# Synthesis and Crystal Structure of a Novel Germanate: $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$

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The novel microporous germanate $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$ was prepared from an aqueous solution containing germanium dioxide, pyridine, hydrofluoric acid, and 2,6-diaminopyridine as a template. The solution was kept at 165 °C in a Teflon-lined autoclave for 4 days. Large crystals were produced and studied by X-ray powder diffraction, FTIR, thermal analysis, and elemental analysis. The structure was determined by single-crystal X-ray diffraction. The crystal is orthorhombic, space group *Pbcn*, with $a = 7.0065(4)$ Å, $b = 11.7976(6)$ Å, $c = 19.5200(14)$ Å, and $Z = 4$. The structure is a layered framework built up from $GeO_4$ tetrahedral and $GeO_3F_3$ octahedral units. The polyhedral units are connected in such a way that they form a zeolite-like porous structure with three- and nine-membered rings. Half of the ammonium ions are located inside the nine-membered rings. The other half are above and below the three-membered rings. The connectivity of the germanium polyhedral units is interrupted along the *c* axis by ammonium ions and water molecules inserted between the layers.

## Introduction

Porous germanates are interesting for several reasons. First, germanium is the closest analogue of silicon. Silicon−oxygen compounds form the largest class of minerals and synthetic silicates, such as clays, feldspar minerals, and zeolites. Only a limited number of germanate structures have been published. The question if germanium−oxygen compounds could form templated open anion frameworks and/or layered structures containing $GeO_4$ tetrahedral units, analogous to those of silicates, is interesting from both a theoretical and a practical point of view. Second, according to the Magnus−Goldschmidt rule,[1] the ratio of the ionic radii of germanium to oxygen is too large for the germanium to fit ideally in a tetrahedral environment. In fact, germanium forms oxygen polyhedra with four- (tetrahedral), five- (square pyramidal, trigonal bipyramidal), and six-coordination (octahedral). A germanium−oxygen compound can consist of a single polyhedron type or a combination of different polyhedral types. The flexibility of coordination numbers for germanium allows for the formation of mixed anion framework germanates. The high coordination numbers offer possibilities to synthesize framework germanates with higher charge densities than silicates.

The first templated germanates were reported in 1991 by Xu et al.[2] Four types of open germanate structures were synthesized. Two of them, $Ge_6O_{12}\cdot NMe_4OH$[2] and $[Ge_{18}O_{38}(OH)_4]^{8-}[(C_2N_2H_{10})^{2+}]_4\cdot 2H_2O$, [3] were solved by single-crystal X-ray diffraction. The other two, 1,3-PDA-$GeO_2$ [4] (PDA = propylenediamine) and DMA-$GeO_2$,[5] could not be determined due to lack of suitable crystals. We have examined the IR spectra and X-ray powder diffraction data (XRPD) of DMA-$GeO_2$ and conclude that the template, dimethylamine (DMA), was not successfully incorporated in the compound. DMA-$GeO_2$ is identical with the previously known $(NH_4)_3[HGe_7O_{16}]\cdot 4-6H_2O$,[6] crystallizing in the structure type of pharmacosiderite.[7] Recently, several new germanate structures were reported, including $(NH_4)_2[Ge_7O_{15}]$,[8] $(DMA)_3[Ge_7O_{14.5}F_2]\cdot 0.86H_2O$,[9] DMA$[(GeO_2)_{10}]\cdot H_2O$,[10] DABCO$[(GeO_2)_{10}]\cdot H_2O$ [10] (DABCO = 1,4-diazabicyclo[2.2.2]octane), and $(C_4H_{12}N)_4[Ge_9O_{14}(OH)_{12}]\cdot 14H_2O$.[11] None of the germanates mentioned above are stable at temperatures above 400 °C, as would be desirable for catalysts.

Here we report the synthesis and crystal structure determination of the novel germanate $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$.

