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3-D Germanate Constructed with Ge_7 Cluster Layers and Nickel–Ethanolamine Linkage

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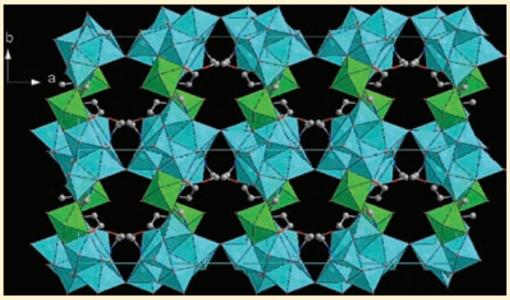
S *Supporting Information*

ABSTRACT: A Ge_7 germanate, $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2Ge_7O_{14}(C_2H_7NO)]\cdot C_2H_5OH$ (**1**), was prepared by the solvothermal method using ethanolamine (C_2H_7NO) as solvent, ligand, and structure-directing agent. Compound **1** shows an unusual GeO framework fused with transition metal complex. The 2-D layers of Ge_7 clusters are linked by a $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2]$ moiety, forming a 3-D architecture. The preparation and structure of **1** are discussed in comparison with the Ge_9 germanates decorated with metal ethylenediamine complexes. The hydroxyl group of the ethanolamine plays an important role in formation of the 3-D structure, in which the ligand ethanolamine is coordinated directly onto the Ge cluster by the hydroxyl group. It is a new type of germanates incorporated with a TM complex bridge. The proton on the flexible amine side can be exchanged by alkali metal ions.



INTRODUCTION

Interest in germanates has been rapidly growing until now, because germanium can be used as a silicon substituent to build various open framework structures and microporous materials. In general, the germanates are typically prepared under hydrothermal/solvothermal conditions in the presence of organic amines (protonated amines) as charge-balance cations or structure-directing agents (SDAs) and templates.[1−8] Recently, transition metal (TM) complexes of diamines and polyamines have been used in the synthesis of germanates,[7a,9,10] because it has been demonstrated that the properties of the metal complexes, such as magnetic and optical properties, can be introduced into the inorganic materials[11] and, more important, the chirality of the metal complexes can be transferred into the inorganic structure.[6c,7a,12] In most cases, the TM complexes are in a discrete state that only acts as a SDA of the open framework structure. In very few of the germanates, TM complexes act as the component of the framework. Three $[M_2(en)_3Ge_9O_{18}(OH)_4]$ (M = Co, Cd, and Zn; en = ethylenediamine) compounds were reported.[10a−c] These compounds prepared by Feng, Yang, and Rao, three different groups, respectively, showed an isomorphous open framework. The structure is constructed from two distinct motifs: a body-centered $[Ge_9O_{18}(OH)_4]$ cluster and a TM complex $[M_2(en)_2(\mu\text{-en})]$, which links the germanate clusters to a 3-D architecture with a neutral framework. Very recentely, two new compounds of the GeO framework with $[Ni(en)_2]^{2+}$-bridged Ge_{10} clusters were reported.[10d] Actually, the contribution of the diversity of TM complexes to the generation of new types of germanates is largely unexplored in a structural sense. It is an attractive way of using TM complexes as linkages in constructing new structures of germanates, because the TM complexes can be made with a wide variety of shapes, charges, and hydrogen-bonding sites and are very versatile as promising SDAs.

We are interested in introducing TM complexes into the main group metal sulfide or oxide frameworks to understand the structure-directing role of the TM complexes in inorganic frameworks.[13] In this manuscript, we report the synthesis and structural characterization of a new germanate compound with formula $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2Ge_7O_{14}(C_2H_7NO)]\cdot C_2H_5OH$ (**1**), in which the TM complex moiety, $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2]$ (C_2H_7NO = ethanolamine), links the 2-D layers of Ge_7 clusters forming a three-dimensional network. Spectra and ion reaction of the compound are discussed.

