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Hydrothermal Synthesis and Structural Characterization of a New Organically Templated Germanate, $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$

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A new open-framework germanium oxide $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$ has been hydrothermally synthesized at 180 °C for 6 days by using the tris(2-aminoethyl)amine (tren) molecule as a structure-directing agent. This compound was characterized by means of single-crystal X-ray diffraction and FTIR. It crystallizes in the noncentric monoclinic system *Cm* ($a = 14.0495(2)$ Å, $b = 12.8058(3)$ Å, $c = 9.2637(2)$ Å, $\beta = 128.406(1)°$, $Z = 4$). Its three-dimensional framework is built up from GeO_4 and $GeO_3(OH)$ tetrahedra connected by vertexes to GeO_5 trigonal bipyramids and GeO_6 octahedra. A pseudo-cubic building unit ("4-3" subunit) consists of four GeO_4 tetrahedra, two GeO_5 trigonal bipyramids, and one GeO_6 octahedron (Ge_7). In the "4-3" block, the GeO_5 trigonal bipyramids share a common edge. This Ge_7 entity is linked to three tetrahedral units GeO_3X (X = O, OH), and this forms an original decameric building unit $Ge_{10}O_{21}(OH)$ which is new in the germanates crystal chemistry. It results in a relatively dense open framework composed of pear-shape cavities ($7^86^25^24^43^2$) encapsulating the triprotonated tren molecule. The inorganic network contains small pores delimited by 7-ring channels running along [001].

Introduction

The synthesis of microporous compounds has been extensively studied because of their industrial applications in the fields of catalysis, ionic exchange, molecular sieves, gas separation, etc. This class of solids was initially zeolites (aluminosilicates), and since the past decades, new series of porous crystalline materials, including phosphates, sulfides, borates, and nitrides, were discovered.[1] The incorporation of many elements (Al, Ga, In, Mg, transition metals, etc.) into the inorganic framework led to a wide structural diversity with new architectures. The utilization of organic molecules (amine, tetralkylammoniums, etc.) as templates under mild hydrothermal conditions facilitated the formation of a great variety of three-dimensional networks.

One of the strategies used for the design of new topologies is related to the observation of the different isomorphic substituted forms of silica SiO_2 (major constituent in zeolites). In the early 1980s, this strategy gave rise to the development of the microporous $AlPO_4$-n family[2] and their derived compounds. More recently, investigations were undergone in the study of the synthesis of germanates, GeO_2. Since the pioneering work reporting the possibility of making some organically templated open-framework germanates by Xu in the beginning of 1990s,[3−6] the research efforts were lately continued with the characterization of several new types of frameworks.[7−19] In contrast with silicon, which is

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usually tetrahedrally coordinated, germanium may adopt three types of coordinations (GeO_4, tetrahedron, GeO_5, square pyramid or trigonal bipyramid, and GeO_6, octahedron) due to its larger atomic radius. It results in longer metal−oxygen distances (≈1.76 Å for Ge−O and ≈1.61 Å for Si−O), which makes possible to have Ge−O−Ge angles smaller than those observed in silicates.[20] Therefore, the occurrence of 3-ring subunits is often encountered in germanate crystal chemistry[21] and may favor the formation of solids with very low framework density.[22] Moreover, the flexibility of the polyhedral configurations for germanium allows for the formation of complex three-dimensional networks; some of them present an extra-large pore system as shown in the germanates FDU-4[23] and ASU-16,[24] which exhibit structures with 24-membered-ring channels. Both phases were prepared from a mixture of organic solvent (dimethylformamide or pyridine) and water in the presence of an amine as template.

We report herein the hydrothermal synthesis and structural characterization of a new germanate $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$ obtained with the tren (tris(2-aminoethyl)amine) molecule in purely aqueous medium. The use of this organic structure-directing agent was previously reported in the synthesis of FDU-4[23] from a dimethylformamide/water mixture as solvent.

