Germanates

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A Germanate Built from a $6^8 12^6$ Cavity Cotemplated by an $(H_2O)_{16}$ Cluster and 2-Methylpiperazine**

Qinhe Pan, Jiyang Li, Kirsten E. Christensen, Charlotte Bonneau, Xiaoyan Ren, Lei Shi, Junliang Sun, Xiaodong Zou, Guanghua Li, Jihong Yu,* and Ruren Xu*

Zeolites and other open-framework oxide materials are interesting because of their catalytic, adsorption, and ion-exchange properties. The pore size and shape of an open-framework material determine its application. An important challenge is to design open-framework oxides with large pores. One approach to constructing open-framework materials with large or extra-large pores is to use large building units, a concept named "scale chemistry".[1] An example of a material constructed by such an approach is the germanate SU-M, which is built from $Ge_{10}X_{28}$ (X = O, OH, F) clusters and which contains 30-ring gyroidal channels and cavities larger than 20 Å.[2a] Thus, it is important to identify large structural motifs as possible building units and to establish a synthesis route that will produce such building units. Recently, much attention has been paid to the synthesis of open-framework germanates.[2–7] Germaniun can be four-, five-, or six-coordinated to form large clusters, such as Ge_7X_{19} (Ge_7),[2,3] Ge_8X_{20} (Ge_8),[2b,4] Ge_9X_{26-m} (Ge_9; $m = 0$–1),[2c,5] and $Ge_{10}X_{28}$ (Ge_{10})[2a,6] (X = O, OH, F). The Ge_7 cluster is of particular interest, as it is found in the 1D tubular germanate JLG-4 (12-rings),[3d] in the 2D layered germanates ASU-19 and ASU-20,[3e] as well as in 3D frameworks with large or extra-large pores,[2,3a–c] such as ASU-12 (16-rings),[3a] ASU-16 (24-rings),[3b] and the silicogermanate SU-12 (24-rings).[3c] Examples of Ge_7 clusters forming large polyhedra (0D objects) remain to be discovered. Herein, we present a tubular germanate, $[(C_5N_2H_{14})_4(C_5N_2H_{13})(H_2O)_4][Ge_7O_{12}O_{4/2}(OH)F_2][Ge_7O_{12}O_{5/2}(OH)F]_2[GeO_{2/2}(OH)_2]$ (denoted JLG-5), with 12-ring channels built from $6^8 12^6$ cavities. JLG-5 was obtained by hydro(solvo)thermal synthesis and was cotemplated by 2-methylpiperazine and an $(H_2O)_{16}$ cluster. The highly symmetric $6^8 12^6$ cavity, built from Ge_7 clusters, is stabilized by an $(H_2O)_{16}$ cluster. This $6^8 12^6$ cavity is the second largest and highest symmetry cavity found in pure germanates as yet.

JLG-5 crystallizes in the $P4/mnc$ space group with $a = 29.0706(6)$ and $c = 22.6849(6)$ Å. The structure is built from two unique Ge_7 clusters and one unique additional tetrahedron. The Ge_7 clusters each consist of one germanium-centered octahedron, two germanium-centered trigonal bipyramids, and four germanium-centered tetrahedra. Twelve Ge_7 clusters are linked together to form a $6^8 12^6$ cavity containing eight 6-ring and six 12-ring windows (formula $[Ge_{84}O_{176}X_{28}]^{44-}$, X = OH, F; Figure 1). The $6^8 12^6$ cavity in JLG-5 has the point symmetry $4/m$ (C_{4h}). As the maximum point symmetry of the $6^8 12^6$ cavity is $m\bar{3}m$ (O_h), the $6^8 12^6$ cavity represents the most symmetric cavity found in a pure germanate. The free diameters of the 12-ring windows are 3.8×3.8 and 3.8×4.5 Å^2, and those of the $6^8 12^6$ cavity are $6.4 \times 7.0 \times 7.0$ Å^3. The $6^8 12^6$ cavity represents the second largest cavity found in a pure germanate, in comparison with the cavity found in SU-M with free diameters of 10.0×22.4 Å^2.[2a]

