Inorg. Chem. **2003**, *42*, 5960–5965

Inorganic Chemistry

Article

Synthesis and Characterization of a Novel Organically Templated Open Framework Zirconogermanate with Three- and Seven-Membered Rings

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Received April 3, 2003

A new organically templated microporous zirconogermanate, $(C_2H_{10}N_2)H_2O[ZrGe_3O_9]$ (denoted as FDZG-3), with a low framework density of 13.6 T/1000 Å^3, has been solvo/hydrothermally synthesized by using $ZrO(NO_3)_2 \cdot 2H_2O$ as a zirconium source and triethylenetetramine (TETA) as a structure direct agent. This compound was characterized by means of single-crystal X-ray diffraction analysis, thermogravimetrical analysis, and IR and UV–vis spectra. Its three-dimensional (3D) framework is built up by 1D sinusoidal germanate chains cross-linked by ZrO_6 octahedra, which forms a network containing three- and seven-membered rings (MRs). Four intersecting 7-MR channels can be observed along the *b* axis, *c* axis, [110], and [–110] directions, respectively. Charge-balancing $(C_2H_{10}N_2)^{2+}$ and extraframework water molecules are encapsulated within 7-MR channels and form hydrogen bonds with framework oxygen atoms. Crystal data for FDZG-3: $M = 533.13$, monoclinic, space group *Cc* (No.9), $a = 11.299(3)$ Å, $b = 7.7649(19)$ Å, $c = 13.835(3)$ Å, $\beta = 104.826(3)°$, $V = 1173.4(5)$ Å^3, $Z = 4$, R1 = 0.0263, wR2 = 0.0529.

Introduction

Recently, germanate-based microporous crystalline materials have raised increasing interest due to their abilities to form extended structures with GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra[1−4] and to the capacities of germinates to form odd membered rings (*x*-MR = *x*-membered ring), such as 3-MRs,[5−7] 5-MRs,[8] 7-MRs,[9] and 9-MRs,[5−7] among which the mixed coordination and 3-MRs are thought to be the keys to achieving large pore or low framework density in crystal structures.[10,11] It is expected that the combination of the zirconium and the germanate group in the same crystalline material may not only generate a new class of materials with novel framework topology but also bring about new properties. However, there is little research carried out on zirconogermanates,[12,13] although their zirconosilicate analogues have been studied much more. Also, in previously works, most of the zirconogermanates were hydrothemally synthesized in the present of NaOH or KOH by using $ZrCl_4$, $Zr(OC_2H_5)_4$, or $Zr(OC_3H_7)_4$[12,13] as the zirconium source. Recently, we successfully synthesized a new open framework zirconogermanate ($(C_4N_2H_{12})$-$[ZrGe_4O_{10}F_2]$, FDZG-1)[14] with cavansite topology structure. In this paper, we report a new organically templated zirconogermanate, $(C_2H_{10}N_2)H_2O[ZrGe_3O_9]$ (denoted as FDZG-3), which was synthesized by using $ZrO(NO_3)_2 \cdot 2H_2O$ as the zirconium source and triethylenetetramine as a structure directing agent. The 3D framework structure of FDZG-3 built up by 1D sinusoidal germanate chains cross-linked by ZrO_6 octahedra is constructed containing a three-membered ring (MR) and four intersecting 7-MR channels, which result in a low framework density of 13.6 T/1000 Å^3.

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10.1021/ic0343612 CCC: $25.00

Experimental Section

Reagents. All reagents were of analytical grade and were used without further purification.

Synthesis. In a typical procedure, FDZG-3 was prepared as follows: 0.20 g (0.75 mmol) of $ZrO(NO_3)_2{\cdot}2H_2O$ was first dissolved in 1.25 g (69 mmol) of H_2O. Then, 5.30 g (67 mmol) of pyridine, 0.22 g (2.06 mmol) of GeO_2, 0.48 g (3.29 mmol) of TETA, and a drop of 40% hydrofluoric acid (0.06 g, 1.16 mmol) were added successively to the solution under vigorous stirring. After stirring at room temperature for 10 h, the solution was transferred into a 23-mL Parr Teflon-lined stainless steel autoclave and heated at 160 °C under autogenous pressure for 7 days. Colorless quadrate platelike single crystals (most of them are aggregates of crystals) with approximately 85% yield (based on GeO_2) were obtained by filtration, washed with water several times, and dried at 80 °C.

