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Hydrothermal Synthesis and Structural Characterizations of Two New Germanates with a Novel Topological Framework and Unusual $Ge_4(OH)_4$ Cubane

Yan Xu,* Liying Cheng, and Wansheng You

Institute of Chemistry for Functionalized Materials, College of Chemistry and Chemical Engineering, Liaoning Normal University, No. 850 Huanghe Road, Dalian 116029, P. R. China

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Two new germanates, $Ge_7O_{12}(OH)_4\,(C_4N_3H_{13})_{0.5}(H_2O)_5$ (**1**) and $Ge_7O_{12}(OH)_4(H_2O)_6$ (**2**) have been synthesized under hydrothermal conditions and characterized by IR spectroscopy, powder XRD, TG, and single-crystal X-ray diffraction. Compound **1** crystallizes in cubic space group $P\bar{4}3m$ (No. 215) with $a = b = c = 7.7119(5)$ Å, $v = 458.65(5)$ Å^3, $z = 1$. Compound **2**: cubic, $P\bar{4}3m$, $a = b = c = 7.7653(17)$ Å, $v = 457.48(17)$ Å^3, $z = 1$. Both germanates keep the same topological novel inorganic framework, which is assembled from $Ge_4(OH)_4$ cubane and chiral intertwined Ge–O double helices.

Introduction

Great efforts have been made to synthesize new porous materials with either pure tetrahedral or mixed polyhedral open frameworks because of their widespread applications in adsorption, ion exchange, catalysis, and radioactive waste remediation. It is therefore vital to design novel porous materials with different topological structure in order to explore their functional properties. In the early 1990s, Xu et al.[1] reported the possibility of synthesizing organically templated porous germanates under hydrothermal conditions. Recently, the research efforts were continued with the synthesis and characterization of new topological germanate frameworks.[2−9] In germanates, not only can Ge adopt Ge/O radius ratios to form polyhedra with coordinations of four, five and six but the Ge−O distances are also significantly longer than Si−O in silicates. Therefore, the flexibility of polyhedral structure for germanium allows for the formation of various open-framework structures with an extra-large pore, such as FDU-4[7a] and ASU-16.[7b] More recently, another topic of interest in materials chemistry has been inorganic materials[4d,10−14] with helical pores or chains because of its particularly desirable applications in enantiotopic selective

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* To whom correspondence should be addressed. E-mail: yanxuweb@yahoo.com.

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separation and catalysis. Among a variety of open-framework materials reported, only limited numbers of phosphates and two germanates [2c, 4d] have such structural features. Here, we report the hydrothermal synthesis and structural characterizations of two novel germanates, $Ge_7O_{12}(OH)_4(C_4N_3H_{13})_{0.5}(H_2O)_5$ (**1**; LNM-1a) and $Ge_7O_{12}(OH)_4(H_2O)_6$ (**2**; LNM-1b), with a particularly interesting structure containing double helical Ge−O chains and unusual $Ge_4(OH)_4$ cubanes.

Experimental Section

General Remarks. All chemicals purchased were of reagent grade and used without further purification. The crystalline product was characterized by thermal analysis, powder XRD, single-crystal XRD, and IR spectroscopy. The C, H, and N elemental analyses were performed on a Perkin−Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded from KBr pellets on a Nicolet 170SXFT/IR spectrometer. TG analyses were carried out on a Diamond TG/DTA instrument (Perkin−Elmer) thermal analyzer under a nitrogen atmosphere at a scan rate of 10 °C/min.

Synthesis of $Ge_7O_{12}(OH)_4(C_4N_3H_{13})_{0.5}(H_2O)_5$ 1 (LNM-1a). Colorless cubic crystals were hydrothermally synthesized from a mixture of GeO_2, H_3BO_3, $CuCl_2\cdot 2H_2O$, diethylenetriamine, HF, pyridine, and H_2O in a molecular ratio of 2:1:2:4:4:74:110. To avoid SU-16,[9c] we added $CuCl_2\cdot 2H_2O$ to induce the formation of LNM-1a. In a typical synthesis, GeO_2 (0.10 g) and H_3BO_3 (0.03 g) were dissolved in a mixed solvent of pyridine (2.80 g) and water (0.91 g), followed by the addition of $CuCl_2\cdot 2H_2O$ (0.16 g) and diethylenetriamine (0.21 g) with constant stirring. Finally, hydrofluoric acid (0.1 mL, 40 wt %) was added to the above mixture. The mixture was kept in a 25 mL Teflon-lined steel autoclave at 170 °C for 7 days. The autoclave was slowly cooled to room temperature; the product was then filtered, washed with distilled water and acetone, and dried at room temperature. Colorless cubic crystals LNM-1a were obtained (0.050 g, yield 40% on the basis of GeO_2). Anal. Calcd for $Ge_7O_{12}(OH)_4(C_4N_3H_{13})_{0.5}(H_2O)_5$: C, 2.70; H, 2.11; N, 2.26. Found: C, 2.64; H, 2.25; N, 2.31. IR (KBr pellet, cm^{-1}): 3209 (m), 1425 (m), 1102 (vs), 774 (s), 531 (m), 475 (s).

