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Two Open-Framework Germanates with Nickel Complexes Incorporated into the Framework

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S *Supporting Information*

ABSTRACT: Two open-framework germanates, SUT-1 and SUT-2, have been synthesized under hydrothermal conditions using ethylenediamine (en, $H_2NCH_2CH_2NH_2$) as templates and $Ni(NO_3)_2 \cdot 6H_2O$ as the transition-metal source. Their frameworks are built with Ge_{10} clusters and $[Ni(en)_2]^{2+}$ complexes. In both structures, Ge_{10} clusters form square nets in the *a*−*c* plane, while the $[Ni(en)_2]^{2+}$ complexes bridge the square nets via Ni−O−Ge bonds to form 3D networks. They present the first examples to incorporate Ni^{2+} complexes into the germanate frameworks. In SUT-2, additional linkages by Ge_2O_7 clusters between the square nets generate a new type of topology.

Since the reports of three open-framework germanates in the early 1990s,[1] a number of germanates with various framework and pore structures have been obtained.[2] During the past decade, much effort has been made toward the introduction of heteroatoms into germanate frameworks, through which a number of new open-framework structures with novel properties have been achieved. For example, the borogermanate $|(CH_3NH_3)_2|[Ge(B_4O_9)]$ has a 3D chiral zeolite-type framework and exhibits second-harmonic-generation response and ferroelectric properties.[3] Because of the variable coordination numbers and excellent behavior in catalytic applications, transition-metal elements are among the favorite heteroatoms to be introduced into germanate frameworks such as cobalt,[4] copper,[5] zinc,[6] zirconium,[7] niobium,[8] and cadmium.[9] Recently, transition-metal complexes, such as $Ni(en)_3 \cdot Cl_2$ (en = ethylenediamine) and $Ni(dien)_2 \cdot Cl_2$ (dien = diethylenetriamine), were used in germanate syntheses.[10] In these reported structures, the nickel complexes mainly act as templates directing the formation of the framework structures and as counterions to balance excess negative framework charges. The interaction between the metal complex and the framework is mainly through hydrogen bonding either between nitrogen atoms of the complex and oxygen atoms of the framework or via bridging H_2O molecules. One exception is FJ-1, in which nickel was found in trigonal-bipyramidal coordination with germanium in $[Ni@Ge_{14}O_{24}(OH)_3]$ clusters.[10c] It would be interesting to directly link nickel complexes to the germanate frameworks like a few other metal-incorporated germanates,[6a,c,11] where the nickel complexes are still accessible from the pores. Here, we present two new nickel-incorporated 3D germanates, SUT-1 and SUT-2 (SUT = Stockholm University transition-metal-incorporated porous materials). To our best knowledge, both SUT-1 and SUT-2 are the first examples where nickel complexes are directly linked to the framework and act as both templates and framework-forming units.

Both SUT-1 and SUT-2 were synthesized under hydrothermal conditions. In a typical synthesis of SUT-1, 66 mg of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 1.2 mL of H_2O, and then the solution was added to a suspension of 100 mg of GeO_2, 8.0 mL of ethylenediamine, and 4.8 mL of H_2O. The mixture with a molar ratio of GeO_2:en:Ni^{2+}:H_2O = 1.00:125:0.24:350 was stirred until a clear pink solution formed, and then the solution was transferred into a 30 mL Teflon-lined stainless steel autoclave. After being kept statically at 160 °C for 10 days, yellow plate crystals were obtained, as shown in Figures 1a and S3a in the Supporting Information. SUT-2 was synthesized under conditions similar to those for SUT-1, except for the addition of pyridine. The starting material has a typical molar ratio of GeO_2:en:pyridine:Ni^{2+}:H_2O = 1.00:18:26:0.23:156. The final product, SUT-2, is lilac slab crystals shown in Figures 1b and S3b in the Supporting Information. Minor variations in the initial composition could result in a mixture of SUT-1, SUT-2, and ASU-14. The addition of pyridine facilitates the formation of SUT-2, while large amounts of templates lead to the formation of SUT-1. Both structures were solved by synchrotron single-crystal X-ray diffraction.[12]

