) are in agreement with those observed in other germanate materials.[21,32,33]

The SBUs are linked together through bridging oxygen atoms to form the framework of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ shown in Figure 2 that contains an intersecting three-dimensional channel system. All the linkages between the SBUs are made through corner-sharing connection of Ge-centered tetrahedra and Ge-centered trigonal bipyramids. The connections in the *ab* plane are through the Ge(3)O_3(OH) and Ge(2)O_5 units, with the connections between SBUs in the [001] direction being made through Ge(5)$O_4$and Ge(4)O_5 units. The two largest channels of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ are directed along the *c* axis. The largest channel is circular in shape, has a pore diameter of 12.64(3) Å (O···O), and is circumscribed by a 16MR, as shown in Figures 2 and 3a. The inner surface of this channel is lined by oxygen atoms, and the channel contains one of the crystallographically independent structure-directing isopropylammonium cations. The N(1) atom of the isopropylammonium cation is most strongly hydrogen-bonded to two of the framework oxygen atoms (N(1)···O(9), 2.775(8) Å; N(1)···O(6), 2.845(8) Å). The wall of the circular 16MR channel consists of alternating pairs of 3MRs and elliptical 8MRs as shown in Figure 3b. The 8MRs have dimensions of 8.81(2) × 5.31(2) Å (O···O) and form the openings of 8MR channels that run in four directions perpendicular to the *c* axis and cross at an angle of 45° between 8MR channels. The second largest channel that runs parallel to the *c* axis appears to be square in shape as seen in Figure 2. This channel is actually delimited by elliptical 14MRs as shown in Figure 4a and has a pore dimension of 6.49(2) × 13.09(3) Å (O···O). The elliptical 14MRs are aligned in two different orthogonal orientations, with alternating rings arranged orthogonally with respect to each other along the channel. Between adjacent elliptical 14MRs that are oriented parallel to each other are pockets leading off from the core of the channel as shown in Figure 4b.The entrance to these pockets from the core of the channel is delimited by a 12MR. The walls of the square channel contain 8MRs, as shown in Figure 3b, which allow passage into the circular 16MR channels and make this a three-dimensional channel system. The internal surface of the square channel is lined with Ge–OH groups, as seen in Figures 2 and 4a. This channel contains the second crystallographically independent structure-directing isopropylammonium cation, hydronium cations, and water molecules. The isolated regions of electron density in this channel were assigned as oxygen-containing species and not nitrogen-containing species as the C:N molar ratio of 3.0 obtained from the CHN analysis indicates no additional N-containing species are present in the material.

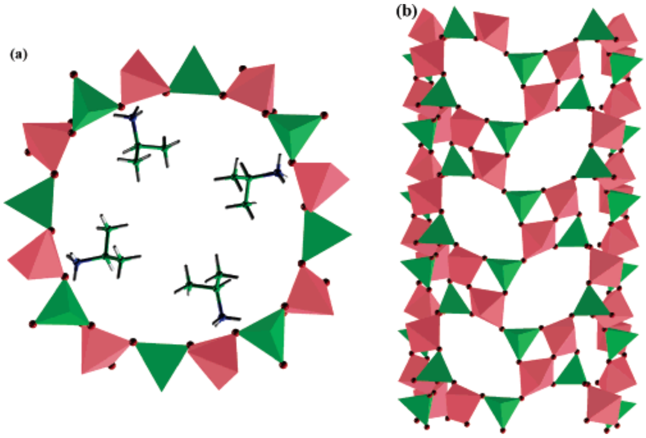

Figure 3. A polyhedral representation of the 16MR circular channel of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ viewed along (a) and perpendicular to (b) the *c* axis. The colors of the polyhedra are green and red for the tetrahedra and trigonal bipyramids, respectively. The isopropylammonium cations in (a) are shown in ball and stick mode, with the gray, green, and blue balls representing the H, C, and N atoms, respectively.