Analytical Procedures. The obtained crystals were initially examined by powder X-ray diffraction, using a Bruker D4 ENDEAVOR diffractometer with Cu Kα radiation, to establish phase identity and purity. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were done on a Hitachi S-520 electron microscope equipped with a LINKS ISIS. The elemental analysis was performed on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric analyses were performed in flowing dry air (5 mL/min) on a Perkin-Elmer TAC 7/DX analyzer, with heating rate of 10 $K{\cdot}min^{-1}$. IR spectra were collected on a Mattson FTIR 5000 spectrometer by using pressed KBr pellets of the samples. The UV−vis diffuse reflectance spectra were recorded at room temperature using a Perkin-Elmer model 330 spectrophotometer equipped with an integrating sphere. Further structural characterization was achieved via single-crystal X-ray diffraction.

Single-Crystal X-ray Diffraction Data Collection, Structure Solution, and Refinement. A colorless single crystal of FDZG-3 with the dimensions 0.200 × 0.200 × 0.05 mm_3 was selected for single-crystal analysis at room temperature. Intensity data were collected on a Bruker Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å), which operated at 50 kv and 20 mA. Empirical absorption corrections based on orientation matrix, Laue symmetry, and appreciable redundancy in the reflection data were applied using the SADABS program. The structure was solved by direct methods followed by successive difference Fourier syntheses. The refinements were performed against all F^2 with anisotropic thermal parameters for all atoms except for the hydrogen atoms of the water molecule. Neutral-atom scattering factors for all atoms were used. Anomalous dispersion and secondary extinction corrections were applied. All calculations were performed using the SHELXTL program.[15] Crystal data and structure refinement parameters for FDZG-3 are listed in Table 1. Atomic coordinates and thermal parameters and a list of selected bond lengths for FDZG-3 are given in Tables 2 and 3, respectively.

Result and Discussion

Synthesis and Chemical Composition. Large single-crystal FDZG-3 can be solvo/hydrothermally synthesized by using the inorganic salt $ZrO(NO_3)_2{\cdot}2H_2O$ as a zirconium source and TETA as a structure directing agent in the presence of HF. A mixture of water and pyridine is used as a solvent. Although hydrofluoric acid does not take part in the structure construction of FDZG-3, it plays a role as pH adjuster. The X-ray powder diffraction (XRD) pattern of the bulk products is in good agreement with that simulated from the atomic coordinates derived from single-crystal X-ray diffraction (Figure 1), confirming that the product is a pure phase. Single-crystal X-ray analysis reveals that its chemical

Table 1. Crystal Data and Structure Refinement Parameters for FDZG-3

	FDZG-3
empirical formula	$C_2H_{12}N_2\,O_{10}Ge_3Zr$
fw	533.13
temp	293(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*Cc*
unit cell dimensions	$a = 11.299(3)$ Å, $\alpha = 90°$ $b = 7.7649(19)$ Å, $\beta = 104.826(3)°$ $c = 13.835(3)$ Å, $\gamma = 90°$
volume, *Z*	1173.4(5) $Å^3$, 4
density (calcd)	3.018 Mg/m^3
abs coeff	8.524 mm^{-1}
F(000)	1016
cryst size	0.200 × 0.200 × 0.05 mm^3
θ range for data collection	3.05−27.11°
limiting indices	$-14 \le h \le 14, -8 \le k \le 9, -17 \le l \le 16$
reflns collected/unique	2760/2133, $R_{int} = 0.0205$
completeness to $\theta = 27.11°$	97.2%
max and min transm	0.6752 and 0.2805
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2133/5/166
extinction coeff	0.00069(10)
GOF on F^2	0.928
final *R* indices [$I > 2\sigma(I)$]	R1[a] = 0.0263, wR2[b] = 0.0529
R indices (all data)	R1 = 0.0307, wR2 = 0.0537
largest diff peak and hole	0.819 and −0.633 e $Å^{-3}$

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 5.74P]$ with $P = (\max F_o^2 + 2F_c^2)/3$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ × 10^3) for FDZG-3 Compound