SUT-1 adopts an orthorhombic space group *Pcan* with a = 10.5529(3) Å, b = 31.5559(5) Å, and c = 20.7333(2) Å. The framework is built from $Ge_{10}(O,OH)_{28}$ (Ge_{10}) clusters, additional GeO_4 tetrahedra, and $[Ni(en)_2]^{2+}$ complexes. The Ge_{10} cluster has four octahedrally coordinated germanium centers surrounded by six GeO_4 tetrahedra. The additional GeO_4 tetrahedron is bonded to three of the GeO_4 tetrahedra, similar

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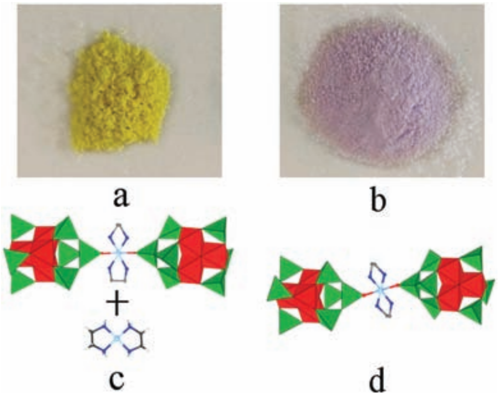

Figure 1. SUT-1 and SUT-2 samples are in (a) yellow and (b) lilac, respectively, because of the different coordination environments of Ni^{2+}. (c) In SUT-1, Ni^{2+} ions are in octahedral and square-planar coordination. (d) In SUT-2, Ni^{2+} only exists in the framework with octahedral coordination.

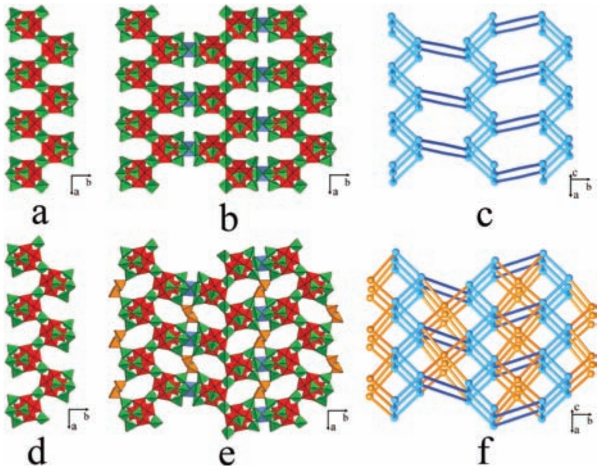

Figure 2. Frameworks of SUT-1 (top) and SUT-2 (bottom) built from Ge_{10} clusters, additional tetrahedra, and $[Ni(en)_2]^{2+}$ complexes. (a and d) Zigzag chains formed by Ge_{10} clusters through sharing of the GeO_4 tetrahedra along the *a* axis. They are further linked to form wavy square nets in the *a*−*c* plane. (b) In SUT-1, the square nets are connected into a 3D framework through $[Ni(en)_2]^{2+}$ complexes to form a framework of the **bnn** net shown in part c, with light-blue knots representing Ge_{10} clusters. (e) In SUT-2, additional Ge_2O_7 clusters (in orange) connect square nets to form a framework with a new underlying topology. The corresponding novel binodal 4,7-connected net is depicted in part f. Ge_2O_7 clusters are shown as orange knots.

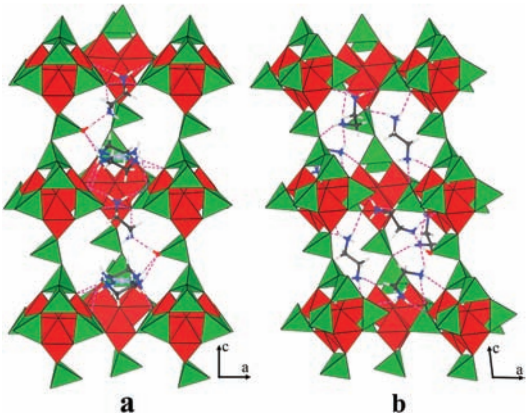

Figure 3. Interaction between the framework and templates: SUT-1 (left); SUT-2 (right). Both $Ni(en)^{2+}$ clusters and en cations can be found in the pores of SUT-1, while only en cations exist in those of SUT-2. The details of these hydrogen bonds are given in Tables S5 and S6 in the Supporting Information.

