Inorganic Chemistry

Communication

pubs.acs.org/IC

$(C_8H_{22}N_4Zn)_2Ge_7O_{14}(OH)F_3$: A One-Dimensional Zinc Germanate Containing Hollow Columns with an 18-Membered Window

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Supporting Information

ABSTRACT: A new zinc germanate incorporating a tetradentate amine ligand has been synthesized by the solvothermal method and structurally characterized by single-crystal X-ray diffraction, solid-state ^{19}F NMR spectroscopy, thermal analysis, and IR spectroscopy. Its structure contains close-packed hollow columns with an 18-membered window, each of which contains six one-dimensional chains formed of Ge_7X_{19} (X = O, OH, F) clusters connected to zinc complexes.

Microporous germanates have been extensively studied because of their potential applications in catalysis, adsorption and separation, and interesting structural chemistry.[1] Organic amines have been used as structure-directing agents in the synthesis of inorganic frameworks, with the organic ammonium cations being located in the voids of the structures. In its compounds, Ge atoms can be four-, five-, or six-coordinate and form well-defined clusters as secondary structural building units, such as Ge_7X_{19} (Ge_7), Ge_8X_{20} (Ge_8), Ge_9X_{25-26} (Ge_9), and $Ge_{10}X_{28}$ (Ge_{10}), where X = O, OH, F.[2−5] The compounds that contain Ge_7 clusters are of particular interest because they form various extended frameworks such as chainlike, tubular, layered, and three-dimensional (3D) structures with extra large pores.[1,2]

The incorporation of heteroatoms into germanate frameworks enhances the structural diversity and generates another class of materials with interesting structures and properties. A good number of germanates containing trivalent, quadrivalent, and pentavalent metals have been synthesized.[6−8] Several germanates containing divalent transition metals were also reported. In particular, the Ni^{2+} cation may form complexes as structure-directing agents or be incorporated into germanate frameworks to form one-dimensional (1D) or 3D structures.[9] In contrast, fewer zinc germanates have been reported, and all of them adopt 3D framework structures.[10] Herein we report the synthesis, structural characterization, and properties of a novel zinc germanate, $(C_8H_{22}N_4Zn)_2Ge_7O_{14}(OH)F_3$ (denoted as **1**), whose structure consists of neutral infinite chains formed of a Zn^{2+} complex containing a tetradentate amine ligand, which is further connected to a Ge_7 cluster. Six such chains are stacked together to form a hollow column with an 18-membered window. These columns are close-packed in space to form the structure.

A reaction mixture of 0.157 g of GeO_2 (1.50 mmol), 0.112 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.50 mmol), 1.00 g of 2-methylpiperazine ($C_5H_{12}N_2$; 10.0 mmol), 1.00 mL of 1,2-bis(3-aminopropylamino)ethane (BAPE; 5.20 mmol), and 0.109 mL of 48% HF(aq) (3.00 mmol) was stirred thoroughly. The slurry was heated in a Teflon-lined steel autoclave under autogenous pressure at 150 °C for 10 days and then slowly cooled in the oven to room temperature. The product was obtained by suction filtration, washed with water, rinsed with ethanol, and dried in air under ambient conditions. The product contained colorless hexagonal-prismatic crystals of **1** and a small amount of unidentified white powder. The colorless crystals were manually separated from the powder to give a pure phase of **1**, as confirmed by powder X-ray diffraction (PXRD; Figure S1 in the Supporting Information, SI). The yield of **1** was 71% based on GeO_2. In this synthesis, 2-methylpiperazine was added to adjust the pH of the reaction mixture and to improve the yield of **1**. We have also carried out retrosyntheses without 2-methylpiperazine under similar reaction conditions; the resulting products contained **1** in a very low yield.

The qualitative energy-dispersive X-ray analysis of several crystals of **1** confirmed the presence of Ge and Zn. Total reflection X-ray fluorescence spectroscopy was applied to determine the relative element content. Analysis results showed that the sample contains Ge and Zn in the molar ratio 3.48:1, which is in good agreement with that determined from single-crystal X-ray diffraction (Figure S3 in the SI). Elemental analysis results were also in good agreement with the stoichiometry [Anal. Found (calcd): C, 15.13 (14.95); H, 3.88 (3.53); N, 8.70 (8.72)]. The IR spectrum showed the presence of an OH group, an amine molecule, and Ge−O and Ge−F bonds (Figure S4 in the SI). The thermogravimetric analysis (TGA) curve, which was measured under flowing N_2 at a heating rate of 10 °C min^{-1}, showed a weight loss of 27.88% from 300 to 530 °C, which agrees well with the calculated value of 27.11% for the removal of two amine molecules per formula unit (Figure S5 in the SI). The weight loss above 700 °C can be ascribed to the removal of volatile germanium compounds.[11]