atom	x	y	z	U_{eq}[a]
Ge(1)	6026(1)	6928(1)	5597(1)	16(1)
Ge(2)	6077(1)	12822(1)	5662(1)	18(1)
Zr(1)	3988(1)	9935(1)	6326(1)	9(1)
Ge(3)	4862(1)	9920(1)	4132(1)	24(1)
O(1)	3733(4)	9999(5)	4764(3)	20(1
O(2)	5712(5)	7965(5)	4407(4)	31(1)
O(3)	4328(7)	10103(6)	2853(3)	50(2)
O(4)	5929(5)	11636(6)	4556(4)	30(1)
O(5)	5322(4)	11844(5)	6462(3)	19(1)
O(6)	7632(4)	13045(5)	6247(4)	33(1)
O(7)	7592(4)	6808(5)	6100(4)	31(1)
O(8)	5280(3)	7989(5)	6360(3)	18(1)
O(9)	5411(4)	4850(5)	5307(4)	26(1)
O(10)	6037(6)	5749(9)	7994(5)	76(2)
N(1)	8552(6)	−161(7)	7137(8)	82(4)
C(1)	7895(9)	−405(11)	7977(7)	76(4)
N(2)	7367(6)	2477(8)	8279(6)	48(2)
C(2)	8085(8)	971(10)	8716(7)	59(3)
H(1A)	8279	793	6796	123
H(1B)	8401	−1063	6727	123
H(1C)	9354	−73	7404	123
H(1D)	7023	−513	7674	91
H(1E)	8171	−1479	8319	91
H(2A)	7528	2734	7698	72
H(2B)	7564	3367	8694	72
H(2C)	6574	2246	8178	72
H(2D)	8946	1270	8923	71
H(2E)	7833	589	9301	71

[a] U_{eq} ($Å^2 10^3$) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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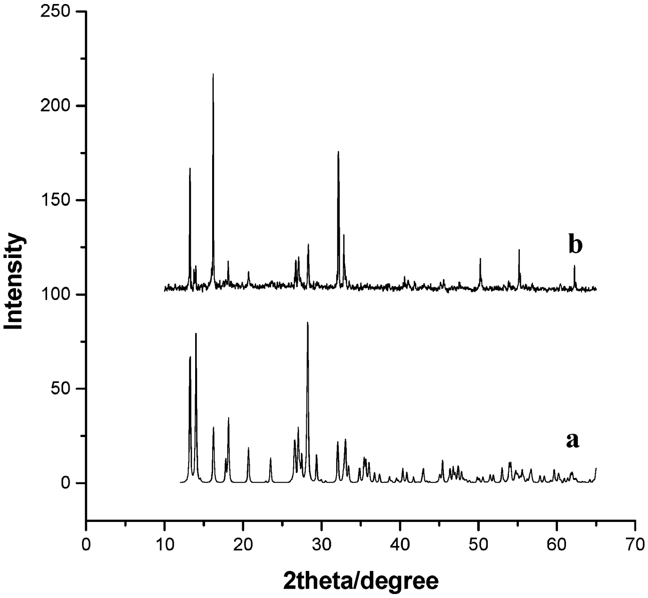

Figure 1. XRD patterns of FDZG-3: (a) simulated and (b) as-synthesized.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the FDZG-3 Compound[a]

Ge(1)−O(8)	1.720(4)	Ge(3)−O(4)	1.793(5)
Ge(1)−O(7)	1.730(4)	Zr(1)−O(7)#4	2.109(4)
Ge(1)−O(9)	1.762(4)	Zr(1)−O(3)#2	2.049(5)
Ge(1)−O(2)	1.784(5)	Zr(1)−O(5)	2.088(4)
Ge(2)−O(5)	1.735(4)	Zr(1)−O(8)	2.093(4)
Ge(2)−O(6)	1.745(4)	Zr(1)−O(6)#3	2.104(4)
Ge(2)−O(4)	1.757(5)	Zr(1)−O(1)	2.106(4)
Ge(2)−O(9)#1	1.760(4)	N(1)−C(1)	1.542(9)
Ge(3)−O(3)	1.722(5)	C(1)−C(2)	1.457(8)
Ge(3)−O(1)	1.723(5)	N(2)−C(2)	1.462(7)
Ge(3)−O(2)	1.784(4)		
O(8)−Ge(1)−O(7)	112.9(2)	O(8)−Zr(1)−O(6)#3	89.55(15)
O(8)−Ge(1)−O(9)	110.6(2)	O(3)#2−Zr(1)−O(1)	177.1(3)
O(7)−Ge(1)−O(9)	110.2(2)	O(5)−Zr(1)−O(1)	88.97(16)
O(8)−Ge(1)−O(2)	109.70(19)	O(8)−Zr(1)−O(1)	87.24(16)
O(7)−Ge(1)−O(2)	109.7(2)	O(6)#3−Zr(1)−O(1)	93.25(19)
O(9)−Ge(1)−O(2)	103.3(2)	O(3)#2−Zr(1)−O(7)#4	95.6(2)
O(5)−Ge(2)−O(6)	110.4(2)	O(5)−Zr(1)−O(7)#4	91.11(15)
O(5)−Ge(2)−O(4)	112.0(2)	O(8)−Zr(1)−O(7)#4	172.72(18)
O(6)−Ge(2)−O(4)	108.4(2)	O(6)#3−Zr(1)−O(7)#4	88.06(17)
O(5)−Ge(2)−O(9)#1	109.0(2)	O(1)−Zr(1)−O(7)#4	86.03(18)
O(6)−Ge(2)−O(9)#1	110.4(2)		
O(4)−Ge(2)−O(9)#1	106.7(2)	Ge(3)−O(2)−Ge(1)	123.4(3)
O(3)−Ge(3)−O(1)	114.1(3)	Ge(2)−O(4)−Ge(3)	125.5(3)
O(3)−Ge(3)−O(2)	108.5(2)	Ge(2)#8−O(9)−Ge(1)	129.8(3)
O(1)−Ge(3)−O(2)	110.5(2)	Ge(3)−O(1)−Zr(1)	126.6(2)
O(3)−Ge(3)−O(4)	107.7(3)	Ge(3)−O(3)−Zr(1)#5	169.0(4)
O(1)−Ge(3)−O(4)	109.3(2)	Ge(2)−O(5)−Zr(1)	135.6(2)
O(2)−Ge(3)−O(4)	106.4(3)	Ge(2)−O(6)−Zr(1)#6	136.6(2)
O(5)−Zr(1)−O(6)#3	177.57(19)	Ge(1)−O(7)−Zr(1)#7	138.2(2)
O(3)#2−Zr(1)−O(5)	88.7(2)	Ge(1)−O(8)−Zr(1)	141.3(2)
O(3)#2−Zr(1)−O(8)	91.2(2)		
O(5)−Zr(1)−O(8)	91.56(17)	C(2)−C(1)−N(1)	115.2(8)
O(3)#2−Zr(1)−O(6)#3	89.2(2)	C(1)−C(2)−N(2)	109.3(8)