Experimental Section

Synthesis. The germanate $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$ was hydrothermally synthesized under autogenous pressure using tris(2-aminoethyl)amine as structure-directing agent. The starting reactants were germanium dioxide (GeO_2, ABCR, 99.98%), orthophosphoric acid (H_3PO_4, Prolabo, 85%), tris(2-aminoethyl)amine or tren ($N_4C_6H_{18}$, Acros, 96%), and deionized water. Typically, the reaction mixture containing the molar ratio 1 GeO_2 (0.363 g), 80 H_2O (4.940 g), 1 H_3PO_4 (0.400 g), 2 tren (1.015 g), was placed in a 23 mL Teflon-lined steel Parr autoclave at 180 °C for 6 days. The synthesis pH was 10. A white powder was filtered off, washed with deionized water, and dried in air at room temperature. A preliminary X-ray powder diffraction pattern showed it to be a mixture of several unknown phases, but crystals of the title compound are easily isolated from the bulk product. Although the title compound did not contain phosphorus, the phosphoric acid is needed for its formation. Some investigations were performed for the synthesis of the germanate without any acid or with other inorganic acids (HCl, H_2SO_4, ...), and our attempts were unsuccessful.

Single-Crystal X-ray Structure Analysis. A colorless platelet crystal was selected under a polarizing optical microscope and glued onto a glass fiber for a single-crystal X-ray diffraction experiment. The diffraction intensities were measured on a Siemens Smart-CCD three-circle diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (monochromated Mo Kα radiation). Slightly more than one hemisphere was recorded with an ω width of 0.3° (exposure time per frame: 10 s). The absorption corrections were based on symmetry equivalent reflections using the SADABS[25] program. On the basis of systematic absences, the space groups were determined to be *C*2/*m*, *Cm*, or *C*2. The examination of the statistics intensity distribution shows that the compound would be compatible with a noncentric space group. The structure was solved in the space group *Cm* by using direct methods, and the topology of the final structure confirmed the noncentric character. The six unique germanium atoms were first revealed, and the remaining atoms (O, C, N) were placed from successive Fourier map analyses. One branch of the template amine is disordered in two equivalent positions, and the corresponding nitrogen (N2) and carbon (C1 and C2) atoms have been refined with a 50% occupancy factor. Some short C−C (1.24(4) Å) or long C−N (1.64(3) Å) distances are abnormally observed for the two branches of the tren molecule. This may reflect the motion of the organic molecule within the cavities of the structure. The positions of the carbon atoms revealed from the examination of the difference Fourier maps may correspond to an average location of the organic molecule. The final refinement including anisotropic thermal parameters of all non-hydrogen atoms converged to R1 = 0.0468 and wR2 = 0.1103. All the calculations were performed by using the SHELX-TL[26] program on the basis of F^2. The crystal data are given in Table 1. The atomic coordinates and selected bond distances and angles are summarized in Tables 2 and 3, respectively.

Table 1. Crystal Data and Structure Refinement for $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$

empirical formula	$Ge_{10}O_{22}N_4C_6H_{22}$
fw	1228.00
temp	293(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, *Cm*
unit cell dimens	$a = 14.0495(2)$ Å
	$b = 12.8058(3)$ Å, $\beta = 128.406(1)°$
	$c = 9.2637(2)$ Å
volume	1306.06(5) Å^3
Z, calcd density	2, 3.067 Mg/m^3
abs coeff	11.433 mm^{-1}
final *R* indices [$I > 2\sigma(I)$]	R1^a = 0.0468, wR2^b = 0.1103
R indices (all data)	R1^a = 0.0568, wR2^b = 0.1174

^{a} R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 $= \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.00635P)^2]$ where $P = [(F_o^2) + 2F_c^2]/3$.

IR Spectroscopy. The IR spectrum was recorded on a Nicolet 550 FTIR spectrometer at room temperature in the range 400−2000 cm^{-1}, using a potassium bromide pellet.