Synthesis of $Ge_7O_{12}(OH)_4(H_2O)_6$ 2 (LNM-1b). A mixture of GeO_2 (0.10 g), H_3BO_3 (0.03 g), pyridine (2.81 g), water (0.91 g), 1,2-diaminopropane (0.21 g), and hydrofluoric acid (0.1 mL, 40 wt %) was sealed in a 25 mL Teflon-lined steel autoclave and heated at 170 °C for 7 days. After the mixture was cooled to room temperature, colorless cubic crystals LNM-1b were obtained (0.048 g, yield 40% on the basis of GeO_2). In addition, ASU-14[3c] topological germanate was prepared without H_3BO_3 under similar conditions. IR (KBr pellet, cm^{-1}): 3195 (m), 1403 (s), 1099 (m), 775 (vs), 481 (s)

X-ray Crystallography. Crystal data for **1**: $C_2H_{20.50}Ge_7N_{1.50}O_{21}$, $M_r = 909.83$, cubic, $P\bar{4}3m$, $a = b = c = 7.7119(5)$ Å, $V = 458.65(5)$ Å^3, $Z = 1$, $D_{calcd} = 3.294$ g cm^{-1}, $\mu = 11.426$ mm^{-1}, $2.64° \le \theta \le 26.38°$ ($-9 \le h \le 9$, $-9 \le k \le 8$, $-8 \le l \le 9$). $T = 293$ K, 2607 measured reflections, 214 independent reflections. R1 (wR2) = 0.0221 (0.0516) for 214 reflections ($I > 2(\sigma)$) and 29 parameters. GOF = 1.126. Crystal dimensions of 0.06 × 0.08 × 0.08 mm^3.

Crystal data for **2**: $H_{16}Ge_7O_{22}$, $M_r = 876.26$, cubic, $P\bar{4}3m$, $a = b = c = 7.7053(17)$ Å, $V = 457.48(17)$ Å^3, $Z = 1$, $D_{calcd} = 3.181$ g cm^{-1}, $\mu = 11.451$ mm^{-1}, $2.64 < \theta < 25.95°$ ($-7 \le h \le 9$, $-9 \le k \le 8$, $-8 \le l \le 9$). $T = 293$ K, 2590 measured reflections, 210 independent reflections. R1 (wR2) = 0.0247 (0.0633) for 198 reflections ($I > 2(\sigma)$) and 22 parameters. GOF = 1.096. Crystal dimensions of 0.06 × 0.09 × 0.09 mm^3.

Table 1. Crystal Data and Structure Refinements for **1** and **2**

	1	**2**
empirical formula	$Ge_7O_{12}(OH)_4(C_4N_3H_{13})_{0.5}(H_2O)_5$	$Ge_7O_{12}(OH)_4(H_2O)_6$
fw	909.83	876.26
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
cryst syst	cubic	cubic
space group	$P\bar{4}3m$	$P\bar{4}3m$
a (Å)	7.7119(5)	7.7053(17)
V (Å^3)	458.65(5)	457.48(17)
Z	1	1
D_{calcd} (g/cm^3)	3.294	3.181
μ (mm^{-1})	11.426	11.451
GOF on F^2	1.078	1.210
R1[a] [$I > 2\sigma(I)$]	0.0229	0.0238
wR2[a] [$I > 2\sigma(I)$]	0.0490	0.0559
R1 (all data)	0.0285	0.0253
wR2 (all data)	0.0518	0.0564

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Data were collected on a SMART APEX2 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Both structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package. All non-hydrogen atoms (except partial occupied atoms: water, C, and N) were refined anisotropically. The H atoms of OH for both structures were located from the difference map, whereas the H atoms for water, C, and N were not located, because of disorder. A summary of the crystallographic data and structural determination for both compounds is provided in Table 1.