The N(2) atom of the isopropylammonium cation is most strongly hydrogen-bonded to two of the framework oxygen atoms (2 × N(2)···O(2), 2.88(2) Å). This isopropylammonium has a 50% crystallographic occupancy and is replaced by a H_2O(14) molecule and a $H_3O(15)^+$ hydronium cation when it is not present. O(15) was assigned to be a hydronium cation as it occupies exactly the same position as the N(2) atom, so as this is the site of positive charge on the organocation, the hydrogen-bonding interactions will be as favorable when the hydronium cation is on this site. The O(14) atom of the H_2O(14) molecule has its strongest hydrogen-bonding interaction with the framework O(8) atom (O(14)···O(8), 2.89(2) Å). Within the center of the square channel are located H_2O(13) molecules. This crystallographic

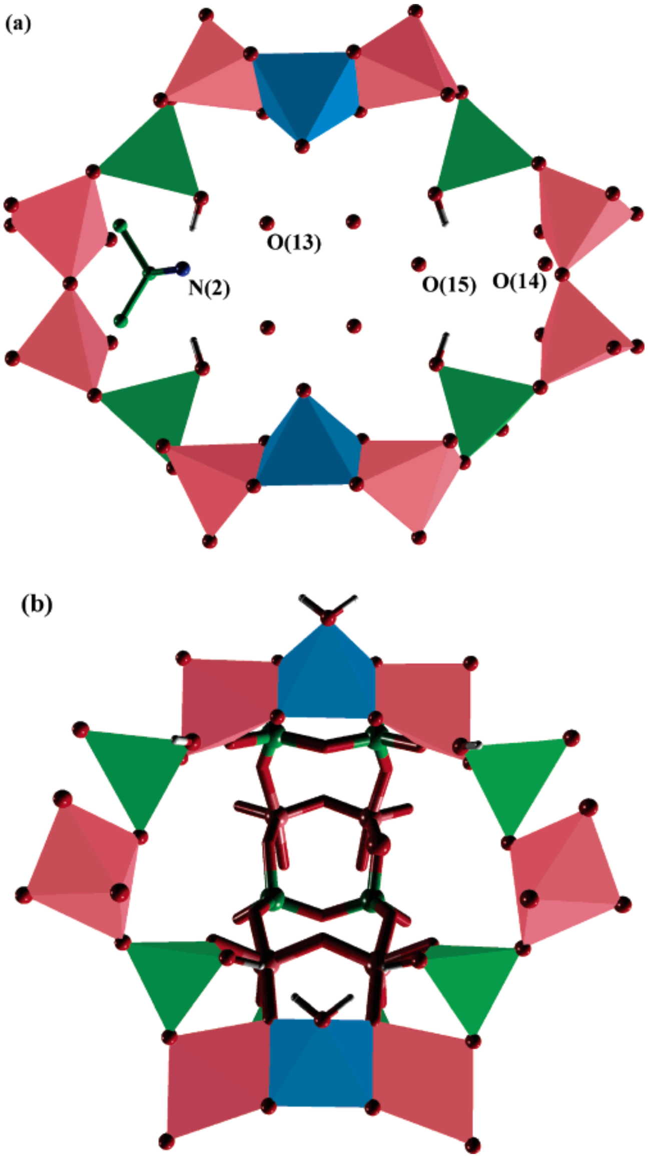

Figure 4. A polyhedral representation of aspects of the square channel of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$: (a) a view of the constituent elliptical 14MR; (b) a view into a side pocket of the square channel through the 12MR entrance to the pocket. The colors of the polyhedra are green, red, and blue for the tetrahedra, trigonal bipyramids, and square-based pyramids, respectively. Certain features within each view are shown in ball and stick mode, and the colors of the balls are gray, green, blue, red, pale green, and pale red for the H, C, N, O, 4-coordinated Ge, and 5-coordinated Ge atoms, respectively. Hydrogen atoms are omitted from extraframework species in (a) for clarity.

