Angewandte Chemie International Edition

DOI: 10.1002/anie.201006500

Zeolite Analogues

A Gallogermanate Zeolite Constructed Exclusively by Three-Ring Building Units**

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Zeolites have microporous structures constructed by tetrahedrally connected atoms (T atoms, e.g., Si, Al, P, and Ge) and have been widely applied in fields such as catalysis, adsorption, and separation.[1] Considerable efforts have been made to synthesize zeolites with extra-large pores and low framework density (FD).[2] One effective approach is to introduce as many small-ring building units (i.e., 3- or 4-rings) as possible into the frameworks.[3] Since Si does not favor the formation of 3-rings because of the high Si-O-Si stress, other elements, such as Be, Zn, and Ge, have been introduced into zeolite frameworks to facilitate the formation of small rings.[4–6] Notably, a series of Ge-containing zeolite structures have been synthesized with double 4-rings (D4Rs),[7] and, more recently, extra-large-pore silicogermanate zeolite ITQ-44 with double 3-rings (D3Rs) and very low FD was reported.[8]

Chiral zeolites would be desirable for potential applications in asymmetric catalysis and separation, but chirality in zeolite frameworks has rarely been reported. Up to now, BEA, BSV, CZP, GOO, JRY, OSO, and STW[9] are the only chiral frameworks among all 194 zeolite types. To introduce chiral features into the inorganic open frameworks, optically pure or racemic mixtures of rigid chiral metal complexes have been widely used,[10] However, few examples of the synthesis of 4-connected zeolitic frameworks with chiral features by such an approach have been reported.

Here we present the synthesis and characterization of a novel three-dimensional (3D) gallogermanate zeolite $[Ni(en)_3][Ga_2Ge_4O_{12}]$ (denoted GaGeO-CJ63, en = ethylenediamine). GaGeO-CJ63 is a strictly 4-connected zeolitic structure constructed exclusively by 3-rings, and its FD is the second lowest among all known zeolite frameworks.[9] GaGeO-CJ63 was synthesized by using racemic $[Ni(en)_3]^{2+}$ cations as structure-directing agent, and chirality transfer could be clearly observed from chiral templates to chiral cages in its framework.

GaGeO-CJ63 was prepared by solvothermal reaction of a mixture of GeO_2, GaOOH, $[Ni(en)_3]Cl_2$, HF, ethylenediamine, ethanolamine, and H_2O in a molar ratio of 1.00:0.86:0.37:1.85:10.00:44.47:74.07 at 180 °C for 8 days in a Teflon-lined stainless steel autoclave. The phase purity was confirmed by the agreement between the experimental XRD pattern and the simulated pattern based on structure analysis (Supporting Information, Figure S1).

GaGeO-CJ63 crystallizes in the cubic space group $Pa\bar{3}$ (No. 205) with $a = 16.5716(3)$ Å. The asymmetric unit contains two unique T atom positions (T = Ge, Ga) and one unique Ni position. Since Ge and Ga atoms cannot be distinguished through X-ray diffraction, each T site in GaGeO-CJ63 is occupied by a Ge or Ga atom with a possible ratio of 2:1, as confirmed by elemental analysis. The T–O distances are in the range of 1.764(4)–1.780(4) Å, and the average T–O bond length of 1.77 Å lies between the ideal Ge–O (1.74 Å) and Ga–O bond lengths (1.82 Å).[6a] Notably, the framework of GaGeO-CJ63 is constructed exclusively by 3-rings. All T-O-T angles are in the range of 125.6(2)–130.3(2)°, which is reasonable for zeolite structures with 3-rings. GaGeO-CJ63 contains two kinds of 3-rings, one of which has C_1 symmetry and the other C_3 symmetry. Each 3-ring with C_3 symmetry is surrounded by three 3-rings with C_1 symmetry, and each 3-ring with C_1 symmetry is surrounded by two 3-rings with C_1 symmetry and one 3-ring with C_3 symmetry. Two 3-rings connect to each other to form a spiro-5 secondary building unit, and the spiro-5 units further construct the whole framework. The FD of GaGeO-CJ63 is 10.5 T/1000 Å^3, which is the second lowest among all known zeolite frameworks and only higher than that of zeolite UCR-20 (FD = 5.2 T/1000 Å^3, zeotype RWY).[9]