Results and Discussion

Crystal Structures of Compounds. The structural analysis reveals that germanate **1** (LNM-1a) is a novel porous structure with interesting one-dimensional eight-membered ring channels. It has a previously unknown topology with space group $P\bar{4}3m$ and is assembled from a network of GeO_4 tetrahedra and $GeO_3(OH)_3$ octahedra. In germanate **1** (LNM-1a), there are two crystallographically independent germanium sites; one of them (Ge(1)) is tetrahedrally coordinated by four oxygen atoms with Ge−O distances of 1.739(4) Å, which are comparable with those reported values for the quartz form GeO_2 (1.741(3) Å). The O−Ge−O angles (107.76−113.0°) are within the expected range for the tetrahedral geometry. Another germanium atom (Ge(2)) exists in a 6-fold coordination (octahedron) characterized by three Ge−O distances of 1.835(4) Å and three Ge−OH distances of 1.965(3) Å, whereas the adjacent germanium atoms are connected by bridging O atoms or OH groups.

The structure can be described from a $Ge_4(OH)_4$ cubane building unit (Figure 1a) attached to six tetrahedral GeO_4 units (Figure 1b). The tetrameric $Ge_4O_6(OH)_4$ unit ($Ge_4(OH)_4$ cubane plus six bridging O atoms) is composed of four edge-sharing $GeO_3(OH)_3$ octahedra. Two adjacent $GeO_3(OH)_3$ octahedra are sharing two bridging OH to generate a three-membered ring; moreover, four O atoms from hydroxyl groups link four Ge atoms to produce a novel $Ge_4(OH)_4$ cubane. To the best of our knowledge, this type of building unit is not found in other reported germanates. The GeO_4 tetrahedra link adjacent $Ge_4(OH)_4$ cubanes along the a, b, and c axes by using three-membered rings that are made from two $GeO_3(OH)_3$ octohedra and one GeO_4 tetrahedron.

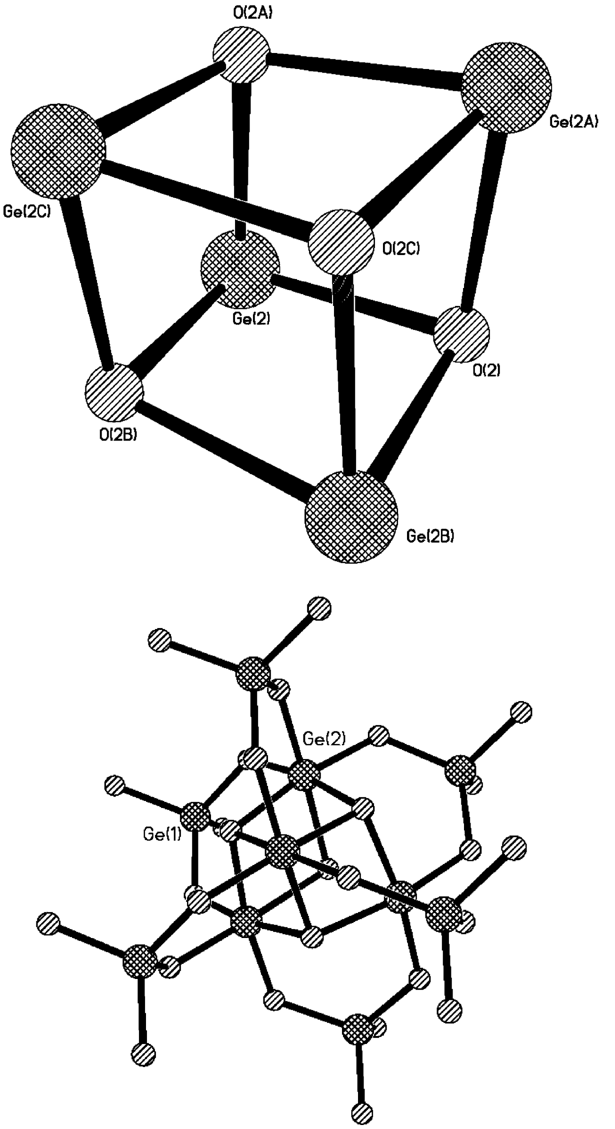

Figure 1. (a) Structure of $Ge_4(OH)_4$ cubane building unit. (b) Second Ge_{10} cluster building unit.

