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Zinc Germanates Incorporating Organic Amine Ligands: Solvothermal Synthesis and Structural Characterization of $Zn_2Ge_4O_{10}(NH_2CH_2CH_2CH_2NH_2)$ and $ZnGe_2O_5(NH_2CH_2CH_2NH_2)$

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Two zinc germanates incorporating bidentate-bridging organic amine ligands have been synthesized under solvothermal conditions by using the amines as solvents. Their structural features are infinite chains formed of edge-sharing ZnO_4N trigonal bipyramids and unbranched vierer single layers with the composition $[Ge_4O_{10}]$ and discrete ZnO_2N_2 tetrahedra and unbranched zweier double chains with the composition $[Ge_2O_5]$, respectively.

Since the discovery of microporous aluninophosphates and silicoaluminophosphates, the synthesis of porous materials to explore their interesting structural chemistry and useful properties, such as molecular separation and heterogeneous catalysis, has been a subject of intensive research.[1] A large number of microporous materials containing other polyhedral elements have been synthesized under solvo/hydrothermal conditions. Recently, there were a good number of reports on the synthesis of metal germanates in the presence of organic amines as structure-directing agents.[2] Most of these germanates contain trivalent and quadrivalent metals, and a few of them contain divalent metals, namely, $[Ge_9O_{18}M_2(OH)_4]\cdot 3NH_2CH_2CH_2NH_2$ (M = Zn, Co, and Cd).[2c,f,i] These compounds are isostructural and were synthesized by employing a solvo/hydrothermal route using water/ethylene glycol (or ethylenediamine) mixtures as solvents.

Recently, we reported several uranium germanates, such as a thermally stable uranyl germanate with 12-ring channels, $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$, a uranium(V) germanate, $Rb_3(U_3O_6)(Ge_2O_7)$, and mixed-valence uranium(V,VI) germanates, $A_3(U_2O_4)(Ge_2O_7)$ (A = Rb and Cs).[3] All of these uranium germanates were synthesized under high-temperature, high-pressure hydrothermal conditions at about 600 °C and 170 MPa. Following the successful synthesis of pure inorganic germanates, we have extended our research to the synthesis of metal germanates incorporating organic amines instead of alkali metals under mild solvothermal conditions below 200 °C. Herein, we report two divalent metal germanates, $Zn_2Ge_4O_{10}(NH_2CH_2CH_2CH_2NH_2)$ (denoted as **1**) and $ZnGe_2O_5(NH_2CH_2CH_2NH_2)$ (denoted as **2**), which were synthesized by using organic amines not only as solvents but also as ligands in their 3D framework structures.

Colorless block crystals of **1** were obtained by heating a mixture of GeO_2 (0.209 g, 2 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.149 g, 0.5 mmol), HF(aq) (0.125 g, 3 mmol, 48% solution), and 1,3-diaminopropane (6.219 g, 83.9 mmol) in a Teflon-lined steel autoclave at 170 °C for 10 days, followed by slow cooling to room temperature at 3 °C/h. A crystal was selected for structure determination by single-crystal X-ray diffraction. The bulk product was monophasic, as judged by the total consistency of its powder X-ray pattern with that simulated from the atomic coordinates derived from the single-crystal X-ray study (Figure S1 in the Supporting Information). The yield was 72% based on zinc. A solvothermal reaction using ethylenediamine instead of 1,3-diaminopropane as the solvent was also performed under the same reaction conditions as those for **1**. The product was a colorless microcrystalline powder, and its powder X-ray pattern was considerably different from those of **1** and **2** (see below). We were unable to characterize its structure by single-crystal X-ray diffraction because of the very small crystal size. Colorless block crystals of **2** were

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prepared by heating a mixture of GeO_2 (0.105 g, 1 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.149 g, 0.5 mmol), and ethylenediamine (4.495 g, 74.8 mmol) under similar reaction conditions. The product contained large colorless block crystals of **2** as a major product and an unidentified white powder. Compound **2** could be manually separated from the side product, giving a pure sample, as indicated by powder X-ray diffraction (Figure S2 in the Supporting Information). The yield was 48% based on zinc. Energy-dispersive X-ray fluorescence spectroscopy analysis confirmed the presence of zinc and germanium in both compounds. Elemental analysis results were consistent with their formulas. Anal. Found (calcd) for **1**: C, 5.61 (5.50); H, 1.60 (1.54); N, 4.31 (4.28). Anal. Found (calcd) for **2**: C, 6.77 (6.85); H, 2.37 (2.30); N, 7.74 (7.99). Their IR spectra were recorded by using the KBr pellet method and revealed the bands characteristic of the organic amine (for **1**, 3313 and 3265 cm^{-1}; for **2**, 3310 and 3105 cm^{-1}) and GeO_4 groups (for **1**, 896 and 798 cm^{-1}; for **2**, 899 and 806 cm^{-1}) (Figures S3 and S4 in the Supporting Information). The TGA curves of **1** and **2**, which were measured in flowing dinitrogen at 10 °C/min, showed several steps of weight loss in the range from 40 to 1000 °C (Figures S5 and S6 in the Supporting Information). The first step of weight loss corresponds to the loss of organic amines (for **1**, an observed weight loss of 11.59% from 300 to 700 °C and a calculated value of 11.31%; for **2**, an observed weight loss of 16.57% from 340 to 740 °C and a calculated value of 17.14%). Subsequent large weight losses can be attributed to the removal of volatile germanium oxide phases.[2f] Powder X-ray diffraction of the final decomposition products showed the presence of $ZnGeO_3$ (JCPDS-34-0763).