The framework of GaGeO-CJ63 has 3D intersecting 10-ring channels running along the [100], [010], and [001] directions. Figure 1a shows the 10-ring channels along the [100] direction. The channel opening has dimensions of 6.7 × 5.6 Å^2. GaGeO-CJ63 is the second zeolite framework constructed exclusively by 3-rings. The first strictly 3-ringed

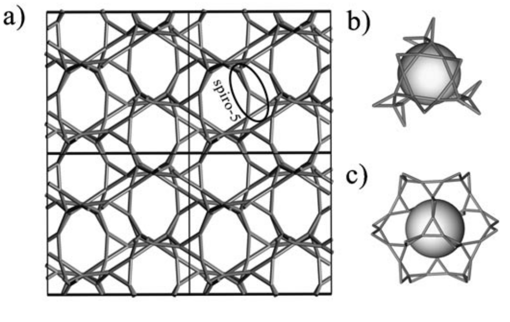

Figure 1. a) Framework of GaGeO-CJ63 viewed along the [100] direction, b) the [3^4.6.10^3] cage, and c) the [3^8.10^6] cage. The gray spheres show the pores in cages. All oxygen atoms are omitted for clarity.

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[**] This work is supported by the National Natural Science Foundation of China and the State Basic Research Project of China (Grants: 2011CB808703 and 2007CB936402) and the Major International Joint Research Project of China.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006500.

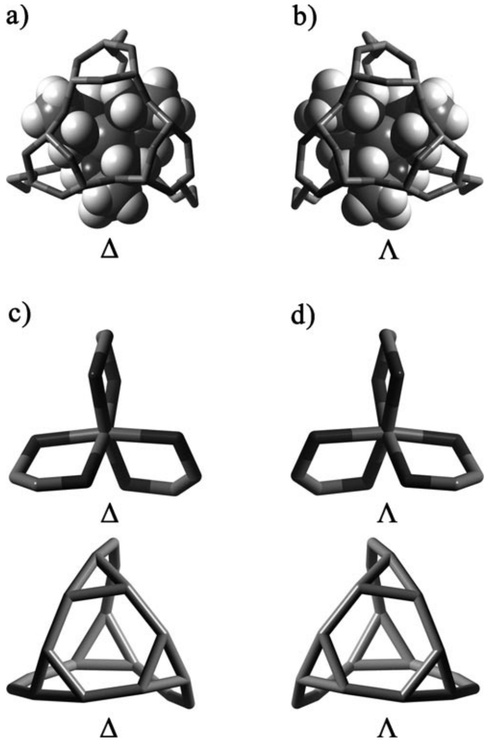

Figure 2. a) The Δ-[Ni(en)$_3$]$^{2+}$ cation in the Δ [3^4.6.10^3] cage, b) the Λ-[Ni(en)$_3$]$^{2+}$ cation in the Λ [3^4.6.10^3] cage, c) the Δ-[Ni(en)$_3$]$^{2+}$ cation and the Δ [3^4.6.10^3] cage shown separately, and d) the Λ-[Ni(en)$_3$]$^{2+}$ cation and the Λ [3^4.6.10^3] cage shown separately.

zeolite framework is OSO,[9] which has 14-ring channels and an FD of 13.4 T/1000 Å^3. The framework of GaGeO-CJ63 contains two kinds of cages, namely, the [3^4.6.10^3] cage (Figure 1b) and the [3^8.10^6] cage (Figure 1c), which have never been found in previously reported zeolitic structures. The structure of GaGeO-CJ63 can be understood as a three-periodic net carried by a unique natural tiling[11] with transitivity of [2442]. The signature of this tiling is 2[3^4.6.10^3]+[3^8.10^6], and the two cages are the two respective tiles in this tiling.