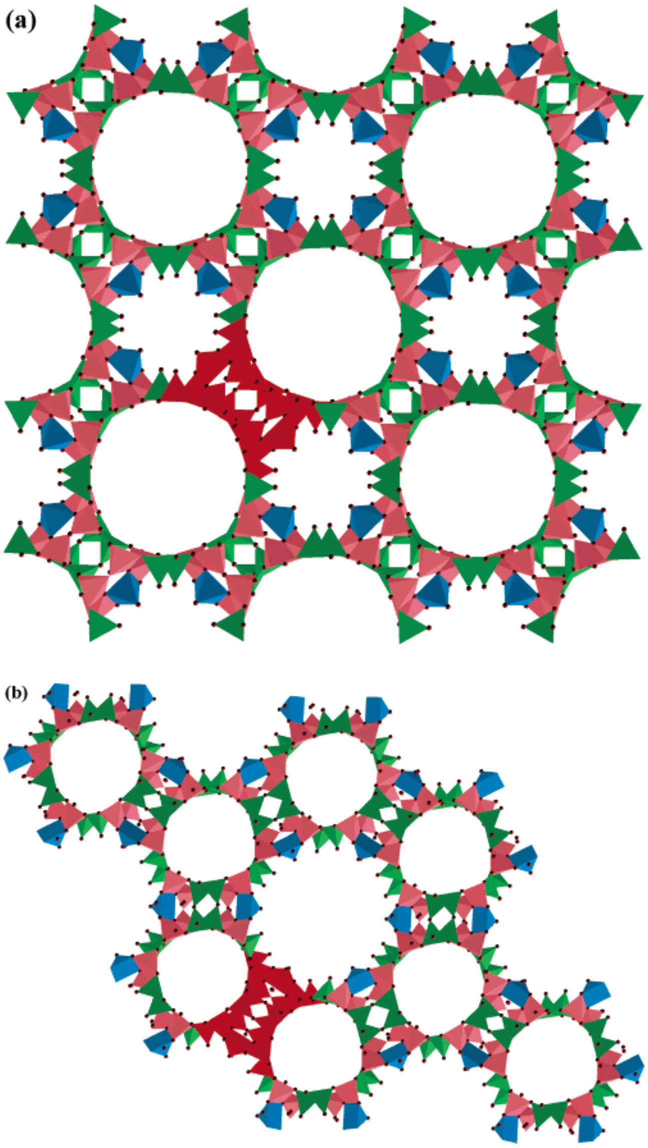

Figure 5. A polyhedral representation of several chains of $[Ge_9(O,OH)_{25}]$ clusters that form the structure of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ (a) and FDU-4 (b). The colors of the polyhedra are green, red, and blue for the tetrahedra, trigonal bipyramids, and square-based pyramids, respectively, with one chain of $[Ge_9(O,OH)_{25}]$ clusters being colored bright red in (a) and (b) for explanatory purposes. All extraframework species are omitted for clarity.

site is again only half-occupied to prevent two $H_2O(13)$ molecules from being too close together to be physically reasonable when this site becomes more than 50% occupied. The $H_2O(13)$ molecule can form hydrogen bonds with other $H_2O(13)$molecules (O(13)···O(13), 2.77(2) Å) and framework oxygen atoms (O(13)···O(1), 2.77(2) Å; O(13)···O(5), 2.82(2) Å). The locations of the extraframework species in the square channel are shown in Figure 4a.

As mentioned previously, the structures of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ and FDU-4 are constructed from the same SBU that is connected to other SBUs through identical atom coordination sequences. If the structures of both materials are considered as being constructed from chains of SBUs directed along the *c* axis, then the channel structure of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ is seen to be derived from the connection of four of these chains to make up both the circular and square channels, as shown in Figure 5a. However, in FDU-4 six of these chains connect to form the walls of the larger 24MR channels, which, due to the size constraints of the chains, only permits three chains to connect to form the smaller 12 MR channels, as shown in Figure 5b. The adoption of both structure types implies that there is a high degree of flexibility in the Ge−O−Ge bond angles of the corner-sharing connections of Ge-centered tetrahedra and Ge-centered trigonal bipyramids that link the SBUs together and that this angle should be substantially greater in FDU-4 (Ge(4)−O(3)−Ge(3), 140.9°) to accommodate the number of chains in the 12MR and 24MR channels compared to the angle in the $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ structure (Ge(3)−O(6)−Ge(2), 131.1(3)°). It is also evident that the differing number of chains forming the walls of the channels in each structure results