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $y + 1$, z; #2, x, $-y + 2$, $z + {}^1/_2$; #3, $x - {}^1/_2$, y - ${}^1/_2$, z; #4, $x - {}^1/_2$, $y + {}^1/_2$, z; #5, x, $-y + 2$, $z - {}^1/_2$; #6, $x + {}^1/_2$, $y + {}^1/_2$, z; #7, $x + {}^1/_2$, $y - {}^1/_2$, z; #8, x, $y - 1$, z.

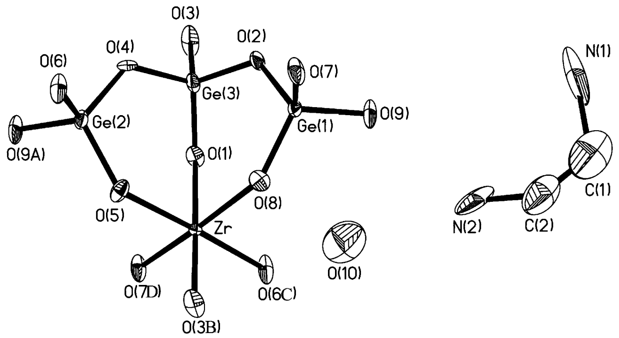

Figure 2. Labeled ORTEP plot of the asymmetric unit of FDZG-3 (50% probability ellipsoid).

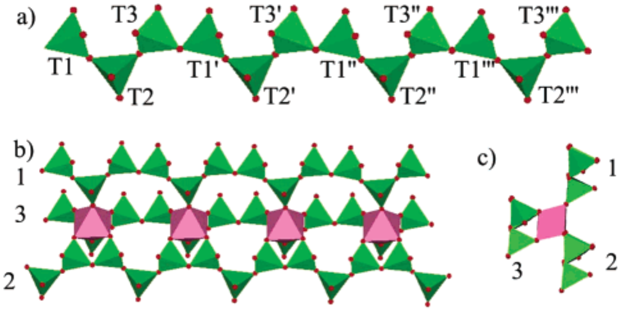

Figure 3. Structure diagram showing the connectivity of the FDZG-3 framework: (a) one germanate chain, and (b) and (c) three germanate chains linked by ZrO_6 octahedra viewed along [101] and the *b* axis direction, respectively.

formula is $(C_2H_{10}N_2)H_2O[ZrGe_3O_9]$. Since we did not add diethylenediamine (DEA) in the initial mixture, it should be derived from the decomposition of TETA in hydrothermal conditions. The elemental analysis of FDZG-3 gives C, H, N contents of 4.55%, 2.21%, 5.47% (calcd values are C, 4.50%; H, 2.25%; N, 5.25%), respectively. Energy-dispersive X-ray analysis (EDX) gives the Ge/Zr ratio as 2.92:1 (calcd 3:1). These results are in agreement with the formula of FDZG-3 found from the single-crystal analysis.

