$[Ni(1,2\text{-}PDA)_3]_2(HOCH_2CH_2CH_2NH_3)_3(H_3O)_2[Ge_7O_{14}X_3]_3$ (X = F, OH): A New 1D Germanate with 12-Ring Hexagonal Tubular Channels

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Recently, increasing attention has been paid to the synthesis of open-framework germanates, because germanium is the closest analog to silicon in the periodic table that can be used as a silicon substituent to build various open-framework structures of zeolites and microporous materials.[1–7] Compared to tetrahedrally coordinated silicon, germanium can display various geometries, including tetrahedron, square pyramid/trigonal bipyramid, and octahedron, because of its larger Ge−O bond distances and smaller Ge−O−Ge bond angles. Particularly, some large and complex second building units (SBUs) can be formed by linkage of various Ge-centered polyhedra, which further link to form interesting framework architectures. Typical SBUs in germanates are $Ge_7(O,OH,F)_{19}$ (Ge_7),[8–15] $Ge_9(O,OH,F)_{26}$ (Ge_9),[16–21] and $Ge_{10}(O,OH,F)_{27}$ (Ge_{10}) clusters.[22] Significantly, open framework structures with extra large pores and low framework densities can be generated by using such large clusters as SBUs, as predicted by Férey on the basis of the concept of "scale chemistry".[23–25] Notable examples are germanates FDU-4 with 24 rings and $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ with 16 rings constructed from Ge_9 clusters,[19,21] germanates ASU-16 and SU-12 with 24 rings, and ASU-12 with 16 rings built from Ge_7 clusters,[8,10,13] germanate STAG-1 with 16 rings comprising Ge_7 clusters and double four rings (D4Rs),[15] germanates SU-8 with 16 rings and SU-44 with 18 rings comprising both Ge_7 and Ge_9 clusters.[14] Remarkably, Zou et al. reported a crystalline mesoporous germanate SU-M with extra large 30-ring channels and the lowest framework density that is built from Ge_{10} clusters.[22]

Organic species play an important structure-directing role in the formation of open-framework germanates. The germanates are typically prepared under hydrothermal/solvothermal conditions in the presence of organic amines as templates or structure-directing agents (SDAs). A few germanates are formed in the presence of metal complexes, such as FJ-6, ICMM-2, FJ-1a, and FJ-1b.[12,26,27] Transition-metal complexes have been used previously as SDAs in the synthesis of open-framework phosphates,[28–33] and a new concept of chirality transfer of the metal complex into the inorganic framework has been demonstrated.[31–33] However, few attempts have been made in the synthesis of germanates by using metal complexes as the SDAs. Here, we present a novel one-dimensional (1D) germanate $[Ni(1,2\text{-}PDA)_3]_2(HOCH_2CH_2CH_2NH_3)_3(H_3O)_2[Ge_7O_{14}X_3]_3$ (X = F, OH) (1,2-PDA = 1,2-diaminopropane) (denoted JLG-4) with a 12-ring tubular structure. The 12-ring tube comprising 10-ring windows is formed by corner-sharing of Ge_7 clusters. The metal complex $[Ni(1,2\text{-}PDA)_3]^{2+}$ is self-assembled during the solvothermal synthesis and acts as the SDA along with 3-amino-1-propanol that plays a dual role of SDA and solvent. To the best of our knowledge, JLG-4 is the first

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example of 1D tubular structure in the family of germanate materials, which is composed of $Ge_7(O,OH,F)_{19}$ clusters linked in a new way to produce a 12-ring tube.

Large single crystals of JLG-4 were prepared by the solvothermal reaction of a mixture of GeO_2, $NiCl_2 \cdot 6H_2O$, H_2O, 3-amino-1-propanol, 1,2-PDA, and HF in a 1:0.42:37.04:43.58:15.47:1.86 molar ratio. Typically, GeO_2 (0.156 g) and $NiCl_2 \cdot 6H_2O$ (0.15 g) were dispersed in a mixture of H_2O (1.0 mL) and 3-amino-1-propanol (5 mL) with stirring. 1,2-Diaminopropane (1,2-PDA) (2.0 mL) and HF solution (40 wt %, 0.12 mL) were then added to this solution. A homogeneous gel was formed after stirring for about 2 h and was then transferred to a 15 mL Teflonlined stainless-steel autoclave and heated at 180 °C for 6 days under static conditions. The red, hexagonal, rod-shaped single crystals were separated by filtration, washed by distilled water, and then dried in the air.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The experimental XRD pattern agrees well with the simulated one generated on the basis of single-crystal structural analysis (Figure S1, Supporting Information). Elemental analysis indicates that JLG-4 contains 10.20, 3.25, and 6.67 wt % of C, H, and N, respectively. These are in agreement with the calculated values of 10.17, 3.18, and 6.59 wt % of C, H, and N, respectively. Fluoride ion selective electrode shows that JLG-4 contains 2.64 wt % of F (calcd: F, 2.68 wt %). Inductively coupled plasma (ICP) analysis for the JLG-4 gave the contents of Ge, 47.78 wt %, and Ni, 3.70 wt % (calcd: Ge, 47.83; Ni, 3.68 wt %). IR (KBr, cm^{-1}): 3447 (OH); 1589 and 1524 (NH_2); 871, 815, and 585 (Ge−O); 777 (Ge−F) (Figure S2, Supporting Information).[12,34] Thermogravimetric analysis shows a total weight loss of 26.38% between 40 and 800 °C, which corresponds to the decomposition of the occluded 3-amino-1-propanol and 1,2-PDA in $Ni(1,2\text{-PDA})_3^{2+}$ complex, and the release of H_2O and HF in the product (calcd: 26.40%) (Figure S3, Supporting Information). XRD analysis reveals that JLG-4 is stable upon calcination at 250 °C and that it collapses upon calcination at 300 °C with the decomposition of occluded organic species. The measured effective magnetic moment is 2.81 μ_B, which is in agreement with octahedral Ni^{2+} complex (calcd. 2.83 μ_B).[35]

