

[Ge₉O₁₄(OH)₁₂](C₆N₂H₁₆)₂·H₂O: A Novel Germanate with Ge–O Helical Chains Formed by Hydrothermal Synthesis that Can Separate *trans* and *cis* Isomers in Situ

Yan Xu,^{*,[a]} Wei Fan,^[a] S. P. Elangovan,^[a] Masaru Ogura,^[a] and Tatsuya Okubo^{*,[a]}

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A novel germanate [Ge₉O₁₄(OH)₁₂](C₆N₂H₁₆)₂·H₂O (**1**; UTM-4) has been synthesized under hydrothermal conditions and its structure characterized by X-ray crystallography [$a = 9.293(2)$, $b = 12.164(2)$, $c = 14.564(3)$ Å, $\beta = 94.96(3)^\circ$, $V = 1640.1(6)$ Å³, $Z = 2$, monoclinic, space group $P2_1/c$]. The structure consists of Ge–O layers of helical chains, which are

linked by hydrogen bonds to form a soft, open framework that exhibits a selectivity for *cis*-1,4-diaminocyclohexane during the synthesis.

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Introduction

Great efforts have been made to synthesize germanium frameworks, as germanium is the closest analog to silicon and is therefore an attractive element to build open-frameworks in zeolite chemistry.^[1–9] In germanates, Ge can adopt different Ge/O radius ratios to form polyhedra with a coordination number of four (tetrahedron), five (square bipyramid) or six (octahedron). The Ge–O distances are also significantly longer than the Si–O bond in silicates. Therefore, the flexibility of the polyhedral structure for germanium allows the formation of various open-framework structures with an extra-large pore, such as FDU-4^[7a] and ASU-16.^[7b] Recent research in the field of materials chemistry has focused on the synthesis of inorganic materials with helical pores or chains as they are desirable for selective enantiotopic separation and catalysis.^[4d,10–14] Among the open-framework materials reported so far, only a limited number of phosphates and germanates^[2c,4d] have such structural features. For examples, the zinc phosphate [NH₃(C₂H₄)NH₂(C₂H₄)NH₃][Zn₄(PO₄)₃(HPO₄)]·H₂O^[10] possesses intersecting helical chains, UCSB-7 has cross-linked helical pores,^[4d] and the vanadophosphate [(CH₃)₂NH₂]₄[V₁₀O₁₀(H₂O)₂(OH)₄(PO₄)₇]^[11] contains interpenetrating double helices. Some other examples include aluminum phosphates, gallium phosphates, boron phosphates, and zinc phosphates.^[12,13] Here we report the hydrothermal synthesis and structural characterization of a novel germanate [Ge₉O₁₄(OH)₁₂](C₆N₂H₁₆)₂·H₂O (**1**) with a par-

ticularly interesting structure containing helical Ge–O chains that is selective for *cis*-1,4-diaminocyclohexane during the synthesis.

Results and Discussion

Germanate **1** was synthesized by a hydrothermal method from an organic-rich gel consisting of germanium dioxide, a mixture of *cis*- and *trans*-1,4-diaminocyclohexane, HF, pyridine, and H₂O in a 25-mL, Teflon-lined autoclave at 175 °C for 7 d. The crystalline product was characterized by thermal analysis (TG-DTA), powder X-ray diffraction (XRD) and single-crystal XRD.

The structural analysis revealed that the novel Ge–O layers are linked by hydrogen bonds to form a three-dimensional structure, and that only *cis*-1,4-diaminocyclohexane is present in **1**. As shown in Figure 1, the Ge–O (or OH) layer is constructed from three units, namely {[GeO₃(OH)₂](GeO₄)–[GeO₄(OH)]}_n helical chains, [Ge(OH)₂]²⁺ fragments connected by different chains, and [Ge(OH)₃]⁺ fragments bonded by three bridging O-atoms from one chain that stabilize the helical chains. In the helical chain, GeO₄OH and GeO₃OH₂ trigonal bipyramids share their edges, and they are linked by corner-sharing GeO₄ tetrahedra. The central axis for every Ge–O helical chain is a twofold screw axis (symmetry: $-x, 0.5 + y, 0.5 - z$). Two bridging O atoms from adjacent GeO₄ and GeO₃OH₂ units in the helical Ge–O chain coordinate to another germanium of [Ge(OH)₂]²⁺, generating a three-membered [Ge₃O₃] ring. These three-membered rings link the right- and left-handed helical Ge–O chains (Figure 1b) to produce a Ge–O layer in the 011 plane (Figure 1a). Adjacent Ge–O layers are connected by hydrogen bonds

^[a] Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
Fax: + 81-3-5800-3806
E-mail: yanxu@chemsys.t.u-tokyo.ac.jp
okubo@chemsys.t.u-tokyo.ac.jp