Results and Discussion

Structure Description. The framework structure is assembled from a network of GeO_4 and $GeO_3(OH)$ tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra. There are six crystallographically inequivalent germanium sites, four of them are tetrahedrally coordinated to four oxygen atoms with Ge−O distances ranging from 1.717(7) to 1.769(5) Å, which are similar to those reported for the quartz form of GeO_2 (1.741(3) Å).[27] The oxygen atom O10, which is

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$

	x	*y*	*z*	*U*(eq)[a]
Ge(1)	9787(1)	6189(1)	1504(1)	16(1)
Ge(2)	8861(1)	6181(1)	−4305(1)	16(1)
Ge(3)	5157(1)	5000	−5556(2)	22(1)
Ge(4)	3657(1)	2785(1)	−7184(1)	16(1)
Ge(5)	1112(1)	3866(1)	−10188(1)	15(1)
Ge(6)	8099(1)	5000	−2221(2)	14(1)
O(1)	8367(6)	6061(6)	−587(9)	18(1)
O(2)	313(9)	5000	−7259(14)	24(2)
O(3)	10851(6)	6684(6)	1284(9)	21(2)
O(4)	9790(6)	7095(6)	2935(10)	23(2)
O(5)	263(6)	3302(6)	−12452(9)	24(2)
O(6)	8210(8)	7053(6)	−6124(10)	29(2)
O(7)	7844(7)	6062(5)	−3868(10)	20(1)
O(8)	9092(10)	5000	4960(14)	21(2)
O(9)	6468(9)	5000	−3277(13)	21(2)
O(10)	5431(13)	5000	−7147(18)	56(4)
O(11)	4336(8)	3887(6)	−5805(11)	30(2)
O(12)	2388(6)	2977(6)	−9438(9)	17(1)
O(13)	2024(8)	5000	−9599(15)	20(2)
O(14)	9827(8)	5000	−1088(13)	14(2)
N(1)	4074(15)	5000	−2160(20)	42(4)
N(2)* [b]	6080(20)	6044(16)	−1110(30)	35(5)
N(3)	6987(9)	7732(8)	−3114(13)	28(2)
C(1)*	5240(20)	5460(20)	−610(40)	39(6)
C(2)*	6240(20)	5400(20)	340(40)	40(6)
C(3)	8060(30)	9070(20)	−3290(40)	105(8)
C(4)	7790(40)	8660(30)	−2370(60)	166(16)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] (*) Site occupancy factor: 50%.

Table 3. Bond Lengths (Å) and Angles (deg) for $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$[a]

Ge(1)−O(1)	1.720(7)	Ge(5)−O(5)	1.799(7)
Ge(1)−O(3)	1.748(7)	Ge(5)−O(12)	1.856(6)
Ge(1)−O(4)	1.759(7)	Ge(5)−O(14)#8	2.048(7)
Ge(1)−O(2)#1	1.768(5)	Ge(6)−O(9)	1.850(10)
Ge(2)−O(7)	1.717(7)	Ge(6)−O(1)	1.890(7)
Ge(2)−O(6)	1.734(7)	Ge(6)−O(1)#4	1.890(7)
Ge(2)−O(5)#2	1.751(7)	Ge(6)−O(7)#4	1.904(7)
Ge(2)−O(8)#3	1.769(5)	Ge(6)−O(7)	1.904(7)
Ge(3)−O(9)	1.738(10)	Ge(6)−O(14)	1.957(9)
Ge(3)−O(10)	1.740(12)	N(1)−C(1)	1.48(3)
Ge(3)−O(11)	1.757(8)	N(1)−C(3)#5	1.64(3)
Ge(3)−O(11)#4	1.757(8)	N(2)−C(2)	1.47(3)
Ge(4)−O(12)	1.724(6)	N(2)−C(1)	1.68(3)
Ge(4)−O(6)#5	1.733(7)	N(3)−C(4)	1.49(4)
Ge(4)−O(11)	1.737(7)	C(1)−C(2)#4	1.56(4)
Ge(4)−O(4)#6	1.765(7)	C(3)−C(4)	1.24(4)
Ge(5)−O(3)#7	1.764(7)	C(3)−N(1)#10	1.64(3)
Ge(5)−O(13)	1.783(5)		