Structure Description. Single-crystal X-ray analysis reveals that the framework structure of FDZG-3 is built up by a zirconium trigermanate secondary building unit (SBU) denoted as 3 = 1, in which a ZrO_6 octahedron is connected to three GeO_4 tetrahedra of a trigermanate chain by forming two 3-MRs which share a side (Figure 2). The two 3-MRs are not in a plane with a torsion angle of about 100°. In this SBU, the Ge−O distances range from 1.720(4) to 1.793(5) Å, which are similar to those reported for the quartz form of GeO_2 (1.741(3) Å).[16] The O−Ge−O angles, 103.3(2)−114.1(3)°, are within the expected range for a tetrahedral geometry. The Ge−O−Ge angles, 123.4(3)−129.8(3)°, are smaller than those in the silicate parent family where the Si−O−Si angles are rather close to 140°. The bond valence sums[16] at Ge and Zr are 3.93−4.00 and 3.86, close to the expected values (4.0 and 4.0).

The overall topology of FDZG-3 can be described as chains of corner-sharing GeO_4 tetrahedra ($[-O-GeO_2-]_n^{2n-}$) running parallel to the *b* axis direction and linked into a 3D network by ZrO_6 octahedra (Figure 3). The sinusoid-like germanate chain repeats every three tetrahedra (T1T2T3T1′T2′T3′......, Figure 3a), and all Ge sites in one germanate chain are in a plane (Figure 3c). Each ZrO_6 octahedron connects three surrounding germanate chains in three different manners: one of the corners of the ZrO_6

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octahedron is shared with a GeO_4 tetrahedron (such as T2, T2′, etc., Figure 3a) of one germanate chain (chain 1, Figure 3b); another two corners are shared with two adjacent GeO_4 tetrahedra (such as T3T1′, T3′T1″, etc., Figure 3a) of the second germanate chain (chain 2, Figure 3b). The rest of the three corners are shared with three GeO_4 tetrahedra (such as T1T2T3, T1′T2′T3′, etc., Figure 3a) of the third germanate chain (chain 3, Figure 3b). Such six corners complete the Zr coordination sphere of a ZrO_6 octahedron. According to the O atoms of ZrO_6 octahedron in SBU (Figure 2), O(3B) is a shared atom of one germanate chain; O(6C) and O(7D) are shared atoms of another germanate chain; O(1),O(5) and O(8) are shared atoms of the third germanate chain. These ZrO_6 octahedra and tetrahedral chains are similar to those in mineral umbite ($K_2Zr_{0.8}Ti_{0.2}Si_3O_9 \cdot H_2O$),[17,18] where this chains were observed for the first time in wollastonite structure.[19] However, the umbite structure contains 8-MRs, whereas the FDZG-3 structure contains 7-MRs. This (4,6)-connected structure of FDZG-3 also shows some similarities to the structure of ASU-15[12] (($(H_2DAB)[ZrGe_2O_6F_2]$), which is constructed by germanate chains and ZrO_4F_2 octahedra; however, two coordination sites of the ZrO_4F_2 octahedron are terminated by two F atoms which result in 4-connected nets in ASU-15.

An instructive way to view the net involves the reorganization of the 3- and 7-MR zirconogermanate layer, which is constructed by germanate chains and ZrO_6 octahedra in the *ab* plane (Figure 4a). Such infinite zirconogermanate layers stack along the *c* axis direction in the eclipsed configuration (AAAA sequence) to form the 3D structure through bridged oxygens, which are shared vertexes of ZrO_6 octahedra in one layer and GeO_4 tetrahedra in adjacent layer (Figure 4b).

Viewing the 3D framework structure of FDZG-3 along the *b* axis, *c* axis, [110] and [$\bar{1}$10] directions, four intersecting 7-MR channels can be observed, respectively (Figures 4 and 5). The window of 7-MR channels along the *c* axis direction is composed of $2(GeO_4)-(ZrO_6)-3(GeO_4)-(ZrO_6)$, and the window of another three 7-MR channels is one and the same, which is composed of $2(GeO_4)-(ZrO_6)-(GeO_4)-(ZrO_6)-(GeO_4)-(ZrO_6)$. The pore aperture and size are shown in Figure 6. When the van der Waals radius of the oxygen atoms (1.50 Å) is taken into account,[20] their free pore diameters are 2.6×3.2 and 2.4×2.7 Å, respectively. It is worth noticing that 7-MRs are rare in zeolite-like materials,[9,21−23] and here, the FDZG-3 structure is a new example with this feature. The FDZG-3 structure also contains considerable 3-MRs with the connection of $(GeO_4)-(ZrO_6)-(GeO_4)$, which may induce the relatively low framework density with a value of 13.6 T/1000 Å^3 that can be comparable with values of 13.4 for OSB-1[24] and STA-1[25] and 13.5 for FDZG-1[14].