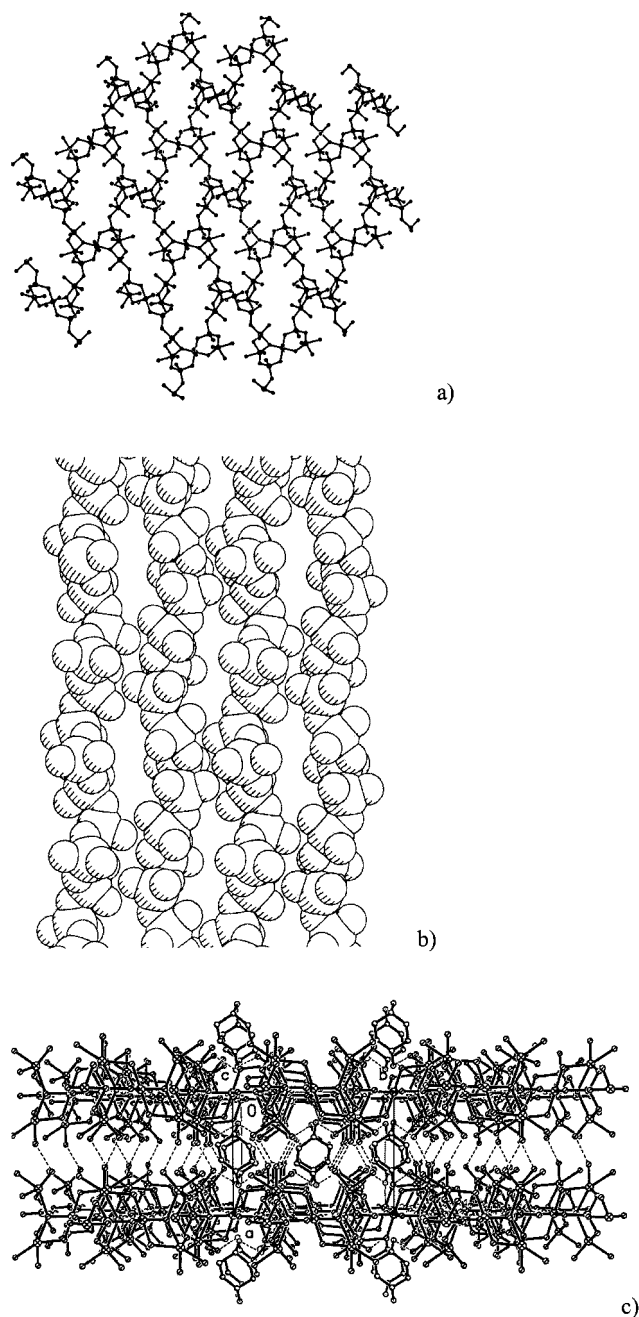


Figure 1. a) View of the Ge–O layer [$\text{Ge}(\text{OH})_3^+$ fragments have been omitted]; b) helical Ge–O chains; c) three-dimensional, hydrogen-bonded structure (*cis*-1,4-diaminocyclohexane has been omitted for clarity)

through terminal OH groups to form a three-dimensional structure (Figure 1c).

The Ge in $[\text{Ge}(\text{OH})_2]^{2+}$ is located at the symmetric center and, therefore, is constrained by symmetry to adopt an octahedral coordination (bonded by four bridging oxygen atoms and two hydroxyl groups), while the Ge of $[\text{Ge}(\text{OH})_3]^+$ is chelated by three bridging oxygen atoms from a helical Ge–O chain, and shares one bridging OH with $[\text{Ge}(\text{OH})_2]^{2+}$, to stabilize the helical chains and layers. There are three unique germanium sites in the helical chains: one regular tetrahedrally coordinated germanium

(GeO_4) is bonded to four oxygen atoms, and two kinds of five-coordinate germanium sites $[\text{GeO}_3(\text{OH})_2]$ and $\text{GeO}_4(\text{OH})$ are coordinated by O atoms and OH groups. Some terminal OH groups are involved in hydrogen-bond interactions between adjacent layers. The shortest $\text{O}\cdots\text{O}$ distance in the two layers is 2.96(2) Å. The Ge–OH distances for these OH groups are 2.038(8) and 2.094(8) Å, which are much longer than the other reported Ge–OH bond lengths. This can be ascribed to the hydrogen bonds between adjacent layers. All the Ge–O bond lengths for the tetrahedral germanium center vary from 1.712(4) to 1.752(5) Å [mean 1.730(4) Å], and are very similar to the reported value for the quartz modification of GeO_2 [1.741(3) Å]. The Ge–O bond lengths for the five- and six-coordinate germanium centers range from 1.683(10) to 2.344(8) Å. These values are in agreement with those observed for known germanates.

A particularly interesting aspect of this reaction is the selectivity for *cis*-1,4-diaminocyclohexane (Figure 2) in the synthesis of germanate 1. The separation of isomers is, in general, very difficult because of their similar physical and chemical properties. For example, the boiling point of both *trans*- and *cis*-1,4-diaminocyclohexane is 197 °C. Here we found that *cis*-1,4-diaminocyclohexane was successfully recovered from the mixture. In order to separate the isomers, a mixture of *trans*- and *cis*-1,4-diaminocyclohexane (approx. 1:1) was used as the reactant in a separation experiment. After hydrothermal synthesis, *cis*-1,4-diaminocyclohexane was found to be concentrated in the Ge–O layers as a guest molecule, with both N-atoms of the organic amine binding to the helical Ge–O chains through $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen-bond interactions, while *trans*-1,4-diaminocyclohexane remained in solution. We analyzed the structures of four different crystals of germanate 1 but did not find any *trans*-1,4-diaminocyclohexane.