O(1)−Ge(1)−O(3)	112.4(3)	O(13)−Ge(5)−O(12)	92.4(3)
O(1)−Ge(1)−O(4)	111.7(3)	O(5)−Ge(5)−O(12)	88.7(3)
O(3)−Ge(1)−O(4)	104.3(3)	O(3)#7−Ge(5)−O(14)#8	92.5(3)
O(1)−Ge(1)−O(2)#1	111.9(4)	O(13)−Ge(5)−O(14)#8	80.2(3)
O(3)−Ge(1)−O(2)#1	110.1(4)	O(5)−Ge(5)−O(14)#8	91.8(3)
O(4)−Ge(1)−O(2)#1	106.0(4)	O(12)−Ge(5)−O(14)#8	171.7(3)
O(7)−Ge(2)−O(6)	105.8(4)	O(9)−Ge(6)−O(1)	89.3(3)
O(7)−Ge(2)−O(5)#2	113.4(4)	O(9)−Ge(6)−O(1)#4	89.3(3)
O(6)−Ge(2)−O(5)#2	107.6(4)	O(1)−Ge(6)−O(1)#4	91.9(4)
O(7)−Ge(2)−O(8)#3	113.2(4)	O(9)−Ge(6)−O(7)#4	91.2(3)
O(6)−Ge(2)−O(8)#3	106.8(4)	O(1)−Ge(6)−O(7)#4	179.3(3)
O(5)#2−Ge(2)−O(8)#3	109.7(4)	O(1)#4−Ge(6)−O(7)#4	88.4(3)
O(9)−Ge(3)−O(10)	113.8(6)	O(9)−Ge(6)−O(7)	91.2(3)
O(9)−Ge(3)−O(11)	105.9(3)	O(1)−Ge(6)−O(7)	88.4(3)
O(10)−Ge(3)−O(11)	111.2(4)	O(1)#4−Ge(6)−O(7)	179.3(3)
O(9)−Ge(3)−O(11)#4	105.9(3)	O(7)#4−Ge(6)−O(7)	91.2(4)
O(10)−Ge(3)−O(11)#4	111.2(4)	O(9)−Ge(6)−O(14)	179.6(4)
O(11)−Ge(3)−O(11)#4	108.5(6)	O(1)−Ge(6)−O(14)	90.4(3)
O(12)−Ge(4)−O(6)#5	107.3(4)	O(1)#4−Ge(6)−O(14)	90.4(3)
O(12)−Ge(4)−O(11)	117.2(4)	O(7)#4−Ge(6)−O(14)	89.1(3)
O(6)#5−Ge(4)−O(11)	104.5(4)	O(7)−Ge(6)−O(14)	89.1(3)
O(12)−Ge(4)−O(4)#6	111.1(3)	C(1)−N(1)−C(3)#5	155.9(17)
O(6)#5−Ge(4)−O(4)#6	108.9(4)	C(1)#4−N(1)−C(3)#5	109.2(14)
O(11)−Ge(4)−O(4)#6	107.4(4)	C(3)#5−N(1)−C(3)#13	93(2)
O(3)#7−Ge(5)−O(13)	122.9(4)	N(1)−C(1)−C(2)#4	109.2(19)
O(3)#7−Ge(5)−O(5)	115.8(4)	N(2)−C(2)−C(1)#4	108(2)
O(13)−Ge(5)−O(5)	120.9(4)	C(4)−C(3)−N(1)#10	113(3)
O(3)#7−Ge(5)−O(12)	94.7(3)	C(3)−C(4)−N(3)	119(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z + 1$; #2 $x + 1, -y + 1, z + 1$; #3 $x, y, z - 1$; #4 $x, -y + 1, z$; #5 $x - {}^{1}/_{2}, y - {}^{1}/_{2}, z$; #6 $x - {}^{1}/_{2}, y - {}^{1}/_{2}, z - 1$; #7 $x - 1, -y + 1, z - 1$; #8 $x - 1, y, z - 1$; #9 $x + {}^{1}/_{2}, y + {}^{1}/_{2}, z + 1$; #10 $x + {}^{1}/_{2}, y + {}^{1}/_{2}, z$; #11 $x, y, z + 1$; #12 $x, -y + 1, z + 1$; #13 $x - {}^{1}/_{2}, -y + {}^{3}/_{2}, z$.