EXPERIMENTAL SECTION

General Remarks. All analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Elemental analysis was carried out on an VARIDEL III elemental analyzer. Room-temperature optical diffuse reflectance spectra of the microcrystal samples were obtained with a Shimadzu UV-3150 spectrometer. Absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function,[14] $\alpha/S = (1 - R)^2/2R$, where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. Thermoanalytical measurements was performed using a DCS-TGA microanalyzer of SDT 2960, and the sample was heated under a nitrogen stream of 100 mL min^{-1} with a heating rate of 20 °C min^{-1}. PXRD of the products was carried out on D/MAX-3C X-ray diffraction meter with Cu Kα (λ = 1.5406 Å)

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radiation. A Varian DUO-220 atomic absorption spectrophotometer was used for determining the quantity of the exchanged Na(I) ion.

Synthesis of [Ni(H_2O)(μ-C_2H_6NO)$_2$$Ge_7O_{14}$($C_2H_7NO$)]·$C_2H_5OH$ (1). Analytically pure GeO_2 (0.0104 g, 0.1 mmol), $NiCl_2·6H_2O$ (0.0056 g, 0.025 mmol), and piperazine (0.0086 g, 0.1 mmol) were mixed in 0.5 mL of ethanolamine (C_2H_7NO) with a small quantity of ethanol. The mixture was placed in a thick Pyrex tube (0.7 cm diameter, 18 cm length). The sealed tube was heated under an autogenous pressure at about 180 °C for 4 days to yield blue block-shaped crystals (30% yield based on GeO_2). The crystals were washed with ethanol and dried. The compound is stable in ambient condition. Anal. Calcd for $C_8H_{27}Ge_7N_3NiO_{19}$ (MW 1036.13): C, 9.27; H, 2.63; N, 4.06. Found: C, 9.56; H, 2.71; N, 4.32. Important IR data (KBr, cm^{-1}): 3466(b), 3361(m), 3195(w), 2919(w), 2872(m), 1699(w), 1626(m), 1550(s), 1366(m), 1284(m), 1090(m), 1033(m), 871(m), 800(vs), 766(vs), 5901(s), 496(m).

X-ray Crystallographic Study. Data collection was performed on a Rigaku Mercury CCD diffractometer using the ω-scan method with graphite-monochromated Mo Kα radiation (λ = 0.071075 nm) at a temperature of 293(2) K. Absorption correction was applied for all compounds using the multiscan correction method. Structures were solved by direct methods using the SHELXS-97 program, and refinement was performed against F^2 using SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of ethanolamine were positioned with idealized geometry and refined with fixed isotropic displacement parameters except those of the amine group, while the hydrogen atoms of the water and solvent molecules were not dealt with. Relevant crystal data, collection parameters, and refinement results can be found in Table 1.

Table 1. Crystal Data and Structural Refinement Parameters for Compound 1

formula	$C_8H_{27}Ge_7N_3Ni_1O_{19}$
fw	1036.13
cryst size (mm^3)	0.20 × 0.18 × 0.10
cryst syst	orthorhombic
space group	$Pca2_1$
a (Å)	16.5087(15)
b (Å)	9.8707(11)
c (Å)	16.4722(14)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
V (Å^3)	2684.2(4)
Z	4
ρ_{calcd} (g cm^{-3})	2.562
F(000)	2008
μ (mm^{-1})	8.081
T (K)	293(2)
R_{int}	0.0689
Flack	0.02(2)
no. of reflns collected	18 274
no. of unique reflns	4946
no. of obsd reflns	4671
no. of params	339
restraints	1
GOF on F^2	1.070
R_1^a /R_1 [$I > 2\sigma(I)$]	0.0518/0.0483
wR_2^b/wR_2 [$I > 2\sigma(I)$]	0.1158/0.1132

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

■ RESULTS AND DISCUSSION

Synthesis. The solvothermal reaction of GeO_2, $NiCl_2·6H_2O$, and piperazine (molar ratio of reactants 4:1:4) in 0.5 mL of ethanolamine at 180 °C for 4 days yielded blue brick-shaped crystals of **1** in about 30% yield. Elemental analysis and X-ray structure determination demonstrate that the piperazine does not enter the final product but is important in adjusting the pH of the reaction mixture. No crystals were obtained if piperazine was not used. The pH of the reaction system is about 10. The cocrystallized ethanol molecules are losable, which dose not change the framework of the compound. The XRD pattern of the powdered microcrystals of **1** is in agreement with that simulated from the data of single-crystal analysis (Figure 1). EDAX analysis showed that the ratio of Ni:Ge is 1:7, in agreement with the structure.