Notably, in GaGeO-CJ63, each [3^4.6.10^3] cage holds one Δ- or Λ-[Ni(en)$_3$]$^{2+}$ cation (Figure 2a, b), while the [3^8.10^6] cage is empty. Hydrogen bonds exist between the N atoms of the [Ni(en)$_3$]$^{2+}$ cations and the bridging O atoms in the [3^4.6.10^3] cages. Each [Ni(en)$_3$]$^{2+}$ cation interacts with the [3^4.6.10^3] cage through three distinct hydrogen bonds with N···O distances of 2.981(7), 2.926(6), and 3.003(6) Å (Supporting Information, Table S1). Interestingly, the symmetry of the [3^4.6.10^3] cage is C_3, which is the same as that of the [Ni(en)$_3$]$^{2+}$ cation. This implies that the [3^4.6.10^3] cage is also chiral, and that its chirality may come from the [Ni(en)$_3$]$^{2+}$ cation it holds. To understand this phenomenon, a molecular mechanics simulation was carried out. For ease of elucidation, hereafter the [3^4.6.10^3] cage holding the Δ-[Ni(en)$_3$]$^{2+}$ cation is referred to as the Δ-cage (Figure 2c), and that holding the Λ-[Ni(en)$_3$]$^{2+}$ cation as the Λ-cage (Figure 2d). First, energy optimization was carried out based on the real structure model in which the Δ-[Ni(en)$_3$]$^{2+}$ cations reside in the Δ-cages and the Λ-[Ni(en)$_3$]$^{2+}$ cations reside in the Λ-cages. After energy optimization, the nonbonding interaction energies, including the H-bond term, the van der Waals term, and the electrostatic term, were calculated. For comparison, the "opposite" structure model was built by exchanging the positions of Δ-[Ni(en)$_3$]$^{2+}$ and Λ-[Ni(en)$_3$]$^{2+}$ cations. By doing so, all of the Δ-[Ni(en)$_3$]$^{2+}$ cations were moved into the Λ-cages and all of the Λ-[Ni(en)$_3$]$^{2+}$ cations into the Δ-cages. After the same energy optimization procedure, the nonbonding interaction energies in this opposite structure model were also calculated. The nonbonding interactions in the real model are much stronger than those in the opposite model (Supporting Information, Table S2). This implies that the Δ-[Ni(en)$_3$]$^{2+}$ cation is more compatible with the Δ-cage, as is the Λ-[Ni(en)$_3$]$^{2+}$ cation with the Λ-cage. According to these results, we believe that molecular recognition exists between the framework of GaGeO-CJ63 and the chiral [Ni(en)$_3$]$^{2+}$ cations, which allows the symmetry and configurational information of the [Ni(en)$_3$]$^{2+}$ cations to be transferred into the cages of GaGeO-CJ63. This phenomenon has been previously observed in some open-framework zinc phosphates.[12]

Up to now, GaGeO-CJ63 and OSO are the only two 4-connected zeolitic structures exclusively formed by 3-rings. Both of these two structures have very low FD. As Brunner and Meier predicted,[3] frameworks with low FD can be formed by small rings. For instance, in Reticular Chemistry Structure Resource (RCSR)[13] database, many 4-connected 3D nets can be found with 3-rings. One of them is net **fud** (Figure 3a), which is in the space group $P\bar{4}3m$ with $a=11.3124$ Å after geometry optimization assuming all the vertices are Si atoms. In **fud**, a new [3^4.6^4] cage can be found (Figure 3b). Eight such cages are connected by 3-rings and form a 3D framework with intersecting 12-ring channels in three directions. The pore dimensions of each channel are 6.1 × 6.9 Å^2, and the FD of this structure is 10.4 T/1000 Å^3. Another example with massive 3-rings is net **lcv** (Figure 3c), which is in the space group $I4_132$ with $a=9.709$ Å after

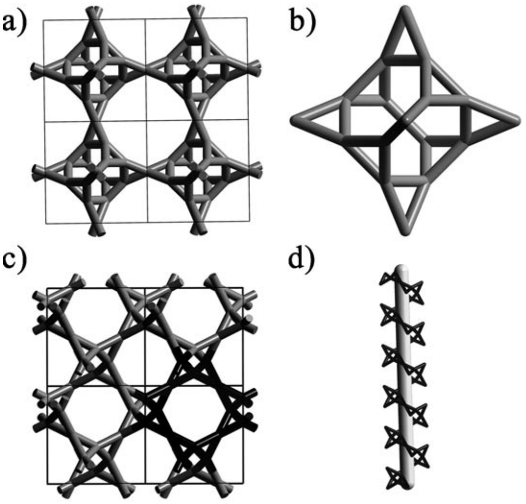

Figure 3. a) Zeolite structure generated from net **fud** viewed along the [001] direction, b) the [3^4.6^4] cage in **fud**, c) zeolite structure generated from net **lcv** along the [100] direction (a 10-ring helical channel is highlighted), and d) the helical channel running along the [100] direction in **lcv**.

geometry optimization. Net **lcv** contains intersecting 10-ring helical channels along the [100], [010], and [001] directions (Figure 3 d). The pore dimensions of the channel are 5.7 × 4.6 $Å^2$, and the FD is 13.1 T/1000 $Å^3$.

