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$[Ge_7O_{13}(OH)_2F_3]^{3-}\cdot Cl^{-}\cdot 2[Ni(dien)_2]^{2+}$: The First Chainlike Germanate Templated by a Transition Metal Complex

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The first chainlike germanate, $[Ge_7O_{13}(OH)_2F_3]^{3-}\cdot Cl^{-}\cdot 2[Ni(dien)_2]^{2+}$, has been solvothermally synthesized by using $Ni(dien)_2^{2+}$ cations as the template and characterized by IR, SEM, TGA, powder X-ray diffraction (PXRD), energy-dispersive X-ray analysis (EDXA), elemental analysis, and single-crystal X-ray diffraction, respectively. This compound crystallized in the monoclinic space group $P2/n$ with $a = 8.8904(2)$ Å, $b = 17.4374(3)$ Å, $c = 13.2110(3)$ Å, $\beta = 101.352(1)°$, $V = 2007.97(7)$ Å^3, and $Z = 2$. Interestingly, the structure contains two types of chiral *mer*-$[Ni(dien)_2]^{2+}$ cations and two types of chiral chains, one left-handed and the other right-handed, which lead to a racemic compound. The orderly separation of achiral *s-fac*-$[Ni(dien)_2]^{2+}$ and chiral *mer*-$[Ni(dien)_2]^{2+}$ isomers was found in the structure. The structure is stabilized by N–H···O(F, Cl) hydrogen bonds.

The interest in germanates has been steadily growing after the discovery of the first germanate with an open framework in 1991.[1] Since then, a number of germanates with 2-D,[2] 3-D,[1,3] or isolated[4] structure have been synthesized. So far, great efforts toward the rational design of these materials have been made. One of the strategies used for the design of germanate materials with new topologies is the selection of structure-directing agents (SDAs) based on the consideration that the shape, size, and charge of SDAs can determine the inorganic framework.

Recently, transition metal complexes as templates have been used in the synthesis of chiral inorganic materials such as aluminophosphates,[5] gallium phosphates,[6] zincophosphates,[7] and borophosphate[8] because they are very versatile and can be made with a wide variety of shapes, charges, hydrogen bonding sites, and particularly chirality.[5e] And more important, it has been demonstrated that the chirality of the metal complexes can be transferred into the inorganic frameworks.[5c,7] However, little attention has been paid to the possibility of using metal complexes as templates in the synthesis of germanates,[3i−k] to our knowledge.

We are interested in introducing metal complexes into the germanate framework and understanding the role of chiral complexes in determining the inorganic framework structures of germanates. In this work, a mixture of the metal

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complex $Ni(dien)_2Cl_2$ has been used in the synthesis of the new germanate $[Ge_7O_{13}(OH)_2F_3]^{3-}{\cdot}Cl^{-}{\cdot}2[Ni(dien)_2]^{2+}$ (denoted **FJ-6**) (dien = diethylenetriamine). **FJ-6** not only fills the gap left by the absence of 1-D structures in the germanate family but also is the first chiral germanate material.

FJ-6 was synthesized under solvothermal condition using pyridine as solvent. The template of $Ni(dien)_2Cl_2$ was prepared by Wold's work.[9] In a typical synthesis, 0.104 g of GeO_2 and 0.031 g of H_3BO_3 were dissolved in the mixed solvent of 3 mL of pyridine and 2 mL of water followed by the addition of 0.336 g of $Ni(dien)_2Cl_2$ with constant stirring. Then, 0.1 mL of hydrofluoric acid (40 wt %) was added to the above mixture. The final mixture with a pH of ~6.0 and the composition GeO_2:H_3BO_3:$Ni(dien)_2Cl_2$:pyridine:HF:H_2O in a molar ratio of 2:1:2:74:4:110 was sealed in a Teflon-lined steel autoclave, heated at 170 °C for 7 days, and then cooled to room temperature. The sole purple prism-like crystals were collected by filtration, washed by distilled water and ethanol, and dried in air without further separation (84.5% yield based on GeO_2). The PXRD pattern of the bulk product is in good agreement with the calculated pattern based on the single-crystal solution, indicating the phase purity of the sample. The elemental analysis, ICP, and EDXA are consistent with the formula $[Ge_7O_{13}(OH)_2F_3]^{3-}{\cdot}Cl^{-}{\cdot}2\,[Ni(dien)_2]^{2+}$.[10]