Suitable crystals of **1** and **2** were selected for single-crystal X-ray diffraction analysis, from which the chemical formulas were determined.[4] The structure of **1** is constructed from the following structural elements: two ZnO_4N polyhedra, four GeO_4 tetrahedra, and one 1,3-diaminopropane molecule. All atoms are in general positions. Each Zn atom is connected to four germanate O atoms and one N atom from a 1,3-diaminopropane molecule in the geometry of a distorted trigonal bipyramid. A five-coordinate MX_5 polyhedron may exhibit three kinds of environments, namely, square pyramid (SP), trigonal bipyramid (TB), and half SP–half TB. The parameter τ defined by Addison et al.[5] as $\tau = (\beta - \alpha)/60$ was calculated (β and α are the largest X–M–X angles of the MX_5 polyhedron) to distinguish different environments. The value is equal to 0 for an ideal SP and to 1 for a TB. The τ values are 0.73 and 0.60 for Zn(1) and Zn(2), respectively. As shown in Figure 1a, each ZnO_4N trigonal bipyramid shares two edges to form zigzag infinite chains parallel to the *c* axis, which are linked by 1,3-diaminopropane molecules so that hybrid organic–inorganic sheets in the *bc* plane with the composition $[Zn_2O_4(NH_2CH_2CH_2CH_2NH_2)]$ are generated. The GeO_4 tetrahedra are connected together by sharing three corners to form layers with the composition $[Ge_4O_{10}]$ containing four- and eight-membered rings (Figure 1b). According to the definition of the layer types based on the periodicity of the fundamental chain from which the layer can be generated by successive linking of these chains, the $[Ge_4O_{10}]$ layer is an unbranched vierer single layer.[6] Similar layers were found in the minerals apophyllite $(KCa_4[Si_4O_{10}]_2(F,OH) \cdot 8H_2O)$[7] and paracelsian $(BaAl_2Si_2O_8)$.[8] They differ, however, in the distribution of tetrahedra pointing up and down, i.e., in the direction of the tetrahedra. The $[Ge_4O_{10}]$ layers in **1** are connected by the $[Zn_2O_4(NH_2CH_2CH_2CH_2NH_2)]$ layers via four μ_3-O atoms to form a 3D neutral framework with the composition $Zn_2Ge_4O_{10}(NH_2CH_2CH_2CH_2NH_2)$ (Figure 1c).

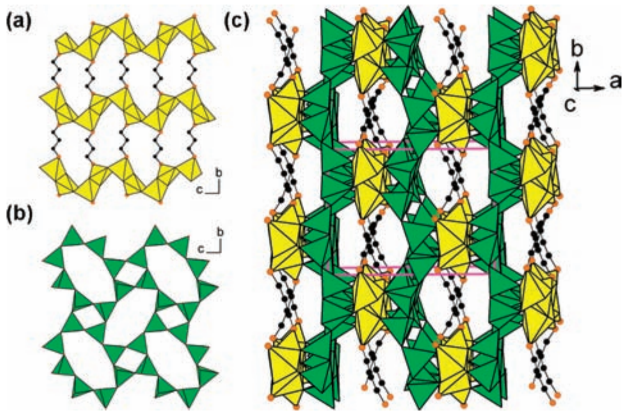

Figure 1. (a) Hybrid organic–inorganic sheet in **1** with the composition $[Zn_2O_4(NH_2CH_2CH_2CH_2NH_2)]$ formed of infinite zigzag chains of edge-sharing ZnO_4N trigonal bipyramids and bidentate-bridging 1,3-aminopropane ligands. (b) Unbranched vierer single layer in **1** with the composition $[Ge_4O_{10}]$. (c) Structure of **1** viewed along the *c* axis. The yellow and green polyhedra are ZnO_4N trigonal bipyramids and GeO_4 tetrahedra, respectively. Black and orange circles are C and N atoms, respectively. H atoms are not shown for clarity.

