The Hydrothermal Synthesis and Crystal Structure of $(H_2O)[Ge_5O_{10}]$ and $[(CH_3)_4N][Ge_{10}O_{20}OH]$, Two Novel Porous Germanates

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Two novel porous germanates, $[Ge_5O_{10}](H_2O)$ (**1**) and $[Ge_{10}O_{20}OH]$ $[(CH_3)_4N]$ (**2**), are synthesized by a hydrothermal method using TMA (tetramethylammonium), and characterized by X-ray crystallography, showing that a novel type of 3 membered rings (two octahedral GeO_6 and one tetrahedral GeO_4) exists in **1**, and the OH^- anions are located in the center of double 4-membered rings in **2**.

Microporous materials have been receiving great attention due to their widespread applications in adsorption, ion-exchange, catalysis and radioactive waste remediation.[1] It is therefore vital to design novel porous materials with different structural characteristics in order to explore their properties. In the last few years one of the most important advanced merits in the zeolitic chemistry was the synthesis of porous germanates, GeO_2. In the early 1990s, Xu[2] reported the possibility to make some organically templated open framework germanates by hydrothermal method. More recently, the research efforts were continued with the synthesis and characterization of several new types of germanate frameworks.[3–11] Compared with silicon, which is usually tatrahedrally coordinated, germanium adopts not only three types of coordinated polyhedra (GeO_4, tetrahedron; GeO_5, square pyramid, and GeO_6 octahedron), but also longer metal–oxygen distances (about 1.76 Å for Ge–O and 1.61 Å for Si–O).[8] Therefore, the flexibility of the polyhedral structure for germanium allows the formation of various open framework structures with an extralarge pore, which exhibit 24-membered ring channels, such as FDU-4[9] and ASU-16.[10] In particular, germanates show great possibility for formation of 3-membered rings, which are postulated to be important to form open frameworks architecture.[11] Replacement of tetrahedral species with octahedral ones can also influence the framework configuration. Some germanates with 3-membered ring have been reported,[12–14] which consisted of three tetrahedral GeO_4 or one octahedral GeO_6 and two tetrahedral GeO_4. Here we present the synthesis and structural investigations on two new germanates as $[Ge_5O_{10}](H_2O)$ (**1**) (UTM-3) and $[Ge_{10}O_{20}OH]$ $[(CH_3)_4N]$ (**2**). X-ray single crystal analysis shows that a novel 3-membered ring exists in **1**, which is built from two octahedral GeO_6 and one tetrahedral GeO_4. In **2**, OH^- anions are located at the center of double 4-membered rings as template.

Germanate **1** [UTM-3 (University of Tokyo, Microporous Materials)] was synthesized as colorless prismatic crystals by the hydrothermal method. GeO_2 (0.12 g) was suspended in a pyridine solution (4.05 g) containing 15% aqueous TMAOH (1.56 g), water (1.05 g), and 47% aqueous HF (0.1 mL). The gel was kept in a Teflon-lined autoclave at 175 °C for 9 days, and then cooled to room temperature to give 6 mg (about 5% yield based on GeO_2) product **1**, as well as some quartz and germanate **2**. As similarly, GeO_2 (0.12 g) was dissolved in 15% aqueous TMAOH (1.50 g) followed by the addition of pyridine (4.01 g), water (1.02 g), and 47% aqueous HF (0.1 mL). After heating for 9 days at 175 °C, only colorless block product **2** (0.065 g, 50% yield based on GeO_2) was synthesized. Both germanates were synthesized without DABCO to avoid the presence of ASU-9[4b] and ICMM5.[7b] The resulting products were washed with deionized water and ethanol, dried at room temperature for 1 day. Single crystal structures were determined from low temperature (−60 °C) data collected on a Rigaku Mercury-CCD diffractometer.[15]

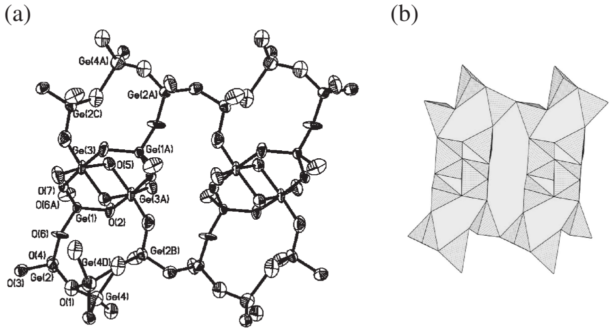

Figure 1. (a) ORTEP view of the building block unit in the structure of UTM-3, atoms labled A, B, C, or D are symmetry generated. (b) polyhedral representation of UTM-3.

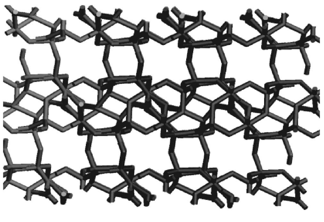

Figure 2. 3-D network of UTM-3 along [1 1 0].