## Experimental Section

Crystals of $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$ of size up to 1.5 × 1.5 × 0.5 mm were synthesized under hydrothermal conditions from a homogeneous mixture of germanium dioxide, pyridine, hydrofluoric acid, 2,6-diaminopyridine, and water in the molar ratio 1.0:34.4:1.53:9.75:38.4. $GeO_2$ was added to a stirred solution of pyridine, hydrofluoric acid, and water. Then 2,6-diaminopyridine, the trial template, was added with continuous stirring and a clear dark brown solution was formed. The solution was transferred to a 23 mL Teflon-lined Parr autoclave and heated at 165 °C for 4 days under autogenous pressure. The product was yellowish brown transparent crystals, which were filtered, washed, first with deionized water and then with ethanol, and dried in air at 40 °C.

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**Table 1.** Crystallographic Data Collection and Refinement Parameters for $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67(H_2O)$

| | |
|---|---|
| empirical formula | $Ge_5O_{9.67}F_6N_4H_{17.34}$ |
| fw | 705.16 |
| space group | *Pbcn* |
| *a* (Å) | 7.0065(4) |
| *b* (Å) | 11.7976(6) |
| *c* (Å) | 19.5200(14) |
| cell vol (Å$^3$) | 1613.52(17) |
| Z | 4 |
| calcd density (g/cm$^3$) | 2.903 |
| radiation | Mo Kα ($\lambda = 0.710\ 73$ Å) |
| $\mu$(Mo Kα) (mm$^{-1}$) | 9.30 |
| *T* (°C) | 20 |
| final *R* value ($I > 2\sigma(I)$) | R1$^a$ = 0.0223, wR2$^b$ = 0.0514 |
| *R* value (all data) | R1$^a$ = 0.0316, wR2$^b$ = 0.0544 |

$^a$ $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0502P)^2]$, where $P = [(F_o^2) + 2F_c^2]/3$.

X-ray powder diffraction analysis was performed on a Guinier-Hägg focusing camera, with Cu K$\alpha_1$ radiation. Fine silicon powder was used as an internal standard. The unit cell parameters were determined to be $a = 7.006$ Å, $b = 11.798$ Å, $c = 19.520$ Å, and $\alpha = \beta = \gamma = 90°$, using TREOR90.[12]

Qualitative energy dispersive spectroscopy (EDS) analysis of single crystals was performed on a JEOL JSM880 scanning electron microscope equipped with a Link ISIS system. Elemental analysis (C, N, and H) was performed on a FISON 1108 element analyzer by Mikro Kemi AB, Stockholm, Sweden.

Thermogravimetrical (TG) analysis was performed in oxygen atmosphere on a Perkin-Elmer TGA 7 from 20 °C up to 400 °C, with a heating rate of 10 °C/min. The IR spectrum was recorded on a Bruker IFS-55 FTIR spectrometer, using a potassium bromide pellet.

Single-crystal X-ray diffraction data were collected at 20 °C, on a STOE IPDS diffractometer equipped with an image plate, using graphite-monochromatized Mo Kα radiation (0.710 73 Å) from a rotating anode generator. A total of 12 895 reflections, of which 1582 were unique, were collected in the region $4.0° < 2\theta < 52.0°$. The space group was determined to be *Pbcn* by analyzing systematic absences ($0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h + k = 2n$) of all reflections. A numerical absorption correction was applied with a linear absorption coefficient of 9.30 mm$^{-1}$, using X-SHAPE.[13] Structure solution and refinement were carried out with the SHELX97 software package,[14,15] using atomic scattering factors for neutral atoms. The crystallographic data and the results of the structure refinement of the title compound are given in Table 1.