to those found in many previously reported germanate frameworks.[2e,f,13] In SUT-1, two adjacent GeO_4 tetrahedra of each Ge_{10} cluster are shared with two other Ge_{10} clusters along the [110] and $[1\bar{1}0]$ directions alternatively, generating a zigzag chain along the *a* axis (Figure 2a). Two opposite GeO_4 tetrahedra in the [001] direction of each Ge_{10} cluster further connect the chains by corner-sharing the GeO_4 tetrahedra into a layer, forming a wavy square net expanding in the *a*−*c* plane, where the Ge_{10} clusters are located at the knots of the net (Figure S4a,c in the Supporting Information). Each layer has a thickness of about 15.52 Å, i.e., half of the *b* axis. Two such layers in the unit cell are symmetrically related by a 2-fold rotation along the *a* axis. The nickel ions in $[Ni(en)_2]^{2+}$ complexes connect two square nets by coordinating to the terminal oxygen atoms in the additional GeO_4 tetrahedra (Figure 1b and Table S3 in the Supporting Information). Each $[Ni(en)_2]^{2+}$ complex has a square-planar configuration and is located on a 2-fold axis along *a* axis. Note that, instead of connecting the closest Ge_{10} clusters of adjacent square layers [$d(Ge^{tetr}-Ge^{tetr})$ = 4.46 Å], $[Ni(en)_2]^{2+}$ complexes bridge Ge_{10} clusters with a displacement of about *c*/2 [$d(Ge^{tetr}-Ge^{tetr})$ = 7.39 Å], due to inconsistent orientations of the tetrahedra. The arrangement and connectivity of Ge_{10} clusters in the final 3D framework of SUT-1 resemble the RCSR **bnn** net describing hexagonal boron nitride if Ge_{10} clusters are considered as knots, as shown in Figure 2c.[14] Elliptic 20-ring channels (19.5 × 10.5 Å) are formed by the pore openings of the framework along the *c* axis (Figure 2b). The channels communicate through 10-ring windows, forming a 3D channel system (Figures S5a,b and S6a in the Supporting Information). The overall composition of SUT-1 is $|2Ni(en)_2\cdot 2(enH)_2\cdot 4.6H_2O|[Ge_{20}O_{40}(OH)_8\cdot Ni(en)_2]$ deduced from X-ray diffraction, elemental analysis,[12] and thermogravimetric analysis (TGA; Figure S7 in the Supporting Information).

SUT-2 crystallizes in a monoclinic space group $P2_1/n$ with a = 10.8907(2) Å, b = 30.9833(5) Å, c = 20.7890(5) Å, and β = 98.228(2)°. It has building units and a framework structure similar to those of SUT-1. The basic square nets of Ge_{10} clusters are also formed in the *a*−*c* plane, which are further connected by square-planar $[Ni(en)_2]^{2+}$ complexes at inversion centers in a manner similar to that in SUT-1 (Figure 1b and Table S4 in the Supporting Information). The difference is that, in SUT-1, the terminal −OH groups point into the 20-ring channel to form hydrogen bonds between each other, whereas in SUT-2, they are connected by additional Ge_2O_7 clusters to form extra linkages between four opposite Ge_{10} clusters, as shown in Figure 2e. Different from SUT-1, only en ions and H_2O molecules are found in the pores in SUT-2: two diprotonated $[enH_2]^{2+}$ ions and two monoprotonated $[enH]^+$ ions. SUT-2 has a composition of $|2(enH_2)\cdot 2(enH)\cdot 9(H_2O)|\,[Ge_{22}O_{45}(OH)_6\cdot Ni(en)_2]$.[12]