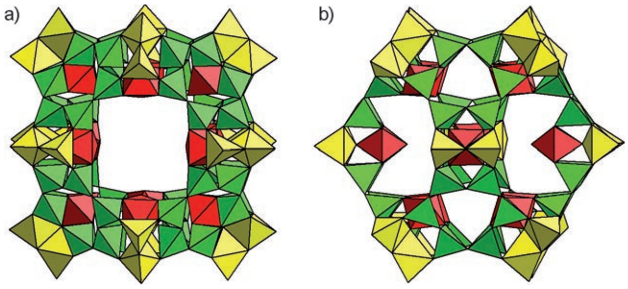

Figure 1. The $6^8 12^6$ cavity, built from 12 Ge_7 clusters, viewed along a) the [001] and b) the [$1\bar{1}0$] directions. The point symmetry of the $6^8 12^6$ cavity is $4/m$ (C_{4h}). The germanium-centered octahedra are red, the germanium-centered trigonal bipyramids are yellow, and the germanium-centered tetrahedra are green.

The $6^8 12^6$ cavities are arranged in a body-centered manner with their 12-ring windows aligned on top of each other (Figure 2a). They are further linked along the c axis by additional $GeO_2(OH)_2$ tetrahedra to form tubes containing 12-ring channels (Figure 2b). The tubes are aligned in parallel to the c axis and are held together through diprotonated 2-methylpiperazine cations via hydrogen bonding (Figure 2b).

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[*] Q. Pan, Dr. J. Li, X. Ren, Dr. G. Li, Prof. J. Yu, Prof. R. Xu
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University
Changchun 130012 (P.R. China)
Fax: (+86) 431-8516-8608
E-mail: jihong@jlu.edu.cn
K. E. Christensen, Dr. C. Bonneau, Dr. L. Shi, Dr. J. Sun, Prof. X. Zou
Structural Chemistry and Berzelii Centre EXSELENT on Porous Materials, Stockholm University, 10691 Stockholm (Sweden)
E-mail: zou@struc.su.se

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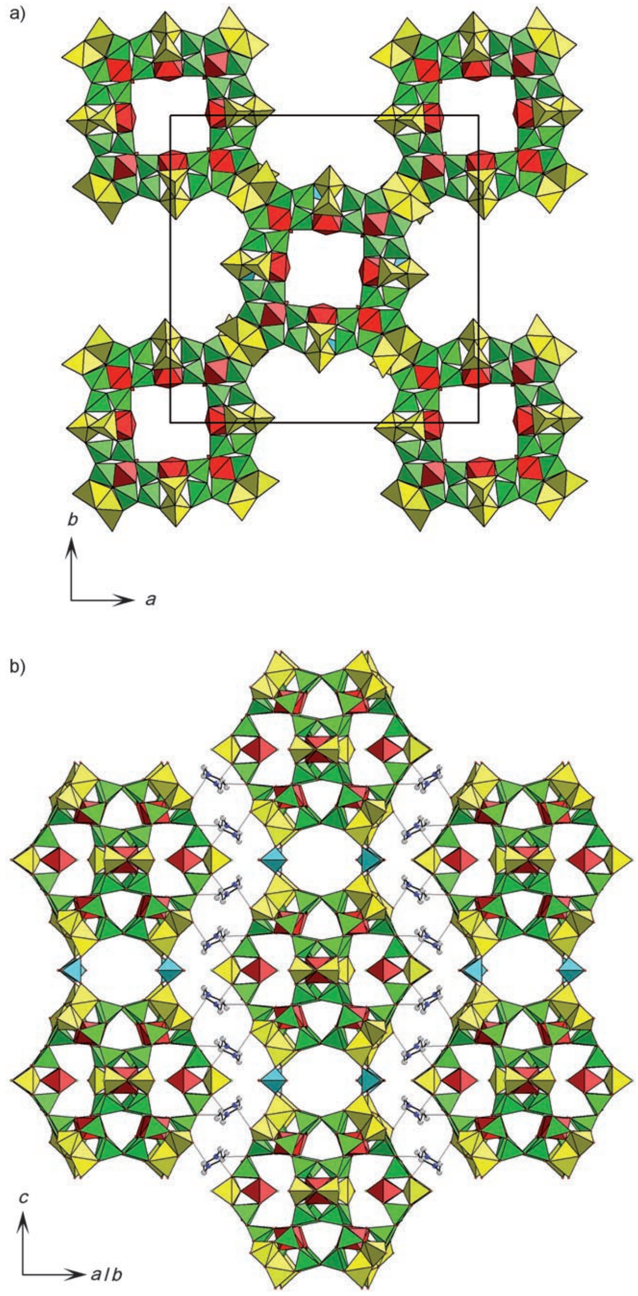