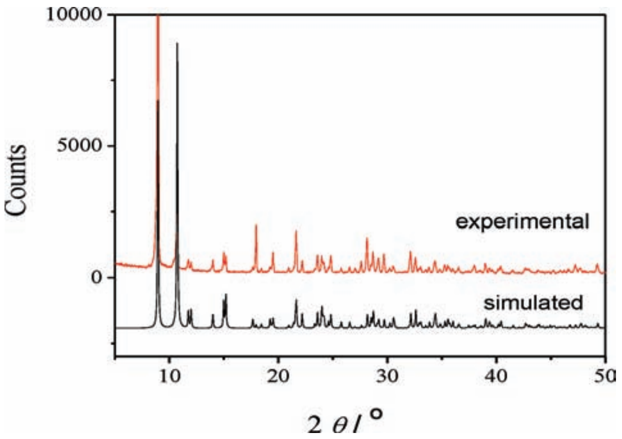

Figure 1. XRD patterns for the experimental and calculated results of compound **1** to ensure their phase purity.

To date, about 100 germanate compounds have been prepared and characterized by single-crystal structural analysis. Most of them grew in the presence of organic amines (protonated amines). Table 2 summarizes the organic amines in the germanates, referring to the CCDC database. Most of them serve as charge-balance cations or structure-directing agents (SDAs). Some chelating amines (diamine and polyamine) coordinate to the transition metal, but the ligands do not coordinate directly to the germanium(IV) atom. Ethanolamine is selected as a SDA because it has both an aliphatic amine group and a germanium affinitive hydroxyl group. Syntheses of new organic–inorganic hybrid germanates are expected.

Table 2. Amines Used in Solvothermal Synthesis of Germanates (Supporting Information)

type of amine	name of amine
monoamine	trimethylamine, ethylamine, *n*-propylamine, *i*-propylamine
diamine	ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopantane, 1,6-diaminohexane, 2-methylpentane-1,5-diammonium
polyamine	diethylenetriamine, tris(ammonioethyl)amine, *N*,*N*′-bis(3-aminopropyl)-ethylenediamine
cycloamine	piperazine, cyclohexane-1,4-diamine, 1,4-diazabicyclo[2,2,2]octane, 4-aminomethylpiperidine

Structure of Compound 1. Compound **1** crystallizes in an orthorhombic system and belongs to the $Pca2_1$ space group with 4 formulas in a unit cell (Table 1). The subunits are composed of seven germanium atoms that show mixed coordination spheres: four tetrahedral GeO_4, two trigonal bipyramidal GeO_5, and one octahedral GeO_6 (Figure 2). One oxygen (O9)

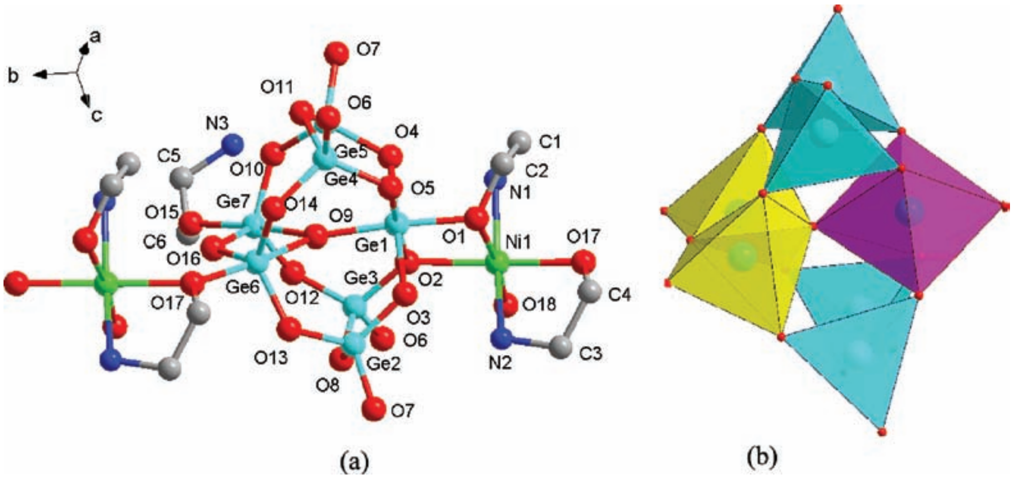

Figure 2. (a) Fundamental structure of compound **1** with labeling scheme; hydrogen atoms have been omitted for clarity. (b) Polyhedron view of the Ge_7 cluster.