Two three-membered rings share the GeO_4 tetrahedron to generate a novel Ge_5 linkage (Figure 2), which is different from $ZrGe_2O_6F_2$.[3e] There are eight-membered ring channels, extending along the *a*, *b*, or *c* axis, as shown in Figure 3. Every eight-membered ring is surrounded by $Ge_4(OH)_4$ cubanes, which are further surrounded by eight-membered rings. The approximate diameter of the narrowest cross-section of eight-membered ring channels is 6 Å. There are also seven-membered ring channels extending along the crystallographic [1 1 0] directions. Interestingly, each eight-membered ring channel is enclosed by chiral intertwined Ge−O double helices of the same handedness, which are connected through Ge−O−Ge linkages (Figure 4). These kind of double helices are particularly rare in inorganic materials, with two reported phosphates being $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]$[10] and $[Zn_2(HPO_4)_4][Co(dien)_2]\cdot H_2O$.[14]

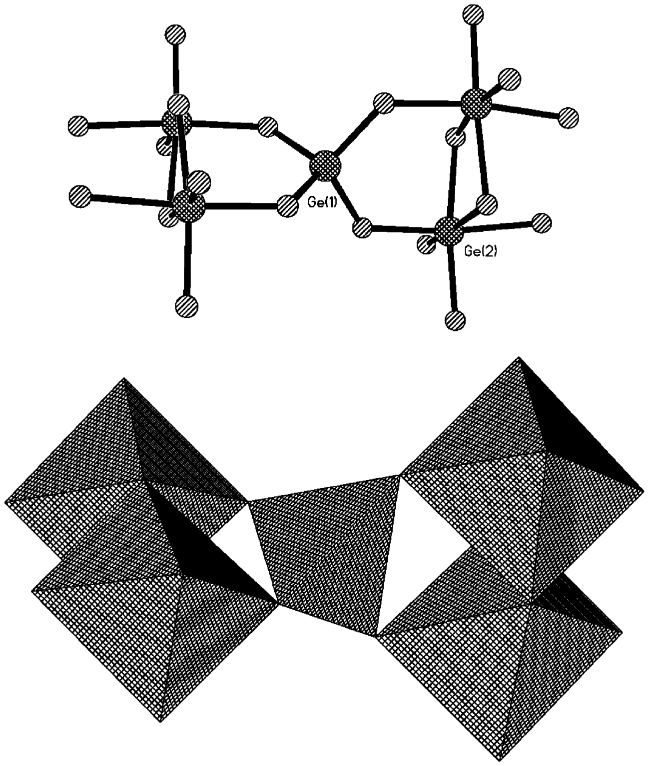

Figure 2. (a) Ge_5 building unit including two three-membered rings. (b) Polyhedral view of the Ge_5 building unit.

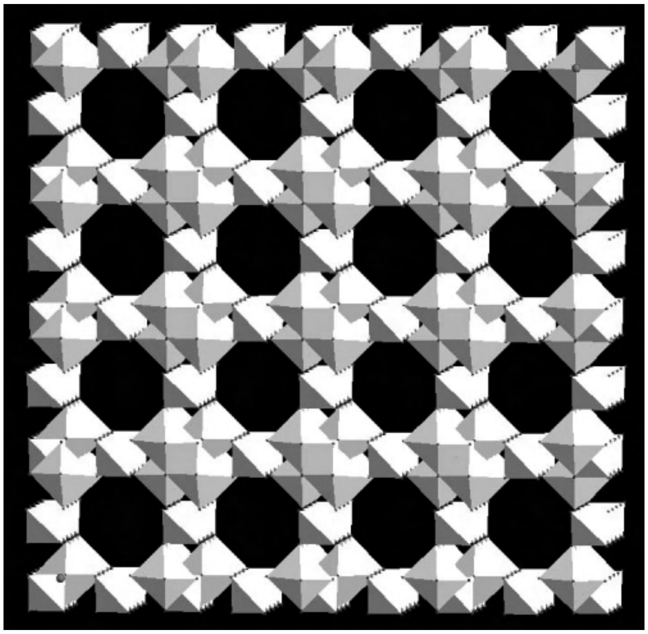

Figure 3. Polyhedral view of the framework along the *a* axis.

In LNM-1a, the diethylenetriamine has a very weak templating effect. The Ge−O inorganic framework adopts the highest possible symmetry and diethylenetriamine molecules conform to the symmetry of the Ge−O inorganic framework by adjusting their orientations and disorder. In LNM-1a, there are five extra framework water molecules per Ge_7 cluster. These water molecules are involved in relatively strong hydrogen bonding with the inorganic framework. The shortest distance between water and an O atom in the inorganic framework is 2.82(2) Å.