## Results and Discussion

**Crystal Structure Solution and Refinement.** The structure was solved by direct methods. All non-hydrogen atoms of the structure were located from the initial solution or through subsequent electron density difference Fourier maps. The atomic coordinates and the thermal displacement parameters for all unique atoms are given in Table 2. Three unique germanium positions and eight framework anions were found. Two unique nitrogen positions and one water oxygen position were located outside the framework (Figure 1). First only oxygen atoms were assigned to the framework anions. During the refinement, the three terminal sites on Ge1, defined as oxygen atoms, displayed negative thermal displacement parameters. When these sites were redefined as fluorine atoms, reasonable thermal displacement parameters were obtained. The presence of fluorine in the structure, as well as germanium, oxygen, and nitrogen, had been confirmed through EDS analysis.

**Table 2.** Final Coordinates and Equivalent Isotropic Displacement Parameters for $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$

| atom | *x* | *y* | *z* | $U_{eq}$ (Å$^2$)$^a$ |
|---|---|---|---|---|
| Ge1 | −0.04830(4) | 0.17712(3) | 0.13389(2) | 0.0079(1) |
| Ge2 | 0.28048(5) | 0.26208(3) | 0.23749(2) | 0.0071(1) |
| Ge3 | 0.5 | 0.48956(4) | 0.25 | 0.0070(2) |
| F1 | 0.0261(3) | 0.28664(18) | 0.07248(11) | 0.0187(6) |
| F2 | 0.0446(3) | 0.07280(19) | 0.07284(11) | 0.0198(6) |
| F3 | −0.2708(3) | 0.17059(19) | 0.08502(11) | 0.0210(7) |
| O1 | 0.5 | 0.1926(3) | 0.25 | 0.0139(10) |
| O2 | 0.1912(3) | 0.1813(2) | 0.17111(12) | 0.0139(7) |
| O3 | 0.1487(3) | 0.2892(2) | 0.31083(12) | 0.0138(7) |
| O4 | 0.3415(3) | 0.3984(2) | 0.20517(12) | 0.0105(7) |
| O5 | 0.3642(3) | 0.5635(2) | 0.30913(12) | 0.0123(7) |
| O6w$^b$ | 0.3759(16) | 0.0519(10) | 0.0014(5) | 0.045(4) |
| N1 | 0.4911(5) | 0.0059(3) | 0.1410(2) | 0.0240(11) |
| N2 | 0.4390(5) | 0.3318(3) | 0.05921(18) | 0.0276(11) |

| atom | *x* | *y* | *z* | $U_{iso}$ (Å$^2$) |
|---|---|---|---|---|
| H1w$^b$ | 0.266(15) | 0.054(13) | 0.030(7) | 0.0671 |
| H2w$^b$ | 0.45(2) | −0.016(9) | 0.009(10) | 0.0671 |
| H3 | 0.544(5) | 0.040(3) | 0.1030(13) | 0.0359 |
| H4 | 0.361(3) | 0.028(3) | 0.1470(19) | 0.0359 |
| H5 | 0.558(5) | 0.028(3) | 0.1818(13) | 0.0359 |
| H6 | 0.496(5) | −0.0744(14) | 0.138(2) | 0.0359 |
| H7 | 0.444(6) | 0.338(3) | 0.0118(9) | 0.0416 |
| H8 | 0.318(3) | 0.304(3) | 0.0728(19) | 0.0416 |
| H9 | 0.463(5) | 0.4023(19) | 0.0804(18) | 0.0416 |
| H10 | 0.534(4) | 0.280(3) | 0.0744(19) | 0.0416 |

$^a$ $U_{eq}$ = one-third of the trace of the orthogonalized **U** tensor. $^b$ Atoms with site of occupancy (SOF) 0.334(11).