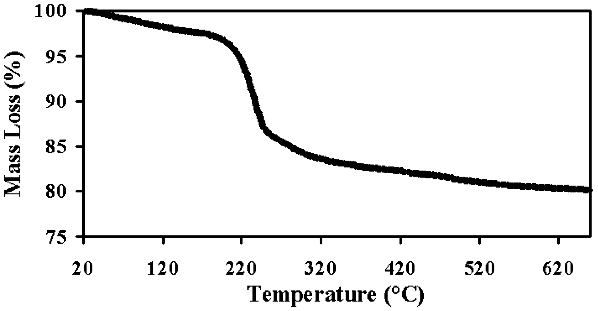

Figure 6. Thermogravimetric trace of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$.

in two similarly sized channels (16MR and a 14MR) in $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ and two dissimilarly sized channels in FDU-4 (12MR and a 24MR). The framework density of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ is 11.7 Ge atoms nm^{-3}, which is slightly higher than that found in FDU-4 (11.1 Ge atoms nm^{-3}) but lower than that of the 16MR-containing germanate material ASU-12 (12.0 Ge atoms nm^{-3}).

The relatively small size of the structure-directing isopropylammonium cations compared to the channel size and shape within $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ implies that the isopropylammonium cations do not template directly the structure of the framework of the material in the close-fitting manner observed for microporous silicate materials. A similar behavior of the organic species is found for the formation of many other large-pore silicon-substituted germanate and germanate frameworks that are formed in the presence of relatively small, simple amines, for instance, dimethylamine (ASU-12),[19] 1,4-diaminobutane (ASU-16),[20] propylamine (SU-12),[18] and 2-methyl-1,5-pentanediamine (SU-M, SU-MB).[22] The role of the isopropylammonium cations may be to stabilize the formation of particular building unit clusters that exist in the reaction gel/solution and then the direction of these clusters during condensation with other clusters to form the resultant framework structure that is also stabilized by the presence of the isopropylammonium cations through electrostatic and hydrogen-bonding interactions. This type of process has been shown to occur for metal phosphate systems[23,24] and would seem to be a plausible mechanism for the formation of the open-framework germanate materials, although, as yet, there are no reports of in situ experimental measurements to clarify the mechanistic aspects of the synthesis of these materials.

3.2. Stability Studies. Mass losses were observed in three main sections in the TGA trace of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$, as shown in Figure 6. The first mass loss of 2.7% between 20 and 180 °C is attributed to the loss of the extraframework water molecules (calculated 2.3%). The second rapid mass loss of 13.9% between 180 and 330 °C is attributed to the loss of the isopropylammonium and hydronium cations (calculated 13.5%). The third mass loss of 3.3% observed between 330 and 660 °C is assigned to the loss of the terminal OH groups from the framework (calculated 4.3%).

The in situ thermodiffraction data are shown in Figure 7. From room temperature up to 180 °C there are only minor changes in the X-ray powder diffraction patterns of the material. From 180 to 200 °C the crystallinity of the material is seen to degrade sharply, with the first peak decreasing in intensity and moving to a higher 2θ value and the remaining peaks all becoming broader and less intense. At 220 °C, only a limited number of the diffraction peaks of the original pattern are still visible. Above 220 °C, the intensity of these diffraction peaks steadily become smaller until at 520 °C the material becomes X-ray amorphous.