X-ray diffraction analysis[11] reveals that the molecular structure of **FJ-6** contains one cluster unit of $[Ge_7O_{13}(OH)_2F_3]^{3-}$ (**1**), two $Ni(dien)_2{}^{2+}$ cations, and one Cl^- ion as shown in Figure 1. Cluster **1** consists of seven Ge atoms with mixed coordination from four to six: one octahedral $Ge(3)O_5F$ [range of Ge−O bond lengths 1.868(4)−2.012(5) Å; Ge(3)−F bond length 1.810(4) Å], two trigonal bipyramidal $Ge(1)O_4F$ [Ge−O bond 1.768(4)−1.980(3) Å; Ge(1)−F bond length 1.823(3) Å], and four tetrahedral GeX_4 (X = O, OH) (two $Ge(2)O_4$ and two $HGe(4)O_4$) [Ge−O bond 1.721(4)−1.760(4) Å, O−Ge−O angle 105.3(2)−113.8 (2)°]. The O(4) atom in the center of **1** is tricoordinated and bonds to one $Ge(3)O_5F$ and two $Ge(1)O_4F$ polyhedra. Each of four GeX_4 is linked to one $Ge(3)O_5F$ and one $Ge(1)O_4F$ by μ_2-O atoms, respectively. The two $Ge(1)O_4F$ polyhedra share one edge, while $Ge(2)O_4$ and $HGe(4)O_4$ groups are linked to each other by the O(2) atom. Unlike Ge(1), Ge(1A), Ge(3), Ge(4), and Ge(4A), which have a terminal ligand (F or OH), the Ge(2) and Ge(2A) centers are connected to neighboring clusters **1** by μ_2-O atoms (O(1) and O(1A)) to form chainlike structure shown in Figures 2 (left) and 3. Such arrangement of polyhedra as described above has been observed in ASU-19,[2d] ASU-20,[2d] ASU-12,[3g] and ASU-16[3h]. In ASU-*n* (*n* = 12, 16, 19, 20), five μ_2-O atoms connect adjacent Ge_7 clusters to form a 3-D or 2-D framework, but in **FJ-6**, the presence of two hydroxyl groups and three fluorine atoms prevents the Ge_7 clusters from further connecting, which only results in 1-D structure only by two μ_2-O(1) atoms. Like $Co(dien)_2{}^{3+}$,[12] $Ni(dien)_2{}^{2+}$ has also *s-fac*-, *u-fac*-, and *mer*-configurations, but only the latter two are chiral. There are two unique Ni sites corresponding to two isomers of *mer*-$Ni(2)(dien)_2{}^{2+}$ and *s-fac*-$Ni(1)(dien)_2{}^{2+}$, respectively; no *u-fac*-$Ni(dien)_2{}^{2+}$ isomer incorporated into the structure of **FJ-6** (Figure 1). The ions of Cl^- and $Ni(dien)_2{}^{2+}$ are located between the chains, and interact with the chains both electrostatically and via extensive H-bonding interactions, with bond distances N···Cl, 3.396(6)−3.589(6) Å; N···O, 2.888(6)−3.299(7) Å; and N···F, 3.023(6)−3.153(7) Å.

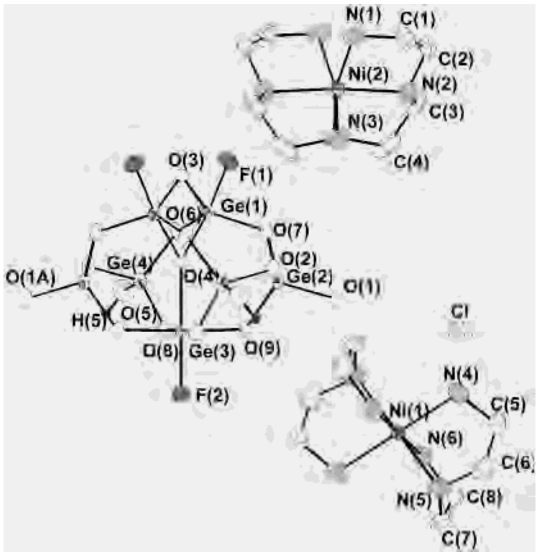

Figure 1. ORTEP plot of the molecular structure of **FJ-6**. Thermal ellipsoids are given at 50% probability.

The most interesting aspect for **FJ-6** is that the structure contains two types of chiral chains and possesses a racemic feature. Because *mer*-$Ni(2)(dien)_2{}^{2+}$ is chiral and susceptible to racemization,[13] it leads to the chirality and racemization of inorganic chains (Figures 2 and 3). It is worth noting that the overall structure of **FJ-6** is not chiral. The chirality and racemization of the inorganic chains are considered to be transferred from the chiral and racemic *mer*-$Ni(dien)_2{}^{2+}$ cations.

As shown in Figure 3, the orderly separation of *mer*-$Ni(2)(dien)_2{}^{2+}$ and *s-fac*-$Ni(1)(dien)_2{}^{2+}$, as well as the absence of *u-fac*-$Ni(dien)_2{}^{2+}$ in the structure of **FJ-6**, indicates that the inorganic network as host has a molecular recognition ability for the metal complexes as guest. From insight into the structures of **FJ-6** and other known Al(Ga,Zn)POs with chiral 1-D,[5a,b] 2-D[5a,c−f,6b,7] and 3-D[6a,7] structures templated by chiral metal complexes, it is found that the chiral metal complexes are responsible for the formation of the chiral framework in the crystallization process and can transfer its