By replacing diethylenetriamine and $CuCl_2\cdot 2H_2O$ by 1,2-diaminopropane in a hydrothermal reaction similar to that for LNM-1a, we obtained germanate **2** (LNM-1b); it keeps

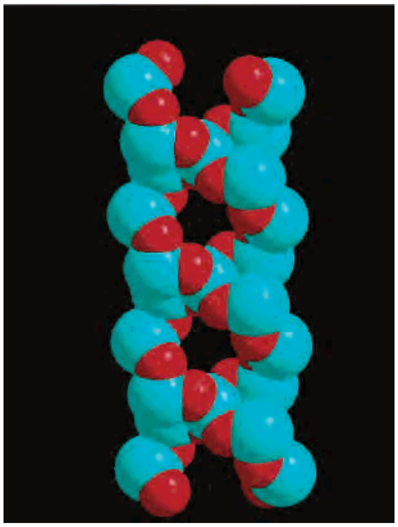

Figure 4. Space-filling diagram of chiral intertwined helices that enclose the eight-membered ring channel (color code: Ge, blue; O, red).

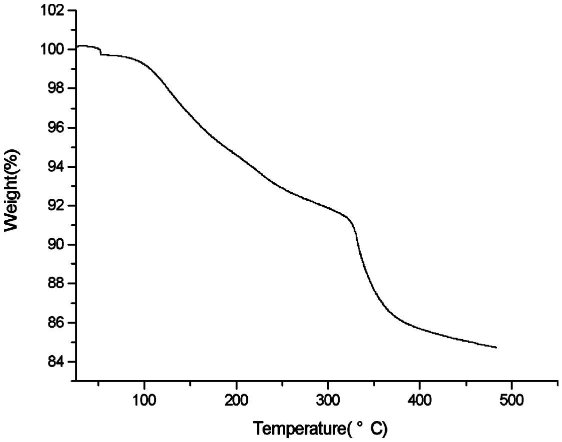

Figure 5. TG curve of $Ge_7O_{12}(OH)_4(C_4N_3H_{13})_{0.5}(H_2O)_5$.

the same topological inorganic framework, but without organic molecules. As thermal and XRD analysis results indicate that diethylenetriamine molecules in LNM-1a cannot be removed without destruction of framework, LNM-1b is more useful.

TG Analyses. The TG curve of **1** (Figure 5) shows a total weight loss of 15.3% in the range 25−500 °C, which agrees with the calculated value of 15.6%. The weight loss of 9.0% in the range 25−320 °C corresponds to the loss of lattice water molecules (calcd 9.9%), whereas the weight loss of 6.3% in the range 320−500 °C arises from the loss of diethylenetriamine (calcd 5.7%).

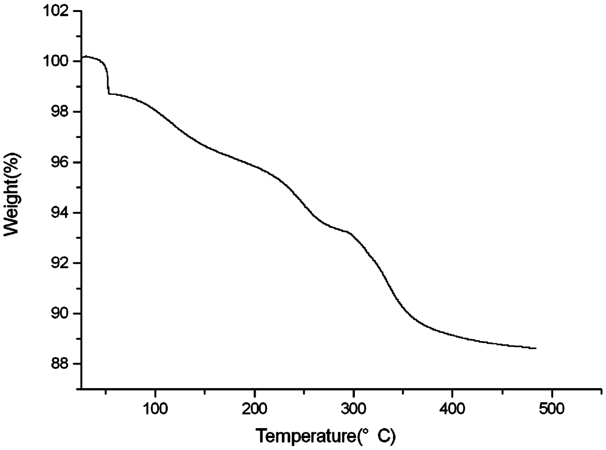

Figure 6. TG curve of $Ge_7O_{12}(OH)_4(H_2O)_6$.

The TG curve of **2** (Figure 6) exhibits a weight-loss stage in the range 25−500 °C, corresponding to the release of all water molecules.The whole weight loss (11.5%) is in agreement with the calculated value (12.3%).

Conclusions

In conclusion, two new germanates with a novel topological inorganic framework have been synthesized. Their framework consists of the novel $Ge_4(OH)_4$ cubanes and chiral intertwined Ge−O double helices. It is particularly interesting that LNM-1b keeps the same topological inorganic framework, but without an organic SDA (structure-directing agent). The present work has great significance for germanium chemistry and chiral porous materials.

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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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