attached to Ge3, is terminal and corresponds to a hydroxyl group (based on bond-valence calculations). The O−Ge−O angles, 104.3(3)−117.2(4)°, are within the expected range for a tetrahedral geometry. However, the observation of a wide variation (from 140.5(4)° to 117.5(4)°) for the Ge−O−Ge angles is often reported in germanate crystal chemistry. This is in contrast to the situation found in the silicate parent family where the Si−O−Si angles are rather close to 140°. The smaller Ge−O−Ge angle value (117.5(4)−118.9(4)°) comes from the existence of 3-ring units in the framework. One germanium atom Ge5 exhibits a 5-fold coordination (trigonal bipyramid) characterized by three equatorial Ge−O distances ranging from 1.764(7) to 1.799(7) Å and two longer axial Ge−O distances 1.856(6) and 2.048(7) Å. Whereas all the germanium polyhedra are connected by their vertexes to each other, two adjacent GeO_5 trigonal bipyramids are linked by a common edge. One oxygen atom of this edge O14 is 3-fold coordinated; it connects two germanium atoms Ge5 with the germanium atom Ge6. The remaining germanium atom Ge6 is octahedrally bound to six oxygen atoms with expected longer Ge−O distances (1.850−1.957 Å).

The structure can be described from a building unit comprising a Ge_7O_{16} species attached to three tetrahedral units GeO_3X (X = O, OH) (Figure 1). The heptameric unit Ge_7O_{16} (Figure 1a) contains four GeO_4 tetrahedra, two GeO_5 trigonal bipyramids, and one GeO_6 octahedron. Two GeO_4 tetrahedra are connected to the pair of edge-sharing trigonal bipyramids by forming a four Ge-center ring. This 4-ring unit is connected to a 3-ring unit composed of the other two GeO_4 tetrahedra and the GeO_6 octahedron. The resulting “4-3” unit was previously observed in the fluorinated germanates ASU-12[8] and ASU-16[24] described by Yaghi and co-workers. The presence of fluorine induces some terminal Ge−F bondings (for the trigonal bipyramidal GeO_4F and octahedral GeO_5F) and generates interrupted open frameworks. This building block is reminiscent of the cubic species 4-4 (or D4R) composed of eight tetrahedral entities encountered in silicates (for instance, zeolite LTA) or in a recent germanate $(Me_3N)_6[Ge_{32}O_{64}]\cdot(H_2O)_{4.5}$.[14] In our compound, two of the tetrahedral centers of the D4R are replaced by one octahedral entity GeO_6. An oxygen atom is located at the center of the “4-3” unit and is linked to the three germanium atoms Ge6 and Ge5 (×2). The location of a central oxygen atom within the cubic unit is similar to that of a fluorine atom within the D4R cage in some fluorinated gallium phosphates such as cloverite,[28] Mu-2,[29] ULM-5,[30] or ULM-18.[31] In these cases, the fluorine was slightly shifted toward the gallium atoms