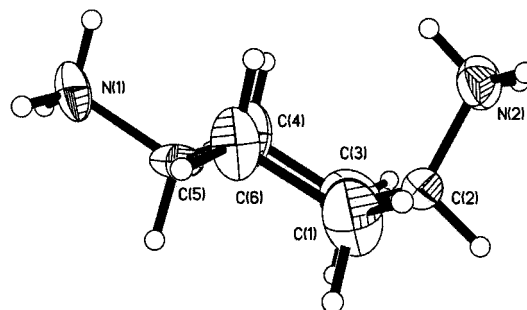


Figure 2. *cis*-1,4-Diaminocyclohexane was selected by germanate 1

Significant changes in the powder X-ray diffraction patterns and TG curve were seen after germanate 1 was stirred in a 1 m solution of NaNO_3 at 50 °C. These ion-exchange results indicate that part of the structure-directing agents (SDAs) can be exchanged.

Thermal analysis of germanate 1 under a 10% O_2 (Ar balance) atmosphere reveals a weight loss of 1.3% between 60 and 226 °C, followed by a further weight loss of 26.7% between 226 and 700 °C. The calculated weight losses for

water (1.35%) and combustion of the SDA and OH (28.6%) are in agreement with these results.

In conclusion, a novel germanate with helical Ge–O chains has been synthesized. This compound can separate *cis*- and *trans*-1,4-diaminocyclohexane in situ during the hydrothermal synthesis. The present work has great significance for germanium chemistry and isomer separation.

Experimental Section

1: Colorless, plate-like crystals of $[\text{Ge}_9\text{O}_{14}(\text{OH})_{12}](\text{C}_6\text{N}_2\text{H}_{16})_2 \cdot 2\text{H}_2\text{O}$ were prepared by a hydrothermal method from an organic-rich solution consisting of GeO_2 , SiO_2 , a mixture of *trans*- and *cis*-1,4-diaminocyclohexane, HF, pyridine, and H_2O in a molar ratio of 1:1:7.5:4.5:51:75. To avoid the formation of $\text{Ge}_7\text{O}_{14}\text{F}_3 \cdot [\text{H}_2\text{DACH}]_{1.5} \cdot 2\text{H}_2\text{O}$ ^[15] (H_2DACH = diaminocyclohexane) SiO_2 was added to induce the formation of germanate **1**. GeO_2 (0.12 g) and SiO_2 (0.60 g) were added to a mixture of pyridine (4.66 g), 1,4-diaminocyclohexane (1.05 g, mixture of *trans* and *cis* isomers), and water (1.55 g). Thereafter, this gel was stirred at room temperature overnight. Finally, a 47% HF solution (0.10 g) was added. The mixture was kept in a 25-mL, Teflon-lined autoclave at 170 °C for 7 d. The product was then washed with deionized water and ethanol, and dried at room temperature for 24 h (0.07 g; yield 41% based on Ge). Germanate **1** can also be synthesized under the same conditions but without SiO_2 powder. $\text{C}_{12}\text{H}_{46}\text{Ge}_9\text{N}_4\text{O}_{27}$: calcd. C 10.81, H 3.45, N 4.20; found C 10.10, H 3.67, N 3.91. X-ray powder diffraction analysis was performed on an M03X-HF (MAC Science) diffractometer, with Cu-K_α radiation, at 40 kV and 20 mA at a scanning rate of 4°/min with a step of 0.02°. Thermogravimetric (TG) analysis of germanate **1** was carried out under an O_2/Ar atmosphere on a Thermoplus TG 8120 (Rigaku) analyzer from 25 to 750 °C, at a heating rate of 10 °C/min.

X-ray Crystallographic Study: $\text{C}_{12}\text{H}_{46}\text{Ge}_9\text{N}_4\text{O}_{27}$, monoclinic, $P2_1/C$ (no.14), $a = 9.293(2)$, $b = 12.164(2)$, $c = 14.564(3)$ Å, $\beta = 94.96(3)^\circ$, $V = 1640.1(6)$ Å³, $Z = 2$, $\mu(\text{Mo-K}_\alpha) = 8.237$ mm⁻¹. Dimensions: $0.12 \times 0.11 \times 0.05$ mm. 3661 Reflections with $I > 2\sigma(I_0)$ and 268 parameters gave $R1$ (wR) = 0.0729 (0.1223). The occupancy factors are 0.5 for O8, O8a, O12, O12a, O13, and O13a. Diffraction data were collected on a Rigaku R-Axis RAPID IP diffractometer at 20 °C in the range $2.76^\circ < \theta < 27.44^\circ$. An empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. The oxygen atoms O5, O10, O11, O12, O12a, O13, and O13a are terminal and correspond to OH, as in other reported germanates. The half-occupied O8 and O8a atoms also belong to OH, because of their low thermal parameters and longer bond distances than other doubly bridging O-atoms.

CCDC-233622 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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