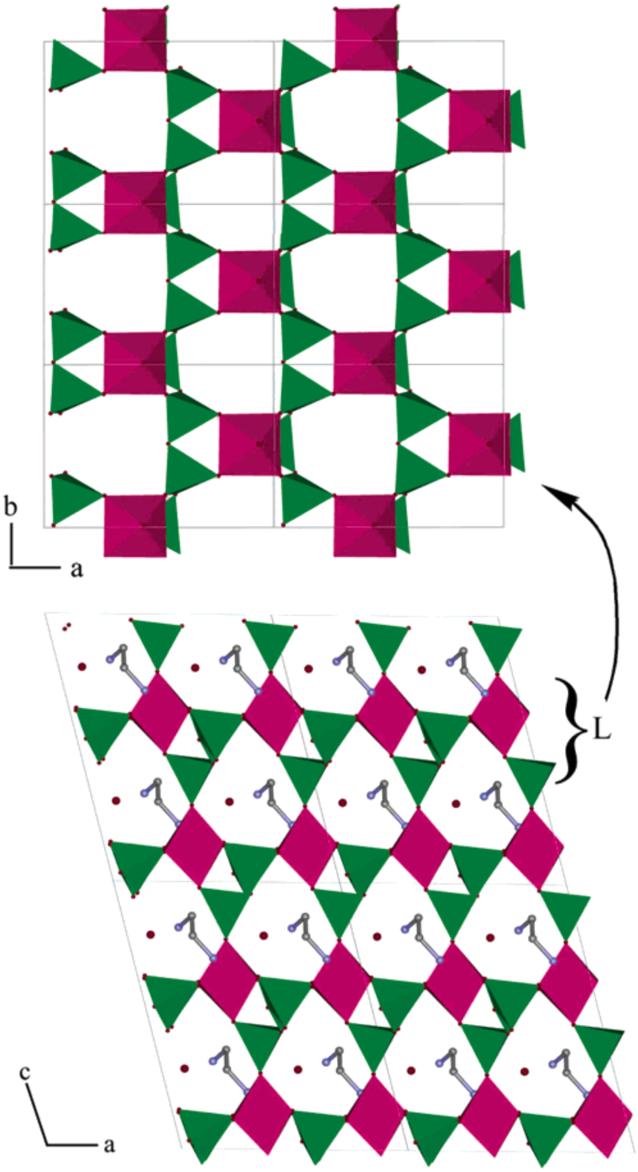

Figure 4. Bottom: View of the structure of FDZG-1 along the *b* axis direction (GeO_4, tetrahedral, ZrO_6, octahedral). Top: Detail of three- and seven-ring zirconogermanate layer (L) viewed along the *c* axis direction (water and DEA molecules are within the 7-MR channels).

Hydrogen Bonds. There are extraframework water and DEA molecules situated in the 7-MR channels (Figures 4 and 5). To compensate for the negative charge of framework, the diethylenediamine should be diprotonated. These species are bonded to the nearest oxygen atoms of the framework through hydrogen bonds. The hydrogen coordinates and equivalent isotropic displacement parameters of the DEA molecule are listed in Table 2, and the hydrogen bonds are

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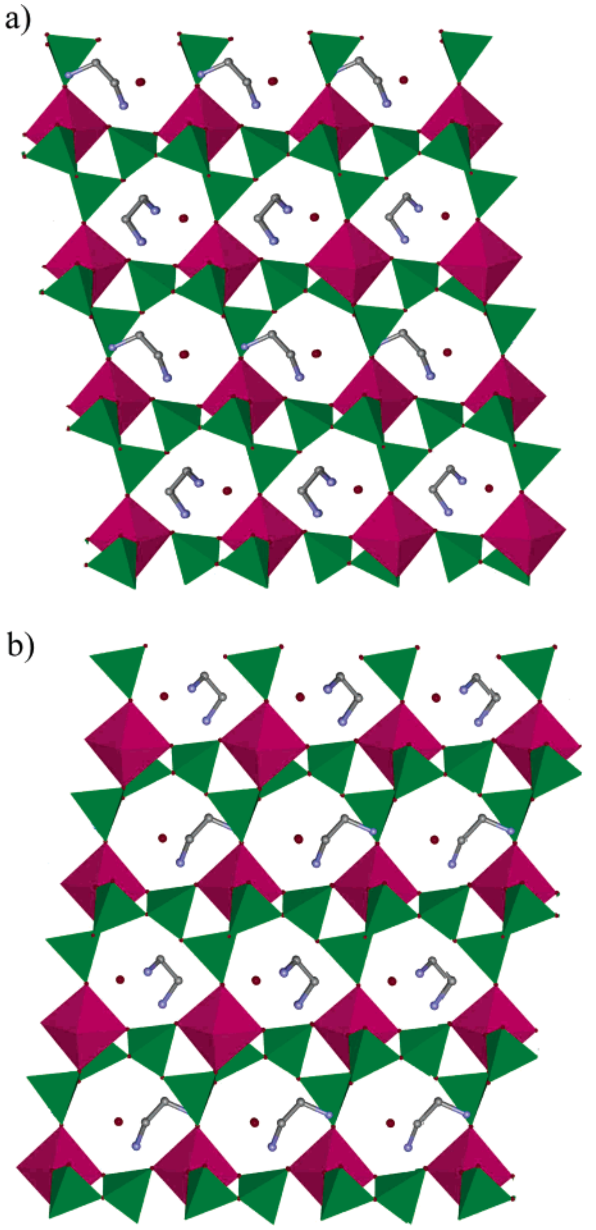