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(10) Anal. Calcd for **FJ-6**, $C_{16}H_{54}N_{12}O_{15}F_3ClNi_2Ge_7$: C, 14.00; H, 3.97; N, 12.24; Ge, 37.03; Ni, 8.55. Found: C, 13.90; H, 3.72; N, 12.07; Ge, 37.11; Ni, 8.51. EDXA gives the Ge:Ni:Cl:F ratio as 6.8:1.9:1:3.1 (calcd 7:2:1:3). These results are in agreement with the formula of **FJ-6** found from the single-crystal analysis. IR (KBr, cm^{-1}): 3478 s (ν_{OH}); 861 s, 967 s (ν_{GeO4}, ν_{GeO6}); 799 s, 715 s (ν_{Ge-F}); 585 s (ν_{Ge-O}) (see Figure S2, Supporting Information).

(11) Crystal data for **FJ-6**: space group $P2/n$, $a = 8.8904(2)$ Å, $b = 17.4374(3)$ Å, $c = 13.2110(3)$ Å, $\beta = 101.352(1)°$, $V = 2007.97\ (7)$ Å^3, $Z = 2$, $R1 = 3.69\%$, $wR2 = 7.62\%$.

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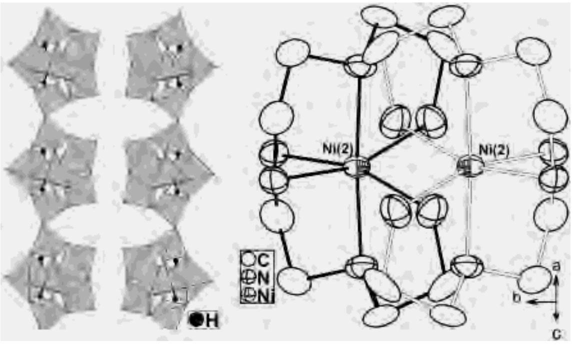

Figure 2. Polyhedral representation of the racemic chains (left) and racemic *mer*-[Ni(dien)$_2$]$^{2+}$ cations (right) in **FJ-6**.

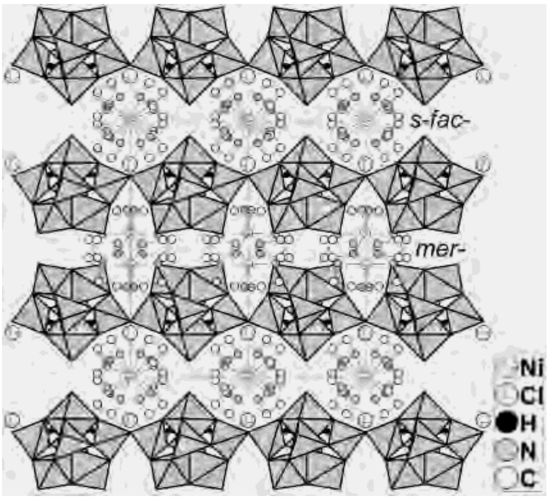

Figure 3. A view of the ABAB... stacking sequence of chains and the relationship between the metal complexes and the chains in **FJ-6** along the [101] direction. All hydrogen positions of C and N atoms are omitted for clarity.

chiral feature in an inorganic framework, as well as lead to the existence of molecular recognition ability between the inorganic host and the chiral metal complex guest. In addition, the H-bonding interactions between the metal complex and the inorganic framework play an important role in the orderly arrangement of the host network and the guest metal complex, as well as the chiral transference.[5c,6c,7]

TGA shows that **FJ-6** is stable up to 350 °C and the weight loss occurs in three steps between 30 and 1000 °C. The total loss of ca. 35% in the first step from 350 to 500 °C corresponds to the loss of four dien, one HF, and one HCl molecule per formula unit (calcd 30.1%, 1.5%, and 2.7%, respectively), resulting in the collapse of the framework, and the latter two steps are assigned to the removal of the volatile germanium oxide phases.[3k]

In summary, we present here the first chiral chainlike germanate with Ni(dien)$_2^{2+}$ complexes.[14] Chiral and racemic metal complexes lead to the chirality and racemization of inorganic chainlike structure. In addition, although the synthesis of germanates using metal complexes as templates is almost unexplored, it offers the possibility of making novel materials with open-framework structures that are useful for chiral separations and other uses. As a major research interest and aim, we are now using other metal complexes as templates and using our 1-D chainlike germanate materials as the building unit to make chiral germanates with 2-D and 3-D structure. Further investigation on this work is in progress.

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Supporting Information Available: SEM image, powder X-ray diffraction patterns, IR spectrum, TGA curve, view along the [101] direction, and CIF for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) During preparation of this Communication, another phase-pure germanate templated by [Co(dien)$_2$]$^{2+}$ cations was obtained as crystallites. Powder X-ray diffraction proves that this germanate, [Ge$_7$O$_{13}$(OH)$_2$F$_3$]$^{3-}$·Cl$^-$·2[Co(dien)$_2$]$^{2+}$, is analogous to **FJ-6**.