located at the core of the cluster is tricoordinated and links the GeO_6 octahedron with the two GeO_5 bipyramidal. The heptamer shows C_{2v} symmetry, which is similar to reported Ge_7 clusters.[1e,9a,16] The Ge−O bond distances of the tetrahedral germanium vary from 1.720 to 1.771 Å. The Ge−O distances (bicoordinated) in the equatorial planes of the bipyramidal coordinated germanium are in the range of 1.769−1.787 Å, and those of the octahedral coordinated germanium are in the range of 1.861−1.903 Å. The bond distances around tricoordinated O9 are in a range of 1.940−2.135 Å, longer than the others, Table 3. It is noticeable that Ge1, Ge6, and Ge7 are coordinated by oxygen from three ethanolamine ligands, respectively, being different from the germanate compounds of ethylenediamine.

The Ni(II) ion in crystal **1** is octahedrally coordinated by two chelating ethanolamine molecules, one water molecule, and an oxygen atom of the Ge_7 cluster, showing a chiral complex. The Ge_7 clusters and the homochiral Ni(II) complexes are alternately connected along the *b* direction (Figure 3). However, the crystal is only a noncentral system and is not a chiral system, because both chains with chirality of Δ and Λ complexes exist.

Through four μ_2-O bridges (O6 and O7), the Ge7 subunits are connected to a 2-D framework being oriented parallel to the *ac* plane (Figure 4), which generates windows of 10-membered (polyhedron) rings. The 2-D sheets are further connected by nickel complex linkage up and down, forming a 3-D framework. Figure 5 and Figure S1 (Supporting Information) show the layered structure and linkage viewed along the *a* and *c* directions. If only considering the Ge−O−Ni framework, the total volume of the cations and solvent is 1449.4 Å^3, about 54.0% of the unit cell volume that was calculated by the PLATON program.[17] The oxygen O1 of the chelating ethanolamine is μ^2-coordinated to Ni1 and Ge1; similarly, O17 is μ^2-coordinated to Ni1 and Ge6. Therefore, the complex moiety of $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2]$ takes a μ^3-bridge mode (see Figure 2) as a linkage and links the Ge7 layers to a 3-D architecture. Another ethanolamine is monocoordinated to Ge_7 via O16 and the amine side is free.

Table 3. Important Ge−O and Ni−N Bond Lengths (Å) and Angles (deg) for 1

bond distance (Å)			
Ge1−O1	1.890(7)	Ge5−O10	1.758(7)
Ge1−O2	1.904(7)	Ge5−O11	1.770(7)
Ge1−O3	1.896(7)	Ge5−O7	1.738(7)
Ge1−O4	1.862(7)	Ge6−O9	1.991(7)
Ge1−O5	1.861(7)	Ge6−O13	1.786(7)
Ge1−O9	1.940(7)	Ge6−O14	1.779(7)
Ge2−O3	1.728(7)	Ge6−O16	1.768(7)
Ge2−O7	1.720(7)	Ge6−O17	1.853(8)
Ge2−O8	1.767(7)	Ge7−O9	2.135(7)
Ge2−O13	1.726(8)	Ge7−O10	1.770(7)
Ge3−O2	1.725(7)	Ge7−O12	1.761(7)
Ge3−O6	1.740(7)	Ge7−O15	1.819(7)
Ge3−O8	1.744(7)	Ge7−O16	1.787(8)
Ge3−O12	1.734(7)	Ni1−O17	2.085(8)
Ge4−O5	1.732(7)	Ni1−O18	2.09(1)
Ge4−O11	1.742(7)	Ni1−N2	2.10(1)
Ge4−O14	1.740(7)	Ni1−O1	2.091(7)
Ge4−O6	1.742(7)	Ni1−O2	2.131(7)
Ge5−O4	1.727(7)	Ni1−N1	2.08(1)
bond angle (deg)			
O1−Ge1−O9	175.1(3)	O9−Ge6−O17	170.2(3)
O2−Ge1−O5	177.2(3)	O13−Ge6−O14	115.9(3)
O3−Ge1−O4	177.9(3)	O13−Ge6−O16	121.1(3)
O3−Ge2−O7	111.1(3)	O14−Ge6−O16	122.9(3)
O7−Ge2−O8	102.2(3)	O9−Ge7−O15	167.4(3)
O7−Ge2−O13	106.7(3)	O10−Ge7−O12	113.7(3)
O2−Ge3−O6	105.4(3)	O10−Ge7−O16	120.7(3)
O6−Ge3−O8	108.0(3)	O12−Ge7−O16	123.8(3)
O6−Ge3−O12	108.2(3)	O17−Ni1−O2	167.3(3)
O5−Ge4−O6	111.2(3)	O18−Ni1−O1	172.0(4)
O11−Ge4−O6	106.0(3)	N2−Ni1−N1	170.0(4)
O14−Ge4−O6	103.7(3)	Ge1−O9−Ge6	135.0(4)
O4−Ge5−O7	107.9(3)	Ge1−O9−Ge7	134.5(4)
O10−Ge5−O7	108.8(3)	Ge6−O9−Ge7	90.5(3)
O11−Ge5−O7	104.1(3)		