Figure 5. Polyhedral representation of 7-MR channels of FDZG-3 viewed along the (a) [110] direction and (b) [$\bar{1}$10] direction.

listed in Table 4. Because the hydrogen atoms on extraframework water molecules are disordered, their hydrogen coordinates and hydrogen bonds are not included in the table. The hydrogen atoms on N atoms (H1A, H1B, H1C on N(1), H2A, H2B, H2C on N(2)) participate in the medium-weak and weak hydrogen bonds with framework oxygen atoms, which can be inferred from the H···A distances of 1.97−2.70 Å.

TG Analysis. Thermogravimetric analysis (Figure 7) shows a gradual weight loss of 3.18% from 25 to 350 °C, resulting from the loss of the extraframework water (calcd 3.38%). The following steps in the range 350−800 °C, which have a sharp weight loss from 350 to 500 °C and gradual weight loss from 500 to 800 °C, correspond to the combustion of DEA molecules (Weight loss: 11.76%. Calcd weight loss: 11.63%).

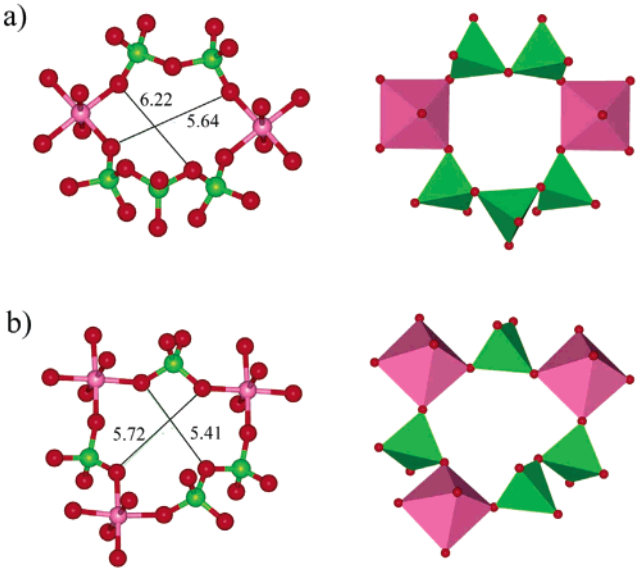

Figure 6. Ball-and-stick and polyhedral representation of two different kinds of windows corresponding to 7-MRs channel along the (a) c axis direction; (b) [110], [$\bar{1}$10], and b axis direction.

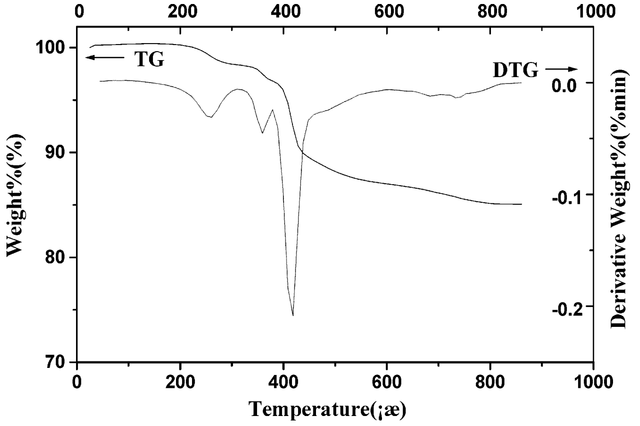

Figure 7. TG-DTG curves of the FDZG-3 compound.