Single-crystal X-ray diffraction analysis reveals that JLG-4 crystallizes in the $P6_3/m$ space group.[36] It has the anionic framework $[Ge_7O_{14}X_3]^{3-}$ (X = F, OH), whose negative charges are compensated by $[Ni(1,2\text{-PDA})_3]^{2+}$, $HOCH_2CH_2CH_2NH_3^+$, and H_3O^+ counterions. The asymmetric unit of JLG-4 is shown in Figure S4 of the Supporting Information.

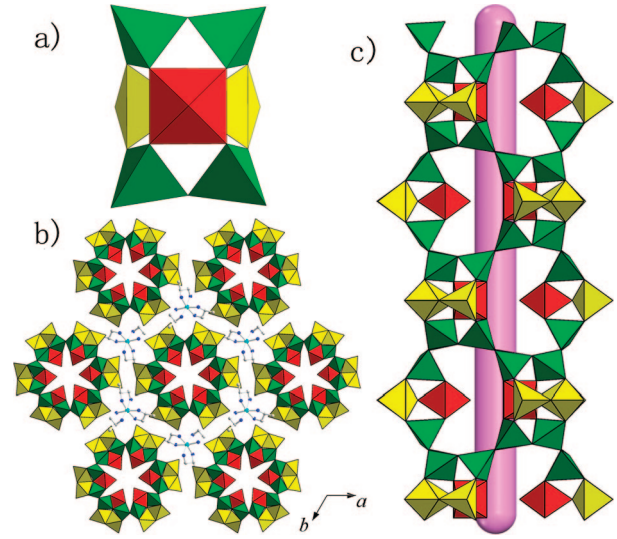

Figure 1. (a) Ge_7 cluster in JLG-4; (b) framework structure of JLG-4 viewed along the [001] direction showing the hexagonal 12-ring tubes (all the hydrogen atoms are omitted for clarity); (c) single 12-ring tube with 10-ring windows. Color code: GeO_5X octahedron, red; GeO_4X trigonal bipyramid, yellow; GeO_4 tetrahedron, green; C, light grey; N, blue; Ni, cyan.

JLG-4 is built from Ge_7 clusters (Figure 1a). The Ge_7 cluster with the point group *m* is composed of four tetrahedral GeO_4 ($Ge-O_{avg}$ = 1.738 Å), two trigonal bipyramidal GeO_4X ($Ge-O_{avg}$ = 1.838 Å and $Ge-F_{avg}$ = 1.802 Å), and one octahedral GeO_5X ($Ge-O_{avg}$ = 1.884 Å and $Ge-F$ = 1.807 Å). One tricoordinated oxygen atom at the core of the cluster links the GeO_5X octahedron and two GeO_4X trigonal bipyramids. The Ge_7 clusters are connected through corner sharing of oxygen atoms of the GeO_4 units to form an infinite 1D hexagonal 12-ring tube running along the 6_3 screw axis (Figures 1b and 1c). Such inorganic tubular structures are rarely reported.[37–39] The terminal X atoms of the GeO_5X units protrude into the 12-ring tube. Three X atoms arrayed in a triangle are at the same level along the tube, and the next three are related by 6_3 screw axis. Six such X atoms along with the wall of 12-ring tube delimitate a large cavity with free diameters of 5.2 × 8.1 Å (Figure S5, Supporting Information). The H_3O^+ cations are encapsulated inside the 12-ring tube. The framework density of JLG-4 is 9.70 Ge atoms per 1000 $Å^3$, which is one of the lowest among the known open-framework materials. As shown in Figure 1c, the wall of the 12-ring tube comprises 10-ring windows that are enclosed by four corner-sharing Ge_7 clusters. The $HOCH_2CH_2CH_2NH_3^+$ cations accommodate in the 10-ring windows with the −OH groups pointing into the 12-ring tube. The $Ni(1,2\text{-PDA})_3^{2+}$ complexes locate among individual tubes, and interact with three nearby tubes through