Figure 2. The structure of JLG-5 viewed along a) the [001] and b) the [$1\bar{1}0$] directions. The $6^{8}12^{6}$ cavities are packed in a body-centered manner, with the 12-ring windows aligned along the three main axes. The $6^{8}12^{6}$ cavities are connected through additional germanium-centered tetrahedra (blue) along the *c* axis to form 12-ring tubes. The tubes are held together by 2-methylpiperazine cations (C gray, N blue) via hydrogen bonding. Within the Ge_7 clusters, the germanium-centered octahedra are red, the germanium-centered trigonal bipyramids are yellow, and the germanium-centered tetrahedra are green. For clarity, only one unique 2-methylpiperazine cation is shown in (b), and the water cluster is omitted.

Inorganic tubular structures reminiscent of carbon nanotubes are of interest,[3d,8] and JLG-5 is the second germanate found to have a tubular structure. The first tubular germanate observed, JLG-4, is also built from Ge_7 clusters and contains 12-ring channels.[3d]

JLG-5 presents a remarkable feature: each $6^{8}12^{6}$ cavity encapsulates a unique hydrogen-bonded $(H_2O)_{16}$ cluster, which stabilizes the cavity (Figure 3). A similar protonated $(H_{41}O_{16})^{9+}$ cluster has been observed in a zeolite A-like silicate, $[\{N(n\text{-}C_4H_9)_4\}H_7(H_2O)_{5.33}][Si_8O_{20}]$, synthesized at room temperature, which has a pseudo-3D framework composed of hydrogen-bonded double-four-ring Si_8O_{20} clusters.[9] In JLG-5, each $(H_2O)_{16}$ cluster is constituted of eight Ow1 atoms linked through hydrogen bonding to form a cube-like $(H_2O)_8$ cluster, with Ow1⋯Ow1 distances of 2.649 and 2.804 Å. Each Ow1 atom then further connects to an Ow2 atom via hydrogen bonding (Ow1⋯Ow2 2.754 Å), leading to the overall formation of a unique eight-clawed cube-like $(H_2O)_{16}$ cluster. A second level of extensive hydrogen-bonding interactions involving the $(H_2O)_{16}$ cluster and the Ge_7 clusters of the $6^{8}12^{6}$ cavity is also observed (Figure 3). Each Ow1 atom is hydrogen-bonded to two Ge_7 clusters, and each Ow2 atom is hydrogen-bonded to three Ge_7 clusters. The $(H_2O)_{16}$ cluster has a point symmetry of $4/mmm$ (D_{4h}), and we believe that the $(H_2O)_{16}$ cluster plays an important templating or structure-directing role in the formation of the $6^{8}12^{6}$ cavity. A similar templating or structure-directing role was played by water aggregates in the formation of MIL-74, $[\{N(CH_2CH_2NH_3)_3\}_8(H_2O)_{34}][Zn_6Al_{12}P_{24}O_{96}]$, in which each sodalite cage encapsulates an $(H_2O)_{17}$ cluster,[10a] and in the formation of the aluminophosphate molecular sieve VPI-5, in which a triple helix of hydrogen-bonded water molecules is located inside an 18-ring channel.[10b]