The extra linkages by Ge_2O_7 clusters make the major difference between SUT-1 and SUT-2. On the one hand, the Ge_2O_7 clusters divide the 20-ring channels into two smaller ones (Figures 2e and S6b in the Supporting Information) and give rise to a novel binodal 4,7-connected net if Ge_{10} and Ge_2O_7 clusters are considered as knots, as shown in Figure 2f and Table S7 in the Supporting Information. To our best knowledge, SUT-2 is the first example of a framework with this underlying topology. Upon removal of the connection by the $[Ni(en)_2]^{2+}$ complexes, the topology of the net becomes the 4,6-connected **sqc125**.[15]

On the other hand, because of strong interactions to the Ge_2O_7 clusters, all Ge_{10} clusters in the square net are tilted, which reduces the symmetry from orthorhombic to monoclinic (Figure 2b,e). This deformation of the framework has significantly changed the pore shape and affected the composition of the guest molecules. In SUT-1, $[Ni(en)_2]^{2+}$ clusters and monoprotonated enH^+ ions alternate along the *c* axis inside the 20-ring channels and thus act as templates anchored to the framework via hydrogen bonds (Figure 3a and Table S5 in the Supporting Information).[12] The coexistence of octahedrally coordinated Ni^{2+} in the framework and square-planar-coordinated Ni^{2+} in the pores results in a yellow color of SUT-1, as shown in Figure 1a.[15] In SUT-2, the enH^+ and enH_2^{2+} ions, together with H_2O molecules, interact with the framework through hydrogen bonds (Figure 3b and Table S6 in the Supporting Information). Thus, only six-coordinated Ni^{2+} ions exist in SUT-2, which gives a lilac color, as shown in Figure 1b.[16]

We have reported two new open-framework germanates, SUT-1 and SUT-2. In both structures, $[Ni(en)_2]^{2+}$ complexes bridge square nets of Ge_{10} clusters to form 3D networks. In SUT-1, $[Ni(en)_2]^{2+}$ complexes in a square-planar configuration were also found in the pores as templating species. The additional connection by Ge_2O_7 clusters in SUT-2 converts the **bnn** net of SUT-1 into a novel 4,7-connected net with a novel topology. SUT-1 and SUT-2 are the first examples where nickel complexes are part of the germanate frameworks.

■ ASSOCIATED CONTENT

Supporting Information. Figures of experimental and simulated powder X-ray diffraction patterns, structural details, and TGA traces, tables of crystallographic information, bond valences, hydrogen bond lengths, and topology, and crystallographic information files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Single-crystal X-ray diffraction data were collected on a Rigaku Saturn724+ diffractometer at 150(2) K using synchrotron radiation ($\lambda = 0.6889$ Å) at the Beamline I19, Diamond Light Source, Ltd., Didcot, U.K. Data reduction and empirical absorption correction were applied with *CrysAlisPro*. The structures were solved and refined by *SHELX* (Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122). Crystal data for SUT-1: *Pcan*, $a = 10.5529(3)$ Å, $b = 31.5559(5)$ Å, $c = 20.7333(2)$ Å, $V = 6904.3(2)$ Å^3, $50 \times 10 \times 2$ μm. A total of 60 673 reflections, of which 7013 are unique, were collected in the region $1.90° < \theta < 25.50°$. $R_{int} = 0.0722$, $R1 = 0.0331$, and $wR2 = 0.0746$ for reflections with $I > 2\sigma(I)$. Crystal data for SUT-2: $P2_1/n$, $a = 10.8907(2)$ Å, $b = 30.9833(5)$ Å, $c = 20.7890(5)$ Å, $\beta = 98.228(2)°$, $V = 6942.6(2)$ Å^3, $30 \times 25 \times 10$ μm. A total of 64 269 reflections, of which 13 967 are unique, were collected in the region $1.59° < \theta < 25.50°$. $R_{int} = 0.0593$, $R1 = 0.0376$, and $wR2 = 0.1085$ for reflections with $I > 2\sigma(I)$. More details are given in Figure S7 and Tables S1−S6 in the Supporting Information.

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