UTM-3 is a novel germanate zeolite-type structure with the interesting 3, 5, and 8-membered rings and it has a previously unknown topology with the space group $C2/m$ (No. 12, standard setting). A single-crystal structural analysis revealed the 3-D open framework constructed from the structural building unit shown in Figure 1. In UTM-3, there are four unique Ge sites. Ge_1 and Ge_2 have regular tetrahedral coordination. Because Ge_4 is disordered with half occupation, it has distorted tetrahedral coordination, and the Ge_4–O distances are 1.698(8)–2.199(9) Å. Ge_3 is located in a symmetric plan and is, therefore, constrained by symmetry to adopt the octahedral model. The core of the structure-building unit is composed of four germanium oxide centers arranged by using crystallographic symmetric center at 0.5, 0.5, 0. The O_2, O_7, O_{2A}, and O_{7A} are bonded two germanium centers to give two octahedral (Ge_3 and Ge_{3A}) and two tetrahedral (Ge_1 and Ge_{1A}) germanium centers. Two germanium atoms in the same core were linked by three GeO_4 sharing corners to form an interesting five-membered ring, which consist of four tetrahedrons and one octohedron. The unusual feature here is that a novel type of 3-membered rings was found in the building unit (Figure 1), which is made from two octahedral GeO_6 (Ge_3 and Ge_{3A}) and one tetrahedral GeO_4 (Ge_1). To the best of our knowledge, this type of 3-membered rings has not been found in other germanate open frameworks. The Ge–O bonds for the tetragonal Ge centers (except disordered Ge_4) are between 1.702(8) and 1.760(7) Å, while Ge–O bonds within octahedral Ge centers vary from 1.784(14) to 1.982(8) Å that are very similar to those found in related structure.[3–10,12–14] The observation of a wide variation [from 102.0(6)° to 143.7(8)°] for angles of Ge–O–Ge is also often reported in the germanate chemistry. Neighboring structural building units are linked by the bridging oxygen atoms along [0 0 1] [1 0 0] and [0 1 0] directions to build a 3-D network (Figure 2). The pores extend along crystallographic [1 1 0] direction, and the water molecules occupied the 3-D 8-membered rings channels as the guest to form hydrogen bonds with the O atoms of the framework.

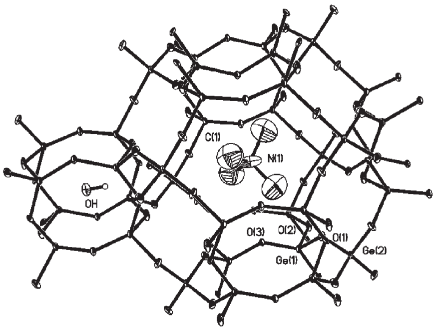

Figure 3. A fragment of structure of $[Ge_{10}O_{20}OH]$ $[(CH_3)_4N]$ **2**.

The framework **2** has been described for $[Ge_{10}O_{20}]$-(DABCO)(H_2O).[4] X-ray single crystal analysis shows a germanate topology (AST[16]) as shown in Figure 3, where the TMA cations reside the central octadecahedron. Nevertheless there are some important differences; (1) anions (OH^-) and cations (TMA^+) are in the different cage, and no any interaction; (2) OH^- anions are located in the center of double 4-membered rings. In some cases, the OH^- is bonded to Ge atoms, but there exist few examples in which the OH^- occupied in germanium cage as template.[7] In the current germanate **2**, the OH anions clearly form a charged framework, and the bond lengths for O–H are 0.81(1) Å, which are comparable with another OH-templated germanate [0.80(1) Å].[7] The IR spectrum shows a band at 3400 cm^{-1} corresponding to the OH group. The O atom of OH^- anion interacts with eight germanium atoms in the double 4-membered rings, and the distances of Ge···OH are 2.73(1) Å. TMA can not be removed without destruction of framework. The thermal gravimetric study in He atmosphere performed on a sample **2** showed the weight loss (total 9.0%) between 520 and 650 °C accompanied by endothermic peak corresponding to the loss of TMA and the OH^- groups, respectively.

In conclusions, two 3-D germanates have been hydrothermally synthesized at similar conditions. The framework of **1** exhibits a new type of 3-membered rings, which is built from two octahedral GeO_6 and one tetrahedral GeO_4. In the framework of **2**, it is demonstrated that OH^- anion plays a very important role in templating 4-membered rings in the synthesis of zeolite-type microporous germanates.

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15 Crystal data for **1**: $H_2Ge_5O_{11}$, monoclinic, $C2/m$ (No. 12), $a = 7.3178(15)$, $b = 14.392(3)$, $c = 7.7401(15)$ Å; $V = 802.6(3)$ Å^3, $Z = 4$, μ(Mo Kα) = 18.57 mm^{-1}. Dimensions: 0.18 × 0.09 × 0.08 mm. Based on 920 reflections with $I > 2s$ (I_0) and 86 parameters gave R_1 (R_{all}) = 0.0629 (0.0646). Crystal data for **2**: $C_4H_{16}Ge_{10}NO_{21}$, tetragonal, $I4/m$ (No. 87), $a = 9.1637(13)$, $b = 14.144(3)$ Å; $V = 1187.7(3)$ Å^3, $Z = 2$, μ(Mo Kα) = 12.555 mm. Dimensions: 0.12 × 0.12 × 0.06 mm. Based on 715 reflections with $I > 2s$ (I_0) and 69 parameters gave R_1 (R_{all}) = 0.0422 (0.0880). The occupied factors are 0.5, 0.5, 0.45(4), 0.55(4), and 0.5 for O_2, O_{2A}, O_3, O_{3A}, and C_1, respectively. Both data were collected on a Rigaku Mercury-CCD at −60 °C in the range $3.16 < \theta < 27.48$ for **1** and $2.65 < \theta < 27.52$ for **2**. An empirical absorption correction was applied. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Only the H atom of OH group was located from different map. CCDC reference number.

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