Table 4. Hydrogen Bonds (Å and deg) between EDA Molecules and Framework Oxygen Atoms in the FDZG-3 Structure[a]

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
N(1)−H(1A)···O(6)#8	0.89	1.97	2.853(8)	170.7
N(1)−H(1B)···O(7)#8	0.89	1.98	2.825(8)	158.2
N(1)−H(1C)···O(10)#7	0.89	1.97	2.844(10)	165.5
N(2)−H(2A)···O(6)#8	0.89	2.06	2.935(9)	169.6
N(2)−H(2A)···O(3)#9	0.89	2.60	3.074(9)	113.9
N(2)−H(2B)···O(1)#9	0.89	2.13	2.970(9)	156.7
N(2)−H(2C)···O(2)#10	0.89	2.17	2.747(8)	121.9
N(2)−H(2C)···O(5)#8	0.89	2.45	2.987(8)	119.1

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $y+1$, z; #2, x, $-y+2$, $z+{}^1/_2$; #3, $x-{}^1/_2$, $y-{}^1/_2$, z; #4, $x-{}^1/_2$, $y+{}^1/_2$, z; #5, x, $-y+2$, $z-{}^1/_2$; #6, $x+{}^1/_2$, $y+{}^1/_2$, z; #7, $x+{}^1/_2$, $y-{}^1/_2$, z; #8, x, $y-1$, z; #9, $x+{}^1/_2$, $-y+{}^1/_2$, $z+{}^1/_2$; #10, x, $-y+1$, $z+{}^1/_2$.

IR and UV−Vis Diffuse Reflectance Spectra. The IR spectrum from the title compound shows a peak centered at 3165 cm^{-1}, which corresponds to the O−H and N−H stretching bands of extraframework water and DEA. The broadening of this peak is indicative of the hydrogen bonding.[26] The peaks at 1604, 1535, 1458, 1078, and 1030

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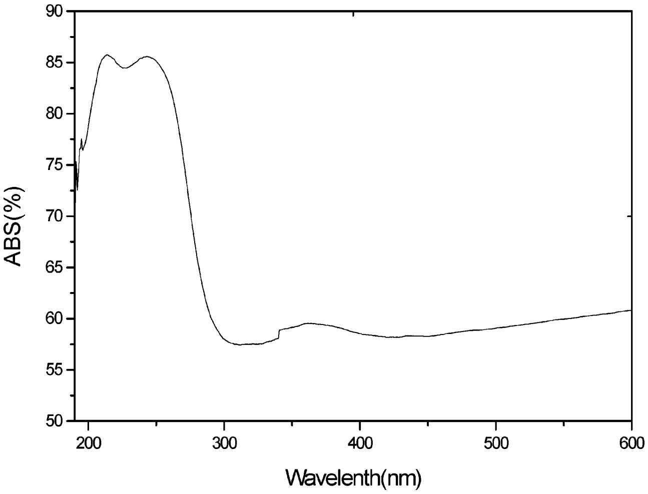

Figure 8. UV−vis diffuse reflectance spectrum of the FDZG-3 compound.

cm^{-1} are due to the bond vibrations from DEA molecules. The peaks at 894, 798, 754 cm^{-1} can be assigned to an asymmetrical stretch of Ge−O of the tetrahedral germanium.[27,28] The absorption bands at 547 and 472 cm^{-1} are overlapping frequencies of symmetrical stretching and bond bending of Ge−O[29] and vibrations of Zr−O.[26,30]

The UV−vis diffuse reflectance spectrum of FDZG-3 is present in Figure 8. There exhibit two interband charge-transfer transitions of $O^{2-} \rightarrow Zr^{4+}$ at 5.08 and 5.79 eV (244 and 214 nm) which are very similar to the behavior of *m*-ZrO_2.[31,32]

Conclusion

We have described the synthesis and characterization of a new organically open framework zirconogermanium, $(C_2H_{10}N_2)H_2O[ZrGe_3O_9]$, FDZG-3. Its framework is a (4,6)-connected net composed of 3-MRs and 7-MRs. Water molecules and diprotonated ethylenediamine situate in its 7-MR channels and form hydrogen bonds with its framework. It has relatively low framework density with a value of 13.6 T/1000 Å^3 that can be comparable with OSB-1, STA-1, and FDZG-1.

Acknowledgment. This work was supported by the NSF of China (Grant 29925309), State Key Basic Research Program of PRC (G2000048001). The continuing help of Dr. Zhou Yaming is gratefully acknowledged.

Note Added during Revision: Plevert et al. report in this issue a similar zirconogermanate.[33]

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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