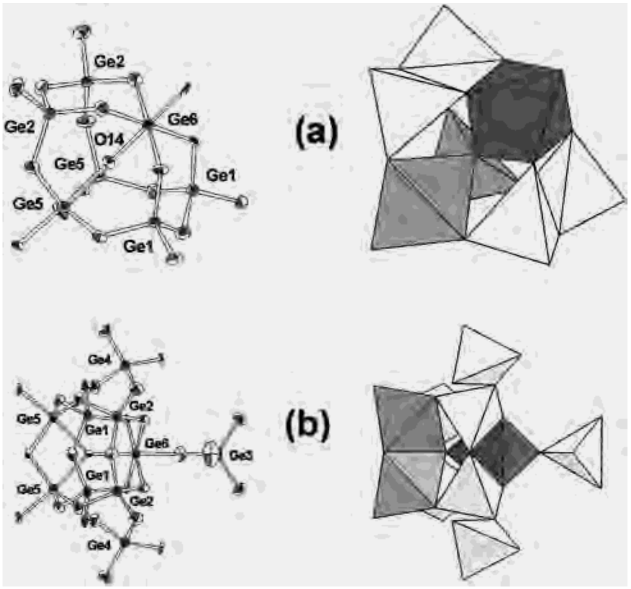

Figure 1. Ball-and-stick (thermal ellipsoids of 50% probability) and polyhedral views of the asymmetric units in $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$: (a) $[Ge_7O_{16}]$ building unit and (b) $[Ge_{10}O_{21}(OH)]$ building unit; GeO_4, white tetrahedra; GeO_5, light gray trigonal bipyramids; GeO_6, dark gray octahedra.

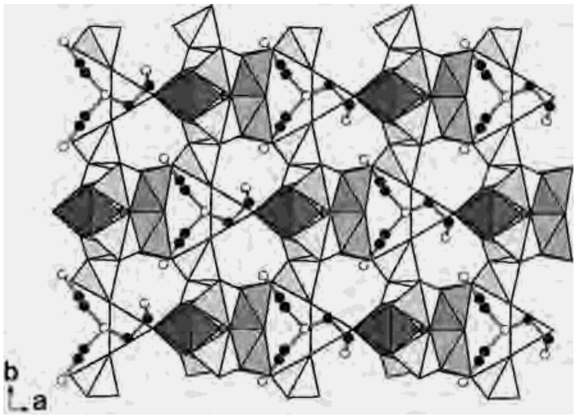

Figure 2. View of the 7-ring channels along [001] of the structure of $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$; GeO_4, white tetrahedra; GeO_5, light gray trigonal bipyramids; GeO_6, dark gray octahedra.

and increased the coordination number of the gallium from 4 to 5. The heptameric unit is connected to three tetrahedral GeO_3X units (X = O, OH), and this generates an original decameric building unit $Ge_{10}O_{21}(OH)$. The Ge_{10} species are linked to each other in order to generate the three-dimensional framework (Figure 2). It results in a relatively dense network (framework density of 15.3 T/1000 $Å^3$) as shown in Figure 3. The largest pore apertures are delimited by seven polyhedra, and 7-ring channels (calculated free diameter: 3 × 2.1 Å, based on an oxygen radius of 1.35 Å) are developed along [001] (Figure 2). The same orientation adopted by all the decameric units in the structure justifies the noncentric space group used in the determination of the structure.

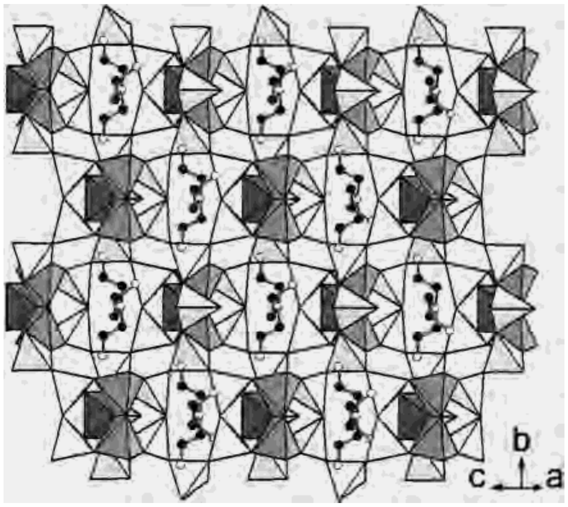

Figure 3. Projection of the framework of $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$ viewed along [101]; GeO_4, white tetrahedra; GeO_5, light gray trigonal bipyramids; GeO_6, dark gray octahedra.