The reported transition metal germanates $[M_2(en)_3][Ge_9O_{18}(OH)_4]$ (M = Co, Cd, and Zn) are isomorphous structures in which the TM complexes coordinate directly to the GeO cluster.[10] The compounds are prepared in en/water mixed solvent by the solvo-/hydrothermal method, which is similar to the method used for compound **1** except for the directing agent. Although ethanolamine is also a chelating ligand that only replaces one amine group of en by a hydroxyl group, its function in building structures differs from that of en. The en-coordinated compound, $[M_2(en)_3][Ge_9O_{18}(OH)_4]$, is a 3-D framework constructed by Ge_9 clusters through μ-O bridges, though the two metal complex centers are connected by an en molecule. In SUT-1 and SUT-2 the Ge_{10} clusters are linked by Ge−O−$Ni(en)_2$−O−Ge bridges.[10d] The ligands (en) in all of these compounds are not directly bonded to the Ge(IV) centers. In contrast, the subunit of the present product **1** is a Ge_7 cluster, $[Ge_7O_{14}(C_2H_7NO)]$, in which the ligand ethanolamine is coordinated onto the Ge atom by the hydroxyl group. It is a new type of germanate incorporated with a TM complex bridge. Ethanolamine is a unique solvothermal solvent for preparing germanates because it has both an aliphatic amine group and a germanium affinitive hydroxyl group. The hydroxyl group is an amphiphilic donor to Ge and Ni atoms that forms the Ge−O_L−Ni−O_L−Ge bridge (L = ligand). This example illustrates the importance of the ligand in the generation of new germanates.

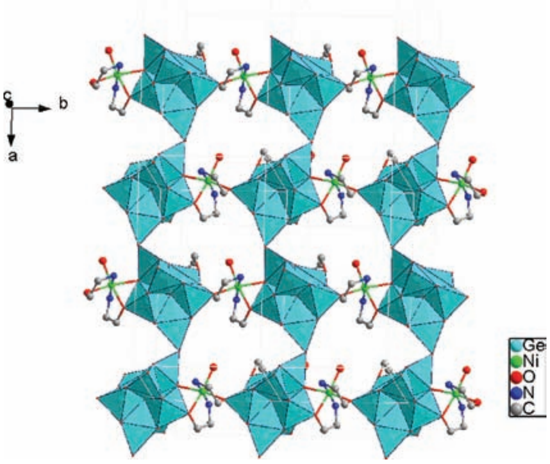

Figure 3. Ge_7 clusters and homochiral Ni(II) complexes are alternately connected along the *b* direction.

Optical Property, Thermal Stability, and Ion-Exchange Property. Because the germanates are generally colorless, their electronic spectra have been less discussed. Incorporating TM−complex cation into the germanate structure can improve the absorption of the materials from the ultraviolet to the the visible range. The optical diffuse-reflection spectrum of **1** was measured at room temperature using $BaSO_4$ as a standard reference (Figure 6).[14] The energy gap of the germanate (3.77 eV) was estimated by extrapolation of the linear portion of the main absorption edge. The absorption bands at 3.28, 2.08, and 1.15 eV are assigned to d−d transition bands of the $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2(\mu\text{-}O)]$ moiety in octahedral coordination. According to the Orgel diagram,[18] there are three d−d transition bands for the Ni^{2+} (d^8) complex, $^3T_{2g} \leftarrow {}^3A_{2g}$ (3.28 eV, 378 nm), $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (2.08 eV, 596 nm), and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (1.15 eV, 1078 nm), respectively. The ultraviolet band $^3T_{2g} \leftarrow {}^3A_{2g}$ and infrared band $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ are not within the visible range. The blue color of the crystals just arises from absorption of $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (2.08 eV, 596 nm).