The structure of **2** is constructed from the following structural elements: one ZnO_2N_2 tetrahedron, two GeO_4 tetrahedra, and one ethylenediamine molecule. Each Zn atom is connected to two germanate O atoms and two N atoms from two ethylenediamine molecules in the geometry of a distorted tetrahedron. As shown in Figure 2a, the amine molecule acts as a bidentate-bridging ligand between two Zn atoms such that infinite chains parallel to the *c* axis with the composition $[ZnO_2(NH_2CH_2CH_2NH_2)]$ are generated. The GeO_4 tetrahedra are connected together by sharing three corners to form unbranched zweier double chains parallel to the *a* axis with the composition $[Ge_2O_5]$ (Figure 2b). The two O atoms of each $ZnO_2(NH_2CH_2CH_2NH_2)$ moiety are joined to GeO_4 tetrahedra of the $[Ge_2O_5]$ chains such that a 3D framework with the composition $ZnGe_2O_5(NH_2CH_2CH_2NH_2)$ is formed (Figure 2c).

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(4) Crystal data for $Zn_2Ge_4O_{10}(NH_2CH_2CH_2CH_2NH_2)$ (**1**): monoclinic, space group $P2_1/c$, $Z = 4$, $M_r = 655.23$, $a = 13.5126(2)$ Å, $b = 10.1471(1)$ Å, $c = 9.8442(1)$ Å, $\beta = 98.001(1)°$, $V = 1336.64(3)$ Å^3, $D_{calc} = 3.256$ g/cm^3, $\lambda = 0.710\,73$ Å, $\mu = 12.463$ mm^{-1}, 2837 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 54.96°$, $R_{int} = 0.023$), GOF = 1.049, $\Delta\rho_{max,min} = 0.55, -0.38$ e/Å^3, R1 = 0.0149, wR2 = 0.0355. Crystal data for $ZnGe_2O_5(NH_2CH_2CH_2NH_2)$ (**2**): monoclinic, space group $P2_1/c$, $Z = 4$, $M_r = 350.65$, $a = 4.9309(1)$ Å, $b = 13.6444(4)$ Å, $c = 11.4385(4)$ Å, $\beta = 93.568(1)°$, $V = 765.08(4)$ Å^3, $D_{calc} = 3.032$ g/cm^3, $\lambda = 0.710\,73$ Å, $\mu = 10.858$ mm^{-1}, 1329 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 52.74°$, $R_{int} = 0.0518$), GOF = 1.192, $\Delta\rho_{max,min} = 1.131, -1.308$ e/Å^3, R1 = 0.0266, wR2 = 0.0911.

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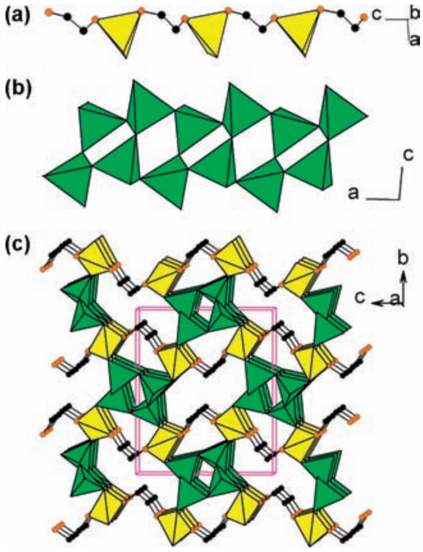

Figure 2. (a) Infinite chain in **2** formed of ZnO_2N_2 tetrahedra and bidentate-bridging ethylenediamine ligands. (b) Unbranched zweier double chain in **2** with the composition $[Ge_2O_5]$. (c) Structure of **2** viewed along the *a* axis. The yellow and green polyhedra are ZnO_2N_2 and GeO_4 tetrahedra, respectively. Black and orange circles are C and N atoms, respectively. H atoms are not shown for clarity.

In the literature, organic amines are usually used as structure-directing agents to direct the formation of inorganic frameworks, with the organic ammonium cations being located in the voids of the structure. A large number of organically templated germanate-based zeolite-type materials, including the pure germanates and those containing tri- or tetravalent metal ions such as Al^{3+}, Ga^{3+}, and Zr^{4+} in their frameworks, have been reported. This work presents two novel zinc germanates incorporating neutral bidentate organic amines as bridging ligands, which were synthesized under solvothermal conditions by using the organic amines as solvents. The 3D frameworks of **1** and **2** are characterized by infinite chains formed of edge-sharing ZnO_4N trigonal bipyramds and unbranched vierer single layers with the composition $[Ge_4O_{10}]$ and discrete ZnO_2N_2 tetrahedra and unbranched zweier double chains with the composition $[Ge_2O_5]$, respectively. These two structures are considerably different from those of previously reported isostructural metal germanates, $[Ge_9O_{18}M_2(OH)_4]\cdot 3NH_2CH_2CH_2NH_2$ (M = Co, Zn, and Cd). Given the large variety of organic amines that could be used in the synthetic regime, one can envisage the synthesis of many more transition-metal germanium oxide frameworks incorporating neutral organic amine ligands by using the amines as solvents in the hope of devising functional materials with interesting structures and properties.

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Supporting Information Available: Crystallographic data of **1** and **2** in CIF format, X-ray powder patterns, IR spectra, and TGA curves. This material is available free of charge via the Internet at http://pubs.acs.org.