The combination of the thermogravimetric and thermodiffraction data suggests that the framework structure of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ remains stable with respect to the loss of the extraframework water molecules as it is heated to 180 °C. Above 180 °C the isopropylammonium and hydronium cations begin to be removed, resulting in a rapid loss of framework stability and crystallinity of the material. Hence, the framework of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ is stable with respect to the removal of the extraframework water molecules but not the extraframework cationic species.

The solvent-accessible volume, calculated using SQUEEZE,[38] of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ including and excluding oxygen-containing extraframework species is 223 and 482 Å^3, respectively. However, nitrogen adsorption experiments performed on a sample degassed overnight at 393 K showed no significant

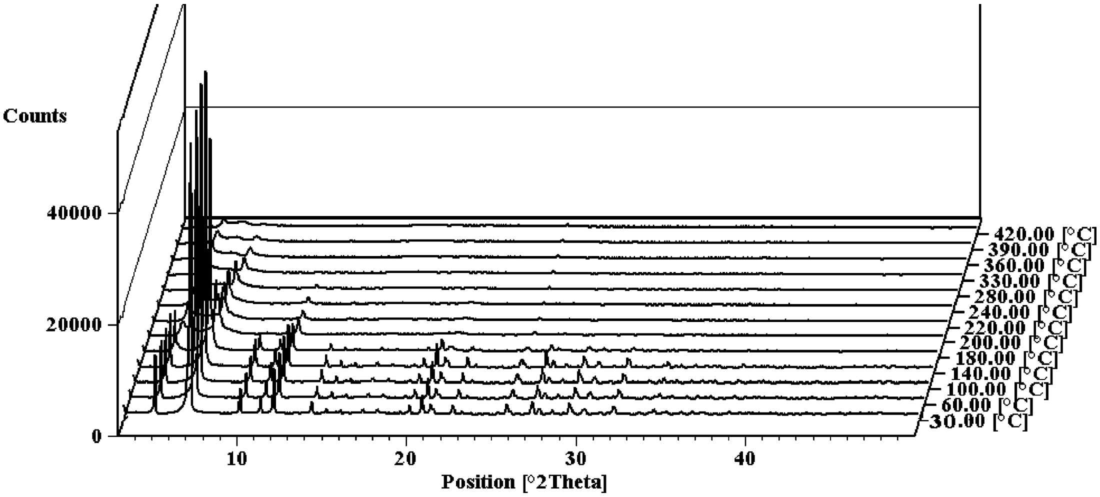

Figure 7. Thermodiffraction patterns of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$.

adsorption of nitrogen into the internal volume of the material.

Experiments in which crystals of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$ were stirred in pure deionized water or a 0.1 M aqueous solution of CsCl resulted in complete dissolution of the solid, indicating the poor hydrolytic stability and fragility of this germanate framework material.

4. Conclusions

We have succeeded in synthesizing the novel open-framework material $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$, containing a three-dimensional channel system. The framework of the material is stable with respect to loss of the extraframework water molecules, but is not stable enough to allow the full potential porous volume to be accessed by removal of the extraframework charge-compensating cations.

The formation of this material further demonstrates that open-framework materials containing large channels may be formed from germania using simple amines as structure-directing agents and that more than one framework material may be formed from the $[Ge_9(O,OH)_{25}]$ SBU. The construction of the title compound and FDU-4 from this SBU illustrates the high degree of bond angle flexibility that the Ge−O−Ge linkages can exhibit, a phenomenon reported for other germanate materials.[20,39]The combination of being able to form framework materials that contain a variety of Ge-centered polyhedra, simple structure-directing agents, and flexible linkages between GeO_n polyhedra exemplifies the great potential for the discovery of a wide array of open-framework materials from this system, some of which may provide the microporous materials with the large pore sizes and internal surface areas required for future applications.

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Supporting Information Available: Tables of extended crystallographic data and structure refinement parameters, atomic coordinates and equivalent isotropic atomic displacement factors, bond lengths and angles, and anisotropic atomic displacement factors, observed and simulated powder X-ray diffraction patterns, and the asymmetric unit of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot3H_2O$ (PDF) and a crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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