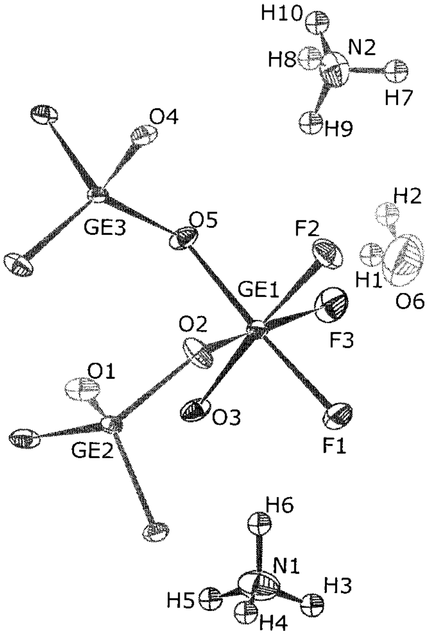

**Figure 1.** Ortep plot of the framework building units. The thermal ellipsoids represent 50% probability.

All non-H atoms were refined anisotropically. The positional parameters of the hydrogen atoms, corresponding to the positive maxima of the difference Fourier synthesis, were refined by taking into account the bond-valence balance and constrained to chemically reasonable hydrogen-bonding distances and angles by means of the DFIX instructions in the SHELXL97 program. Hydrogen atoms were restrained to a distance of 0.95 Å to their

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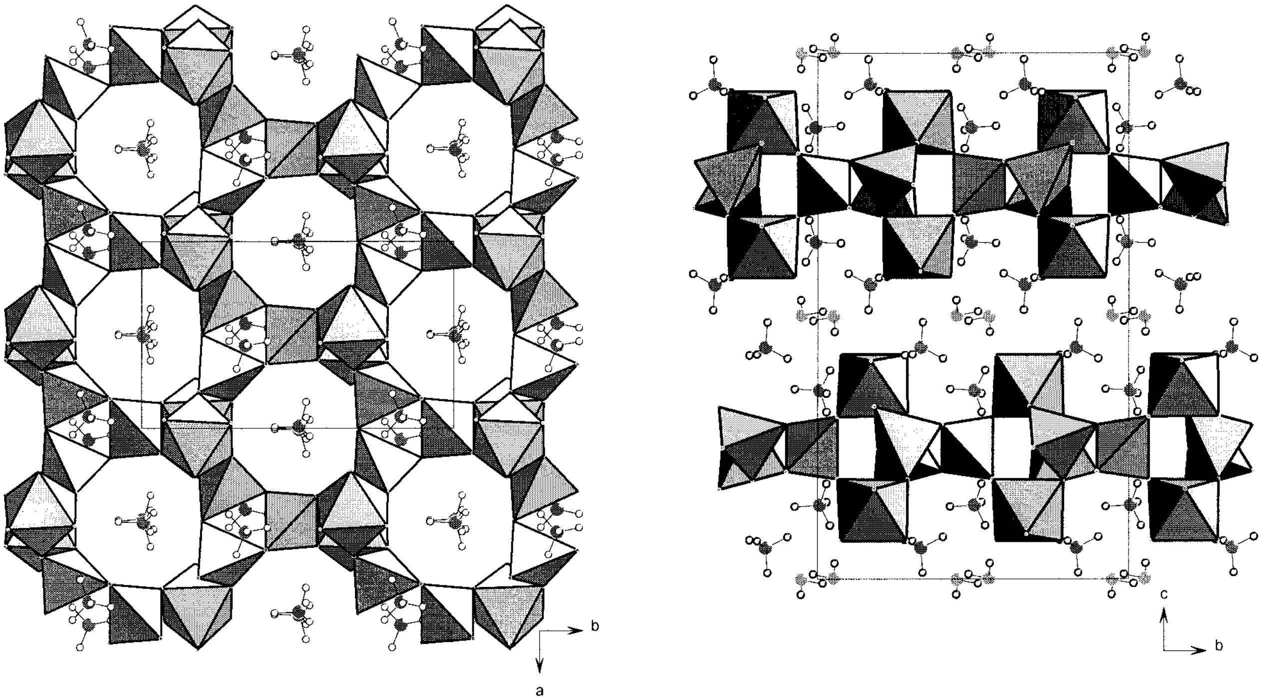

(a) (b)