The magic-angle-spinning (MAS) ^{19}F NMR spectrum of **1** (Figure 1) showed three resolved resonances with approximately equal intensity, which correspond to three unique F atoms in the structure (vide infra). The resonance at −139.59 ppm is assigned to F(1), which possesses a local environment very different from those of the other two F sites. The other two resonances are assigned to F(2) and F(3). The ^{19}F NMR chemical shifts of **1** are in good agreement with those of

Received: June 7, 2012
Published: August 10, 2012

dx.doi.org/10.1021/ic301216q | *Inorg. Chem.* 2012, 51, 9150−9152

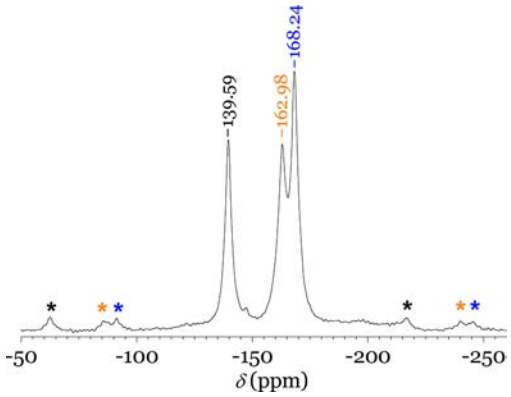

Figure 1. MAS ^{19}F NMR spectrum of **1** acquired at a spinning speed of 29 kHz. The chemical shifts are referenced to that of $CFCl_3$ (at 0 ppm). The asterisks denote the spinning sidebands.

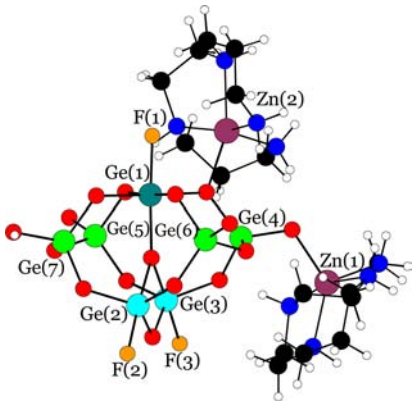

Figure 2. Ball-and-stick representation of the structural building unit in **1**. The red, blue, and black circles are O, N, and C atoms, respectively; the open circles are H atoms.

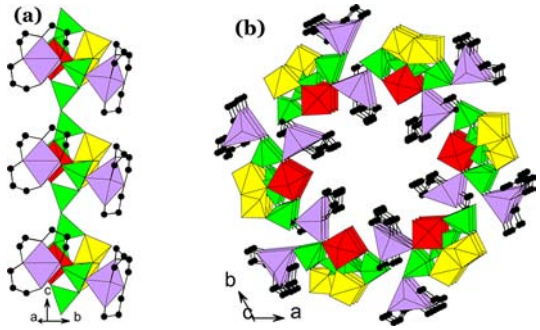

Figure 3. Section of a 1D chain viewed along the ⟨110⟩ direction (a) and the stacking of six chains viewed along the *c* axis (b). The red, yellow, violet, and green polyhedra are GeO_5F octahedra, GeO_4F trigonal bipyramids, $ZnON_4$ polyhedra, and GeO_4 tetrahedra, respectively. H atoms are omitted for clarity.

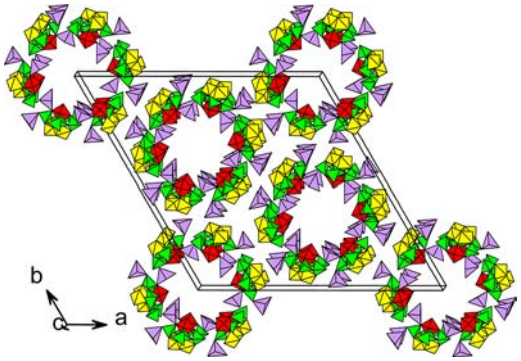

Figure 4. Close-packed hollow columns of zinc germanate in the structure of **1**. C and H atoms are omitted for clarity.

germanium(IV) fluoride complexes such as GeF_4L_2 with L = dimethoxyethane, which shows peaks at −131.0 and −151.1 ppm or at −166.2, −166.7, and −178.8 ppm for L = tetrahydrofuran.[12]

A suitable crystal of **1** was selected for single-crystal X-ray diffraction from which the structure and chemical composition of **1** were determined.[13] The terminal atom of the six-coordinate Ge and that of each five-coordinate Ge are assigned as F atoms, whereas that of a four-coordinate Ge as hydroxo O based on the results from bond-valence-sum calculation.