The thermal stability of **1** was investigated using thermogravimetry analysis (Figure 7). The compound decomposes in approximately two major steps with a total weight loss of 76.5%. Since the cocrystallized ethanol molecules were lost during drying, no weight loss was found below 200 °C. The first step covers a temperature range starting at 200 °C and finishing at 600 °C with a weight loss of 19.2%, which is in agreement with that calculated for removal of the organic molecules (calcd 18.5%). Vigorous decomposition was recorded from 380 to 410 °C. At this temperature, the crystals collapse during decomposition, because the structure of the germanate is supported by the TM complex. The second step from about 600 to 930 °C with a weight loss of 56.7% is assigned to removal of the volatile germanium oxide phases.[9a,10b]

From structural analysis we know that one of the ethanolamines is not a chelating ligand. It coordinates to the Ge(IV)

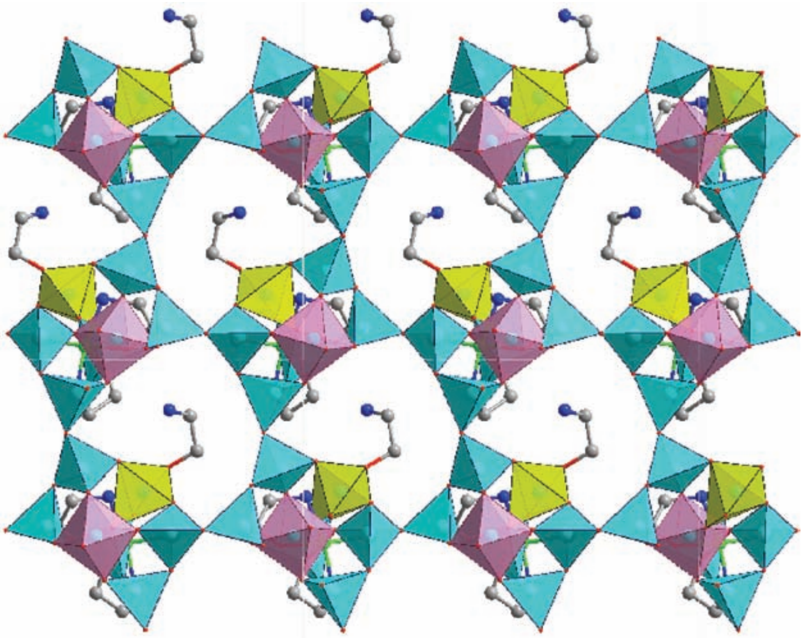

Figure 4. 2-D structure of compound **1**; viewed along the *b* direction.