GaGeO-CJ63, OSO, and other 3-ringed structures, such as **fud** and **lcv**, demonstrate that a low FD may result from an abundance of 3-rings according to the Brunner–Meier principle.[3] To synthesize a zeolitic structure with low FD and possibly extra-large pores, other elements, such as germanium, can be used to replace silicon, since such elements could greatly facilitate the formation of small rings. Furthermore, the successful synthesis of GaGeO-CJ63 shows that novel zeolites with chiral features could be obtained through chirality transfer from rigid chiral metal complexes to inorganic frameworks.

Experimental Section

Synthesis: $[Ni(en)_3][Ga_2Ge_4O_{12}]$ (GaGeO-CJ63) was prepared under solvothermal conditions. GeO_2 (0.156 g) was dispersed in a mixture of H_2O (2 mL) and ethanolamine (4 mL), and then self-made GaOOH (0.137 g) and $[Ni(en)_3]Cl_2$ (0.173 g) were added with stirring. Finally, ethylenediamine (1 mL) and HF (40 wt %, 0.12 mL) were added. A homogeneous gel was formed after stirring for 2 h. The gel was sealed in a 15 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 days under static conditions. Large pink single crystals were separated from the remainder of the product by filtration, washed with distilled water, and then dried in air. Ethylenediamine is necessary for the preparation of GaGeO-CJ63 to maintain the stability of the nickel amine complex in the reaction system. Energy-dispersive X-ray (EDX) analysis, carried out on a JSM-6700F field-emission scanning electron microscope, gave an average molar ratio of Ge/Ga of 2/1. GaGeO-CJ63 collapsed at 350 °C with decomposition of the occluded metal complexes.

Structure determination: A suitable single crystal of GaGeO-CJ63 with dimensions of $0.4 \times 0.4 \times 0.3\ mm^3$ was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A total of 32 165 reflections, of which 1889 were unique ($R_{int} = 0.0775$), were collected in the region $2.13 < \theta < 28.28°$. The structure was solved in space group $Pa\bar{3}$ (No. 205). Unit-cell dimensions: $a = 16.5716(3)$ Å, $V = 4550.86(14)$ $Å^3$, and $\rho_{calcd} = 2.513\ g\,cm^{-3}$. The structure of GaGeO-CJ63 was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL97. All Ge, Ga, Ni, O, C and N positions were easily located. According to elemental analysis and the requirement of charge balance, the occupancies of Ge and Ga were fixed at 0.67 and 0.33 for each T position, respectively, which is in agreement with EDX analysis. All H atoms were placed geometrically and refined with a riding model. Experimental details for the structure determination are presented in Supporting Information, Table S3. The atomic coordinates are presented in Supporting Information, Table S4. CCDC 796382 (GaGeO-CJ63) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Topological analysis: The natural tiling was calculated by using the free software TOPOS[11] (Supporting Information, Figure S2). The coordination sequences were calculated by using the software Systre[14] (Supporting Information, Table S5), and the program 3dt[15] was used for visualization of all the tiles. Energy optimization was performed with Accelrys Materials Studio 4.0.[16] Dreiding 2.21 force field[17] was used to calculate the interactions between metal complexes and the framework of GaGeO-CJ63. During energy optimization, the framework of GaGeO-CJ63 was kept fixed and all the Ni complexes were treated as rigid bodies.

Received: October 16, 2010
Revised: December 18, 2010

Keywords: chirality · gallogermanates · nickel · solvothermal synthesis · zeolite analogues