**Figure 2.** (a) The mixed framework sheet viewed along the *c* axis. Half of the ammonium ions are located in the middle of the nine-membered rings and the other half in the interlayer, below and above the three-membered rings. The water molecules are omitted for clarity. (b) Complete structure model viewed along the *a* axis, showing the connectivity between the octahedra and the tetrahedra within the layers. N atoms are shown by solid dark circles, O atoms by solid gray circles, and H atoms by open circles. The structure models were drawn using DIAMOND.[16]

bound atom (N or O). The distances between all the four hydrogen atoms bound to each nitrogen atom were restrained to 1.55(1) Å, giving a regular tetrahedral shape to the ammonium ion. The distances between the hydrogen atoms of the water molecule were treated in the same way. The isotropic displacement parameters of the hydrogen atoms were fixed to be 1.5 times that of the atom to which the hydrogen atoms were bound and forced to be identical in the same groups. The model, including the hydrogen atoms, was refined by full-matrix least-squares techniques against $F^2$ until $\Delta/\sigma_{\max}$ was less than 0.005. The final agreement factors ($R$ values) were $R = 0.0223$ and $R_w = 0.0514$. The occupancy of the water molecule (both the oxygen and the hydrogen atoms) was refined to be 0.334(11). The thermal displacement parameters of the hydrogen-bound water oxygen were, as expected, larger than those of the framework oxygen atoms (Figure 1).

**Crystal Structure Description.** $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$ is a 2D framework structure, layered perpendicular to the *c* axis. The framework is built by three- and nine-membered germanium polyhedral rings. The three-membered rings are built up of tetrahedra. These rings are connected by pairs of octahedra, in such a way that they form a nine-membered ring (Figure 2a). The nine-membered rings are formed by six $GeO_4$ tetrahedra ($T_d$) and three $GeO_3F_3$ octahedral pairs ($O_h$), in the sequence $2T_d{-}O_h{-}2T_d{-}O_h{-}2T_d{-}O_h$ (Figure 2a). Each octahedron is corner-shared with three tetrahedra from three different 9-rings. The three terminal fluorine atoms point toward the interlayer. Each unit cell contains two layers. Within each layer, the tetrahedra are located in the middle of the layer and the octahedra situated on each side of the tetrahedra, as shown in Figure 2b.

The 9-rings form channels along the *c* axis with a diameter of 5.3 Å, calculated as the shortest oxygen to oxygen distance across the ring. This corresponds to an approximate accessible pore size of 2.3 Å, when the van der Waals radius of the oxygen atoms (1.50 Å) is taken into account.[17] Two charge balancing ammonium ions are located within each ring. In the projection along the *c* axis, these ammonium ions are located exactly in the middle of the 9-ring channel (Figure 2a). In a projection perpendicular to the *c* axis, they are at a similar height (*z* coordinates) as the $GeO_3F_3$ octahedra (Figure 2b).

The 3-rings are built up by three tetrahedra with Ge−O−Ge angles of 124.5° for the Ge2−O1−Ge2 bond and 121.5° for the two Ge3−O4−Ge2 bonds (Table 3, Figure 2a). While the 9-rings continue through the layers, the 3-rings and the octahedra alternate through the layers, resulting in 3-ring cavities, open to the interlayer at both sides. Structures with three-membered rings have been predicted to have low framework density[18] and, thus, very open structures. Until today, only a few silicate[19] and germanate[20] structures containing 3-rings have been reported.

The interlayer has a thickness of 3.4 Å, calculated as the shortest fluorine to fluorine distance between the layers. The remaining two ammonium ions are located between the framework layers, one on each side of the three-membered cavities (Figure 2b). The water molecules are inserted in the middle of the interlayer, in the channels formed by the 9-rings (Figure 2a).