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Table 1. Various Connection Modes of Ge_7 Clusters[a]

mode of linkage	n-connection	example	ref
T^2	2	FJ-6 (1D)	12
P^2O	3	unknown	
T^4	4	ASU-20-DACH (2D)	11
		ASU-20-DAPe (2D)	11
		STAG-1	15
		JLG-4 (1D)	this work
T^2P^2	4	SU-44 (3D)	14
		SU-MB (3D)	22
T^2PO	4	unknown	
T^4P	5	ASU-12 (3D)	8
		ASU-16 (3D)	10
		ASU-19 (2D)	11
		SU-12 (3D)	13
T^4O	5	ASU-19	11
T^4P^2	6	SU-44 (3D)	14
T^4PO	6	SU-8 (3D)	14
T^4P^2O	7	$Ge_{10}O_{21}(OH)\cdot N_4C_6H_{21}$ (3D)	9

[a] T = tetrahedron, P = trigonal bipyramid, O= octahedron.

H-bonds. Each 12-ring tube is surrounded by six pairs of enantiomers of $Ni(1,2\text{-}PDA)_3^{2+}$ cations with Δ- and Λ-configurations. The adjacent tubules and counterions are assembled via H-bonds to form a 3D supramolecular network. It is believed that the co-structure-directing role of metal complex $Ni(1,2\text{-}PDA)_3^{2+}$ and 3-amino-1-propanol is very important for the formation of the unique tubelike structure of JLG-4.

It is noted that a number of known germanate structures are built from the $Ge_7(O,OH,F)_{19}$ clusters. Such Ge_7 cluster possesses diverse nodes of linkage of oxygen sites coming from four tetrahedra, two trigonal bipyramids, and one octahedron (named T, P, and O sites), respectively. This indicates that the Ge_7 cluster may exhibit many different ways of connections with adjacent clusters to form various interesting open-framework structures. Up to now, 2-, 4-, 5-, 6-, and 7-connected Ge_7 clusters have been found in the known germanates ranging from 1D to 3D structures, with seven types of linkage modes of Ge_7 clusters including T^2, T^2P^2, T^4, T^4P, T^4O, T^4P^2, T^4PO, and T^4P^2O. Table 1 also lists several possible connection modes of Ge_7 clusters, such as P^2O and T^2PO which have not been found in known germanates. The various ways of linkage of Ge_7 clusters in germanates are presented in Figure 2. For a given connected number, the distinct linkage sites among Ge_7 clusters may result in different structures. For example, the 4-connected Ge_7 cluster is found to exist two ways of linkages, i.e., T^2P^2 in SU-44[14] and T^4 in ASU-20[11]. JLG-4 reported in this work shows the T^4 mode of linkage as with ASU-20; however, their different structures are a result of different arrangements of the Ge_7 clusters. Theoretically, various linkage modes of Ge_7 clusters can be generated. By using the auto assembly secondary building unit (AASBU) approach developed by

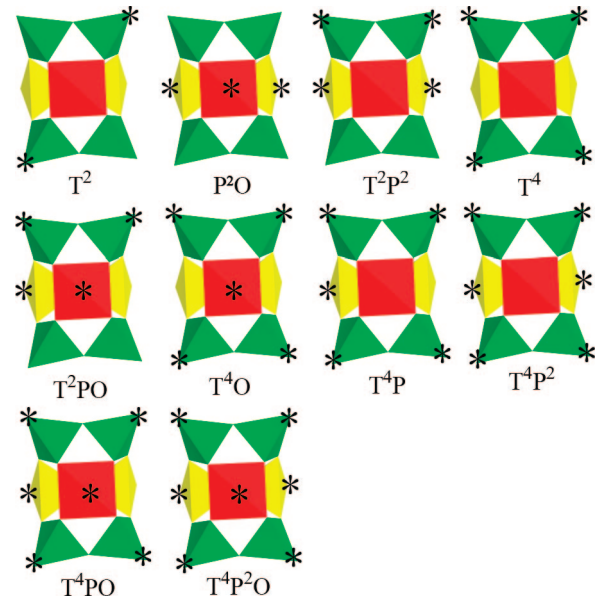

Figure 2. Various connection modes of the Ge_7 cluster (T= tetrahedron, P = trigonal bipyramid, O= octahedron, the polyhedra signed by asterisks (*) indicate the connected sites). Color code: GeO_5X octahedron, red; GeO_4X trigonal bipyramid, yellow; GeO_4 tetrahedron, green.

Férey et al.,[40–42] new open-framework germanate structures can be designed by using Ge_7 clusters as SBUs.

In summary, JLG-4 is the first example of 1D tubular germanate with 12-ring channels and low-framework density. Its structure is built up from Ge_7 cluster building units. We have shown that the Ge_7 cluster possesses various connection modes. By using the AASBU approach, it is possible to design many more new open-framework germanates with large pores and low-framework density by using Ge_7 clusters as SBUs.

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Supporting Information Available: Table of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement paramteters, selected bond lengths and angles, selected hydrogen bonds, experimental and simulated X-ray powder diffraction patterns, TGA curve, IR spectrum, ORTEP plot, graphic showing the cavity delimitated by six F atoms and six Ge_7 clusters (PDF). Crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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