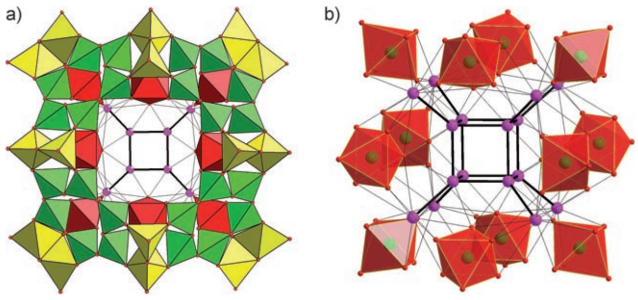

Figure 3. a) The $6^{8}12^{6}$ cavity viewed down the *c* axis, showing hydrogen bonding within the cube-like $(H_2O)_{16}$ cluster (thick lines; O pink) as well as between the water cluster and the $6^{8}12^{6}$ cavity (thin lines). The germanium-centered octahedra are red, the germanium-centered trigonal bipyramids are yellow, and the germanium-centered tetrahedra are green. b) A complete view of the hydrogen-bonding pattern formed by the cube-like $(H_2O)_{16}$ cluster inside the $6^{8}12^{6}$ cavity. For clarity, only the germanium-centered octahedra (Ge green, O red) of the Ge_7 clusters are shown in (b). No hydrogen atoms are shown.

There are four unique 2-methylpiperazine molecules in JLG-5, and they also play an important structure-directing role (see Figures S1 and S2 in the Supporting Information). One 2-methylpiperazine molecule is located at the 12-ring window, perpendicular to the *a* or *b* axis, and holds four Ge_7 clusters together. Another 2-methylpiperazine molecule is located at the 10-ring window between two $6^{8}12^{6}$ cavities and is hydrogen-bonded to Ge_7 clusters and additional tetrahedra. The third 2-methylpiperazine molecule is located between the tubes and holds adjacent tubes together via hydrogen bonding

(Figure 2b). The fourth 2-methylpiperazine molecule is located between two 6-rings from two adjacent tubes and only interacts weakly with the tubes.

The $6^{8}12^{6}$ cavity can be easily identified as a cuboctahedron (Figure 4a and b) with each of its 12 vertices decorated by a four-coordinated Ge_7 cluster (Figure 4c). In JLG-5, the cuboctahedra are two-coordinated in one dimension to form tubes. We, therefore, expect that the $6^{8}12^{6}$ cavity can be further used as a building unit to build 3D framework structures with extra-large pores. The reo-e net corresponds to the primitive cubic packing of six-coordinated cuboctahedra (Figure 4d).[11] If each vertex of the reo-e net is decorated by a six-coordinated Ge_7 cluster, a new, hypothetical 3D germanate framework ($Pm\bar{3}m$, $a = 22.9078$ Å) with two types of cavities, the $6^{8}12^{6}$ cavity and a $6^{8}10^{6}12^{12}$ supercavity, is formed (Figure 4e). The $6^{8}10^{6}12^{12}$ supercavity has a free diameter of 17.8 Å and corresponds to a rhombicuboctahedron (rco; Figure 4f and g) decorated by Ge_7 clusters (Figure 4h). The $6^{8}12^{6}$ cavities themselves adopt a primitive cubic arrangement. Each $6^{8}12^{6}$ cavity is connected to six other cavities by linking their six 12-rings through additional germanium-centered tetrahedra, in a similar way as in JLG-5. The arrangement of the $6^{8}12^{6}$ cavities in the hypothetical structure is similar to that of the β cages ($4^{6}6^{8}$) in zeolite A, which results in α cavities ($4^{12}6^{8}8^{6}$).