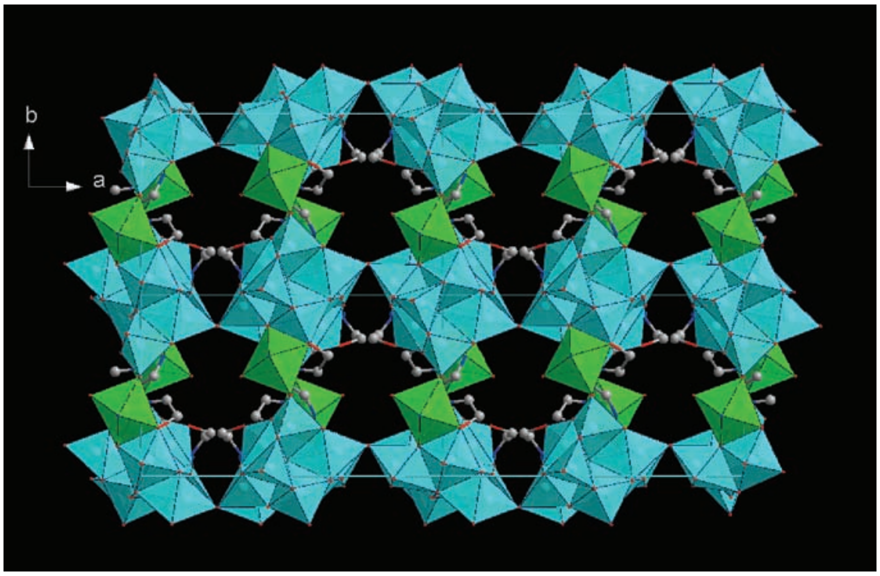

Figure 5. GeO cluster-assembled 2-D layers are further connected by nickel complex linkage of $[Ni(H_2O)(\mu\text{- }C_2H_6NO)_2]$ up and down, forming a 3-D framework; viewed along the *c* direction.

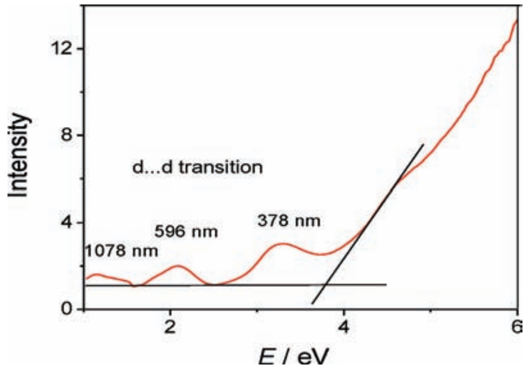

Figure 6. Solid-state absorption spectrum of **1** measured at room temperature using $BaSO_4$ as a standard reference.

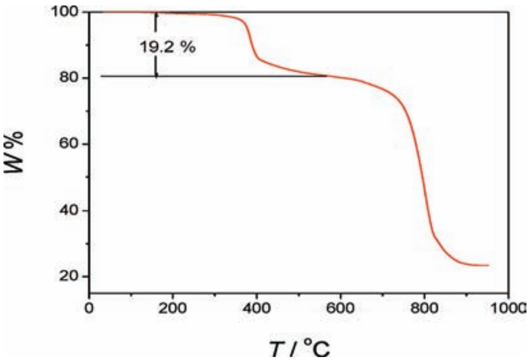

Figure 7. Thermal gravimetric result of **1**.

atom by the alkoxide side and the side of protonated amine is free and protrudes into the hole of the 2-D layer (Figure 4). The proton on the amine group can be neutralized by metal hydroxide using the immersion method, and then the metal ions synchronously enter into the structure. Crystals of **1** were immersed in 0.10 mol·L NaOH at 60 °C for 3 days; then crystals were washed by ethanol and dried for measurements. The content of the Na(I) ion in the sample was measured by an absorption spectrophotometer, and the result is 2.5% in weight percent. The calculated weight percent is 4.0% if all protons are neutralized. A schematic figure (Figure 8) illustrates the cooperating process of ion entering and neutralization.

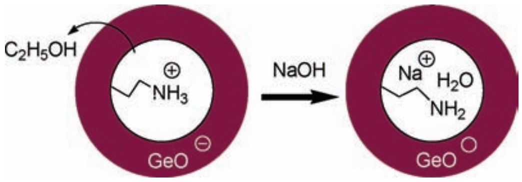

Figure 8. Cooperating process of ion entering and neutralization.

■ CONCLUSIONS

In summary, the reported compound **1** is a unique germanate with Ge_7 clusters. The transition metal complex moiety in this compound not only acts as a structure-directing agent or a charge-balance cation but also as a structure linkage. The 2-D sheets of Ge_7 clusters are linked by $[Ni(H_2O)(\mu\text{-}C_2H_6NO)_2]$ complex, forming a 3-D framework. Such transition metal complex-fused germanates are uncommon and have only been found in Ge_9 and Ge_{10} germanates, which were obtained by the solvo-/hydrothermal route in ethylenediamine. The new 3-D germanate was prepared using ethanolamine instead of ethylenediamine in similar reaction conditions. Ethanolamine is a unique solvothermal solvent for preparing germanates due to the affinity of the hydroxyl group to germanium, which offers the possibility of making new materials with open-framework structures and novel properties. Compound **1** is a new type of germanate incorporated with a TM complex bridge. The proton on the flexible amine side can be exchanged by alkali metal ions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data of **1** and **2** in CIF format and figures of molecular packing and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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