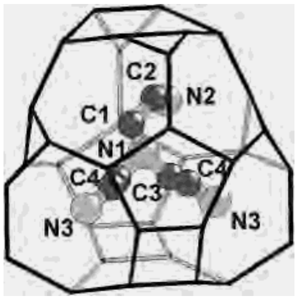

Figure 4. Representation of the tren molecule encapsulated in the cavity ($7^86^25^24^43^2$). Each node of the cage represents a germanium center. Oxygen atoms are omitted for clarity.

The tren molecule is encapsulated in the middle of a pear-shape cage (Figure 4) delimited by eight 7-ring, two 6-ring, two 5-ring, four 4-ring, and two 3-ring windows (cage $7^86^25^24^43^2$). This complex cavity has internal dimensions of 10 × 8.3 Å (calculations based on an oxygen radius of 1.35 Å). One branch (C1, C2, and N2) of this tetraamine is disordered in two equivalent positions due to the symmetry of the structure. The three terminal nitrogen atoms of the branched amine are protonated, and the positive charges of these ammonium groups balance the negative charges from the inorganic framework. Only the central nitrogen atom is not protonated with respect to its very low pK_a value ($pK_a < 2$). The tren molecule interacts through hydrogen bonds with the terminal ammonium groups and some oxygen atoms of the framework. The N···O observed distances range from 2.73(3) to 3.10(1) Å and involve only the N2 and N3 atoms. The N1···O interactions are much weaker and are characterized by N···O distances greater than 3.77(2) Å. Upon calcination, the decomposition of the organic molecule induces the collapse of the structure from 340 °C. It results in the formation crystalline germanium oxide at 500 °C.

IR Analysis. The FTIR spectrum of $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$ is shown in Figure 5. The peaks at 1603, 1532, and 1507 cm^{-1} correspond to the asymmetric and symmetric bond-bending frequencies of the terminal ammonium groups

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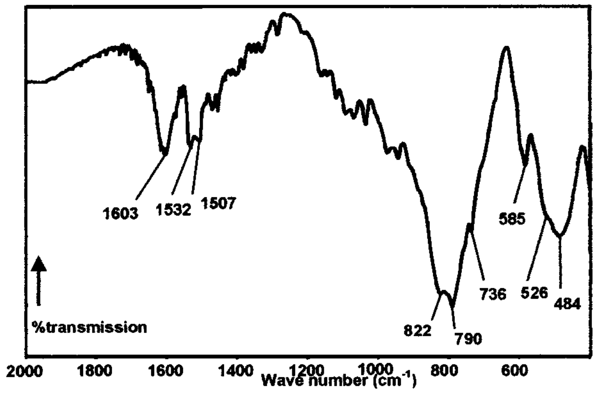

Figure 5. FTIR spectrum of $Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$.

(RNH_3^+) of the encapsulated tren molecule. The absorption bands at 822, 790, and 736 cm^{-1} can be assigned to the asymmetric stretching vibrations of Ge−O bonds.[32] The peaks at 585 and 526 cm^{-1} are attributed to the symmetrical stretch of Ge−O bonds.[33] A Ge−O bending vibration is observed at 484 cm^{-1}. The presence of a terminal hydroxyl group bound to the germanium atom Ge3 is not confirmed by this technique since the signature of such a species overlaps with that of RNH_3^+ in the range 3050−3500 cm^{-1}.

Conclusion

A novel germanate with a 5/11 Ge/O ratio has been synthesized hydrothermally at 180 °C using tren as a structure-directing molecule. This specific stoichiometry slightly differs from that observed in the dense phase quartz type GeO_2. It was recently reported in the germanate with a layered anionic network $Ge_5O_{11}H$[19] intercalated by protonated Dabco molecules. The structure shows another type of building unit which has not been previously encountered in other templated germanates. It consists of a pseudo cubic unit with seven germanium centers forming a “4-3” entity attached to three tetrahedral units GeO_4. The resulting decameric unit $Ge_{10}O_{22}$ units are linked to each other by generating a three-dimensionnal network composed of a pear-shape cavity hosting the triprotonated tren molecule.

Supporting Information Available: Tables of supplementary crystal data and structure refinement and anisotropic displacement parameters. Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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