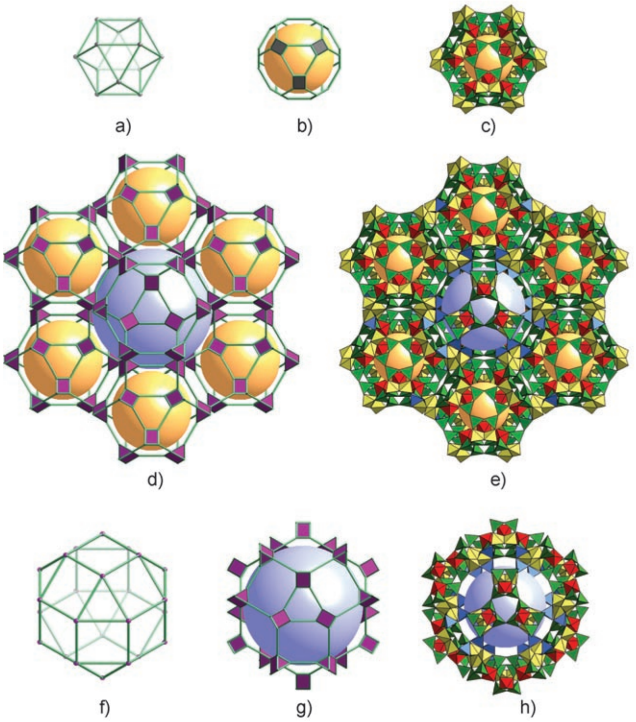

Figure 4. Abstraction of the $6^{8}12^{6}$ cavity and a hypothetical 3D framework built from the cavity. a) A cuboctahedron. b) Augmented cuboctahedron with four-coordinated nodes (gray). c) The $6^{8}12^{6}$ cavity resulting from the decoration of each node of the cuboctahedron by a four-coordinated Ge_7 cluster. d) Augmented reo-e net with six-coordinated nodes (violet). e) A hypothetical 3D framework resulting from the decoration of each node of the reo-e net by a six-coordinated Ge_7 cluster. f) The rhombicuboctahedron found in (e). g) Augmented rhombicuboctahedron with six-coordinated nodes (violet). h) A $6^{8}10^{12}12^{6}$ cavity resulting from the decoration of each node of the rhombicuboctahedron with a six-coordinated Ge_7 cluster. The yellow and blue spheres represent the $6^{8}12^{6}$ and $6^{8}10^{12}12^{6}$ cavities with free diameters of 7.1 and 17.8 Å, respectively. The germanium-centered octahedra are red, the germanium-centered trigonal bipyramids are yellow, and the germanium-centered tetrahedra are green. The additional germanium-centered tetrahedra are blue.

In summary, we have discovered a large cubic building unit consisting of a $6^{8}12^{6}$ cavity formed by 12 Ge_7 clusters. A tubular germanate JLG-5 with 12-ring channels has been obtained by hydro(solvo)thermal synthesis. Notably, a unique hydrogen-bonded $(H_2O)_{16}$ cluster is present in each $6^{8}12^{6}$ cavity and possibly supports the formation of the cavity. This work provides a remarkable example of the templating role played by $(H_2O)_n$ clusters in the synthesis of open-framework materials. We believe that more exotic germanate structures can be formed by using inorganic building units such as the Ge_7 cluster or cavities built from the Ge_7 cluster. It is important to understand the formation of the building units and to be able to control the packing of such building units. One challenge would be to obtain a 3D germanate framework containing both the $6^{8}12^{6}$ cavity and the even larger supercavity $6^{8}10^{6}12^{12}$ with a free-diameter of 17.8 Å, as proposed herein.