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**Table 3.** Selected Bond Distances (Å) and Angles (deg) for $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O^a$

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| $GeO_3F_3$ Octahedron | | | |
| Ge1−F1 | 1.838(2) | Ge1−O2 | 1.829(2) |
| Ge1−F2 | 1.833(2) | Ge1−O3_a | 1.846(2) |
| Ge1−F3 | 1.829(2) | Ge1−O5_c | 1.847(2) |
| $GeO_4$ Tetrahedron | | | |
| Ge2−O1 | 1.7599(17) | Ge2−O3 | 1.733(2) |
| Ge2−O2 | 1.726(2) | Ge2−O4 | 1.780(2) |
| $GeO_4$ Tetrahedron | | | |
| Ge3−O4 × 2 | 1.776(2) | Ge3−O5 × 2 | 1.732(2) |
| Bond Angles | | | |
| Ge−O−Ge | | | |
| Ge2−O1−Ge2_b | 124.5(2) | Ge2−O4−Ge3 | 121.51(13) |
| Ge1−O2−Ge2 | 130.21(13) | Ge1_d−O5−Ge3 | 125.79(12) |
| Ge1_a−O3−Ge2 | 123.61(13) | | |
| $GeO_3F_3$ Octahedron | | | |
| F1−Ge1−F2 | 86.98(10) | F2−Ge1−O2 | 87.17(10) |
| F1−Ge1−F3 | 86.05(10) | F2−Ge1−O3_a | 175.21(10) |
| F1−Ge1−O2 | 88.85(10) | F2−Ge1−O5_c | 91.27(10) |
| F1−Ge1−O3_a | 89.18(10) | F3−Ge1−O2 | 171.91(10) |
| F1−Ge1−O5_c | 175.81(10) | F3−Ge1−O3_a | 90.59(10) |
| F2−Ge1−F3 | 86.29(10) | F3−Ge1−O5_c | 90.03(10) |
| $GeO_4$ Tetrahedron | | | |
| O1−Ge2−O2 | 99.42(10) | O2−Ge2−O3 | 121.94(10) |
| O1−Ge2−O3 | 115.91(8) | O2−Ge2−O4 | 108.66(11) |
| O1−Ge2−O4 | 105.08(12) | O3−Ge2−O4 | 104.71(11) |
| $GeO_4$ Tetrahedron | | | |
| O4−Ge3−O5 | 106.85(10) | O4_b−Ge3−O5 | 108.67(11) |
| O4−Ge3−O4_b | 105.48(11) | O5−Ge3−O5_b | 119.50(11) |
| O4−Ge3−O5_b | 108.67(11) | O4_b−Ge3−O5_b | 106.85(10) |

[a] Symmetry transformations: (a) $-x, y, {}^1/_2 - z$; (b) $1 - x, y, {}^1/_2 - z$; (c) $-{}^1/_2 + x, -{}^1/_2 + y, {}^1/_2 - z$.

Selected framework bond distances and angles are given in Table 3. The octahedron is quite regular with similar Ge−O and Ge−F distances (1.83−1.85 Å). Both tetrahedra are slightly distorted, with Ge−O distances ranging from 1.73 to 1.78 Å. The Ge2 tetrahedron has bond angles between 99 and 122°, while the Ge3 tetrahedron is less distorted with angles ranging from 105 to 120°.

**Hydrogen Bonds.** There are 10 symmetrically unique H positions. Hydrogen bonding plays two distinct roles in the structure: (1) the $NH_4^+$ cations within the 9-rings are hydrogen bound to the framework, and (2) H bonds bridge between the mixed anion framework sheets and the interlayer $NH_4^+$ cations and $H_2O$ molecules, providing the only linkage between the layers.

The four hydrogen atoms (H3, H4, H5, and H6) of the $NH_4^+$ cation within the 9-rings participate in medium-weak and weak hydrogen bonding in the structure. The medium-weak interactions are N1−H3···F3 and N1−H6···F1 with H···F distances of 2.04 and 2.09 Å, respectively. The weak hydrogen bonds are between this $NH_4^+$ cation and all the oxygen atoms from both the framework and the water molecule, with H···O distances between 2.17 and 2.39 Å.