The 1D structure of **1** is constructed from the following structural elements: one GeO_5F octahedron, two GeO_4F trigonal bipyramids, two $ZnON_4$ polyhedra, and four GeO_4 tetrahedra. All atoms are in general positions. The Zn atoms are bonded to four N atoms from the tetradentate BAPE molecule and one germanate O atom to form a distorted $Zn(1)ON_4$ trigonal bipyramid and a $Zn(2)ON_4$ square pyramid according to the calculated geometric parameters of 0.652 and 0.021, respectively, as defined by Addison et al.[14] The Zn−O bonds are shorter than the Zn−N bonds. The bond-valence sums of Zn(1) and Zn(2) are 1.86 and 1.97 valence units, respectively.[15]

Ge(1) is octahedrally bonded to one F and five O atoms. The Ge(2) and Ge(3) atoms are each bonded to one F and four O atoms to form trigonal bipyramids. The other Ge atoms are bonded to four O atoms in tetrahedral geometry. The bond-valence sums of these Ge atoms are in the range from 4.00 to 4.12 valence units.[15] The germanate polyhedra share common vertices and edges to form a Ge_7X_{19} (X = O, OH, F) unit with a three-coordinate O atom, O(5), in the center of the unit. This Ge_7X_{19} unit is connected to two zinc complexes via O atoms to form a $(C_8H_{22}N_4Zn)_2Ge_7X_{19}$ cluster (denoted as Zn_2Ge_7) as the secondary building unit of the structure (Figure 2). Each Zn_2Ge_7 unit is connected to two others via two O atoms to form neutral infinite chains along the [001] direction (Figure 3a). Six such chains are stacked together to form a hollow column with an 18-membered window. The terminal F atoms of the $Ge(1)O_5F$ octahedra are directed toward the center of the column (Figure 3b). The distance between two F atoms across a column is 12.25 Å. The columns are close-packed in space to form the structure of **1** (Figure 4). Neighboring columns are held together by strong hydrogen bonds. The void volume of the structure calculated using the *SOLV* tool in the *PLATON* program is 839.5 $Å^3$ per unit cell.

1D structures of germanates are rare. Three 1D germanates, FJ-6,[9a] JLG-4,[9b] and JLG-5,[2b] were reported, but all of them contain negatively charged chains that are counterbalanced by metal complexes or protonated organic amines. Compound **1** is the first example in the literature containing neutral infinite chains, which are stacked together by hydrogen bonds to form closed-packed columns.

Several 3D structures of zinc germanates incorporating amine ligands have been reported. For instance, the structure of $[Ge_9O_{18}Zn_2(OH)_4]\cdot 3NH_2CH_2CH_2NH_2$ contains a zinc complex bonded to a Ge_9 cluster.[10a] There are two different types of ethylenediamine molecules in the structure. One acts as a bis-

dx.doi.org/10.1021/ic301216q | *Inorg. Chem.* 2012, 51, 9150−9152

chelating ligand to a Zn atom, and the other serves as a bridge between two symmetry-related Zn atoms. Recently, we also reported two zinc germanates with 3D framework structures, namely, $Zn_2Ge_4O_{10}(NH_2CH_2CH_2CH_2NH_2)$ and $ZnGe_2O_5(NH_2CH_2CH_2NH_2)$. One type of connectivity of the amine molecule that acts as a bridging ligand between two Zn atoms was observed in these two compounds.[10b]

In summary, we have successfully synthesized and structurally characterized a 1D zinc germanate incorporating a tetradentate amine ligand. Its structure contains neutral chains of metal germanates that are stacked together to form 18-ring channels. This is the first example of a transition-metal germanate containing extra-large empty channels in the literature. For the first time, the presence of F atoms in the germanate cluster is characterized by solid-state ^{19}F NMR. The synthesis of this compound suggests further opportunities to synthesize new germanates with extra-large pore and low framework density by incorporating different metal complexes into the frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of **1** in CIF format, PXRD patterns, a photo of crystals, an IR spectrum, and a TGA curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Crystal data of **1**: A total of 29584 reflections of a colorless prismatic crystal with dimensions of 0.1 × 0.04 × 0.04 mm^3, trigonal, $R\bar{3}$ (No. 148), a = 46.5858(13) Å, c = 8.8708(3) Å, V = 16672.5(9) $Å^3$, Z = 18, d_{calc} = 2.305 g cm^{-3}, and μ(Mo Kα) = 6.952 mm^{-1} were measured on a Kappa APEXII diffractometer at 296 K, which gave 9234 independent reflections with R(int) = 0.0625. An empirical absorption correction based on the symmetry-equivalent was applied with T_{min}/T_{max} = 0.6381/0.7457. The H atoms of the amine molecule and the hydroxo group were positioned geometrically and refined using the riding model. The final cycles of refinement converged at R1 = 0.0396 and wR2 = 0.0923 for 6262 reflections with $I > 2\sigma(I)$. GOF = 1.016; ρ_{max} and ρ_{min} = 1.565 and −0.753 e $Å^{-3}$.

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