Experimental Section

Synthesis and characterization: JLG-5 was synthesized under hydro(solvo)thermal conditions with pyridine and H_2O as the solvents. Typically, GeO_2 (0.156 g) was dispersed in a mixture of H_2O (1.5 mL) and pyridine (5 mL) with constant stirring. Then, 2-methylpiperazine (0.7 g) and HF (40 wt%, 0.12 mL) were added to this mixture. A homogeneous gel with a composition of GeO_2/H_2O/pyridine/2-methylpiperazine/HF in a molar ratio of 1:58.6:43.2:4.7:1.6 was formed after stirring for about 2 h. The gel was finally transferred to a 15-mL teflon-lined stainless-steel autoclave and heated at 160 °C for 5–6 days under static conditions. JLG-5 could be prepared in the composition range of (0.7–1.3) GeO_2:58.6 H_2O:43.2 pyridine:(4–5.3) 2-methylpiperazine:1.6 HF. Colorless rod-shaped single crystals of JLG-5 were separated by filtration, washed with distilled water and acetone, and finally protected from desolvation.

Powder X-ray diffraction was performed on a PANalytical X'Pert Pro Alpha-1 equipped with a PIXcel detector (see Figure S3 in the Supporting Information). Inductively coupled plasma analyses were performed on a Perkin–Elmer Optima 3300DV spectrometer (calcd (wt%): Ge 52.46; found: Ge 51.52). Elemental analyses were conducted on a Perkin–Elmer 2400 elemental analyzer (calcd (wt%): C 9.86, H 2.72, N 4.60; found: C 9.81, H 2.99, N 4.40). Fluorine analysis was conducted with a fluoride-ion selective electrode (calcd (wt%): F 2.50; found: 2.45). A Perkin–Elmer TGA 7 unit was used for thermogravimetric analysis in air with a heating rate of 20 °C min^{-1}. A total weight loss of 25.89% was detected between 40 and 800 °C, which corresponds to the loss of free water, the decomposition of occluded 2-methylpiperazine, and the release of terminal hydroxy groups and fluorine atoms in the form of H_2O and HF, respectively (calcd 24.41%; see Figure S4 in the Supporting Information).

A suitable single crystal of JLG-5 with dimensions of 0.21 × 0.02 × 0.01 mm^3 was selected for single-crystal X-ray diffraction. Single-crystal X-ray diffraction data were collected at 100 K on an Xcalibur 3 diffractometer equipped with a Sapphire CCD camera and using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The data were reduced with the CrysAlis software package. The structure of JLG-5 was solved by direct methods and refined on F^2 by full-matrix least squares using SHELX97. All germanium, fluorine, oxygen, carbon, and nitrogen atoms were located. Fluorine and oxygen atoms were distinguished by their atomic displacement parameters. Two of the three unique fluorine atoms (F2 and F3) are terminal atoms in the octahedra of the two unique Ge_7 clusters and are hydrogen-bonded to the water clusters within the cavity. The other fluorine atom (F1) acts as the terminal atom in one of the trigonal bipyramids. Three of the four unique 2-methylpiperazine are disordered, each with two possible orientations. No hydrogen atoms were added. Experimental details concerning the structure determination are presented in Table S1 in the Supporting Information. The atomic coordinates are presented in Table S2 in the Supporting Information.

Crystal data for JLG-5: $M_r = 3043.99$, tetragonal, $P4/mnc$ (no. 176), $a = 29.0706(6)$, $c = 22.6849(6)$ Å, $V = 19171.0(8)$ Å^3, $Z = 8$, $\mu = 6.879$ mm^{-1}, $\rho_{calcd} = 2.077$ g cm^{-3}, 146053 reflections measured, 3885 unique (Rint = 0.1446). The final $R1$ ($I > 2\sigma(I)$) was 0.0507, and the final wR_2 (all data) was 0.1406. CCDC-681515 (JLG-5) 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. The 3D structure model with the supercavity $6^8 10^6 12^{12}$ was geometrically built from the $6^8 12^6$ cavity in JLG-5 packed in a primitive cubic lattice and was finally geometry optimized by the Forcite module in Materials Studio.

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