The hydrogen atoms of the interlayer $NH_4^+$ cation interact mainly with the fluorine atoms in the $GeO_3F_3$ octahedron. The hydrogen bonding is medium-weak and involve N2−H10···F3, N2−H9···F2, N2−H8···F1, and N2−H7···F2 with H···F distances of 1.89, 2.02, 2.05, and 2.08 Å, respectively. The water molecule is strongly hydrogen-bound to the framework through O6−H1···F2, with distances H1···F2 of 1.78 Å and O6···F2 of 2.72 Å and an O6−H1−F2 angle of 170.92°.

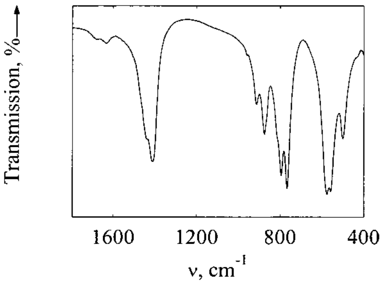

**Figure 3.** FTIR spectrum of $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$.

**IR Analysis.** The FTIR spectrum from the title compound is shown in Figure 3. The peaks at 1411 and 1439 cm$^{-1}$ correspond to the bond-bending frequencies of the ammonium ions. The peaks at 876 and 914 cm$^{-1}$ can be assigned to Ge−O vibrations of the tetrahedral and octahedral germanium polyhedra, respectively.[21] The sharp peaks at 766 and 794 cm$^{-1}$ are due to the symmetrical and asymmetrical vibrations of Ge−F, respectively.[22] The absorption bands at 558 and 576 cm$^{-1}$ are caused by a symmetrical stretch of Ge−O. The peak at 500 cm$^{-1}$ is due to bending vibrations of Ge−O. FTIR spectroscopy did not show any peak due to terminal hydroxyl groups. This strengthens our assertion that fluorine atoms, instead of hydroxyl groups, are bound to germanium.

**TG Analysis.** Thermogravimetrical analysis showed a gradual weight loss (>1.5%) between 40 and 110 °C, resulting from the loss of the crystal water. The structure decomposed between 250 and 400 °C with a weight loss of 26%. XRPD showed that the residual phase was pure $GeO_2$. The theoretical weight loss, calculated from the composition determined by X-ray diffraction, is 26%. The exact match of the calculated weight loss with the experimental one confirms the composition of the title compound. The decay of the framework at low temperature is caused by the breaking of all stabilizing hydrogen bonds between the layers, as the water molecules and ammonium ions leave the compound. The elemental analysis, performed as double tests, gave N at 7.7, 7.7 wt %, H at 2.8, 3.0 wt %, and C at <0.3, <0.3 wt %, which are in good agreement with the calculated values N at 7.9 wt %, H at 2.5 wt %, and C at 0 wt %. The nitrogen and carbon content confirms that ammonium ions, instead of the template 2,6-diaminopyridine, act as framework charge balancing cations.

The compound has a high charge density, with 0.8 ammonium ion/germanium atom, which corresponds to an ion exchange capacity of 5.67 mmol/g. The layering perpendicular to the three- and nine-membered rings gives a very open structure, well suited for ion exchange.

## Conclusion

A novel germanium framework compound, $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$, consisting of three- and nine-membered rings, has been synthesized and characterized. The compound has a 2D mixed framework, in which germanium exhibits both 4- and 6-coordination. The ability to form a variety of different ring structures, including three-membered, shows the potential in using germanium as polyhedral building blocks in the synthesis of open framework compounds.

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**Supporting Information Available:** Listings of crystal data and details of the structure determination, final coordinates, anisotropic and equivalent isotropic displacement parameters for the non-hydrogen atoms, coordinates and isotropic displacement parameters for the hydrogen atoms, bond distances and bond angles, torsion angles, contact distances, hydrogen bonds, and powder X-ray diffraction data and an X-ray powder diffraction pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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