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[1] a) D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley, New York, **1974**; b) J. Čejka, A. Corma, S. Zones, *Zeolites and Catalysis: Synthesis, Reactions and Applications*, Wiley, Weinheim, **2010**.
[2] J. Jiang, J. Yu, A. Corma, *Angew. Chem.* **2010**, *122*, 3186 – 3212; *Angew. Chem. Int. Ed.* **2010**, *49*, 3120 – 3145.
[3] G. O. Brunner, W. M. Meier, *Nature* **1989**, *337*, 146 – 147.
[4] A. K. Cheetham, H. Fjellvåg, T. E. Gier, K. O. Kongshaug, K. P. Linllerud, G. D. Stucky, *Stud. Surf. Sci. Catal.* **2001**, *135*, 158.
[5] M. J. Annen, M. E. Davis, J. B. Higgins, J. L. Schlenker, *J. Chem. Soc. Chem. Commun.* **1991**, 1175 – 1176.
[6] a) X. Bu, P. Feng, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 11204 – 11205; b) Y. Li, X. D. Zou, *Angew. Chem.* **2005**, *117*, 2048 – 2051; *Angew. Chem. Int. Ed.* **2005**, *44*, 2012 – 2015; c) A. Corma, M. Díaz-Cabañas, J. L. Jordá, C. Martínez, M. Moliner, *Nature* **2006**, *443*, 842 – 845; d) L. Shi, K. E. Christensen, K. Jansson, J. Sun, X. Zou, *Chem. Mater.* **2007**, *19*, 5973 – 5979; e) J. Su, Y. Wang, Z. Wang, J. Lin, *J. Am. Chem. Soc.* **2009**, *131*, 6080 – 6081.
[7] a) T. Conradsson, M. S. Dadachov, X. D. Zou, *Microporous Mesoporous Mater.* **2000**, *41*, 183 – 191; b) L. Q. Tang, L. Shi, C. Bonneau, J. L. Sun, H. J. Yue, A. Ojuva, B. L. Lee, M. Kritikos, B. Zoltán, J. Mink, R. G. Bell, X. D. Zou, *Nat. Mater.* **2008**, *7*, 381 – 385; c) A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, F. Rey, G. Sastre, G. Strihmaier, *J. Am. Chem. Soc.* **2008**, *130*, 16482 – 16483; d) J. Sun, C. Bonneau, Á. Cantín, A. Corma, M. J. M. Díaz-Cabañas, M. Moliner, D. Zhang, M. Li, X. Zou, *Nature* **2009**, *458*, 1154 – 1157.
[8] J. Jiang, J. L. Jorda, M. J. Diaz-Cabanas, J. Yu, A. Corma, *Angew. Chem.* **2010**, *122*, 5106 – 5108; *Angew. Chem. Int. Ed.* **2010**, *49*, 4986 – 4988.
[9] C. Baerlocher, L. B. McCusker, D. H. Olson, *Atlas of Zeolite Framework Types*, 6th rev. ed., Elsevier, Amsterdam, **2007**; IZA Structure Commission website: http://www.iza-structure.org/databases/.
[10] a) K. Morgan, G. Gainsford, N. Milestone, *J. Chem. Soc. Chem. Commun.* **1995**, 425 – 426; b) Y. Wang, J. Yu, M. Guo, R. Xu, *Angew. Chem.* **2003**, *115*, 4223 – 4226; *Angew. Chem. Int. Ed.* **2003**, *42*, 4089 – 4092; c) Z. Lin, J. Zhang, J. Zhao, S. Zheng, C. Pan, G. Wang, G. Yang, *Angew. Chem.* **2005**, *117*, 7041 – 7044; *Angew. Chem. Int. Ed.* **2005**, *44*, 6881 – 6884.
[11] V. A. Blatov, O. Delgado-Friedrichs, M. O'Keeffe, D. M. Proserpio, *Acta Crystallogr. Sect. A* **2007**, *63*, 418 – 425.
[12] a) J. Yu, Y. Wang, Z. Shi, R. Xu, *Chem. Mater.* **2001**, *13*, 2972 – 2978; b) Y. Wang, J. Yu, Y. Li, Z. Shi, R. Xu, *Chem. Eur. J.* **2003**, *9*, 5048 – 5055.
[13] M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.* **2008**, *41*, 1782 – 1789.
[14] O. Delgado-Friedrichs, M. O'Keeffe, SYSTRE.http://gavrog.org/ (accessed **2006**).
[15] O. Delgado-Friedrichs, M. O'Keeffe, *Acta Crystallogr. Sect. A* **2003**, *59*, 351 – 360.
[16] Accelrys. Materials Studio, Release 4.0. **2006**, Accelrys Software Inc., San Diego.
[17] S. L. Mayo, B. D. Olafson, W. A. Goddard, *J. Phys. Chem.* **1990**, *94*, 8897 – 8909.