Microporous Germanates

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A Germanate Framework Containing 24-Ring Channels, Ni–Ge Bonds, and Chiral [Ni@$Ge_{14}O_{24}(OH)_3$] Cluster Motifs Transferred from Chiral Metal Complexes**

*Zhi-En Lin, Jie Zhang, Jing-Tai Zhao,
Shou-Tian Zheng, Chun-Yang Pan,
Guo-Ming Wang, and Guo-Yu Yang**

Microporous materials have been extensively studied due to their widespread applications in ion exchange, separation, and catalysis.[1] Since the discovery of the first aluminum phosphates (AlPOs) VPI-5 with 18-membered rings (18-MR) in 1988, some porous materials with larger rings, such as JDF-20 (20-MR), cloverite (20-MR), VSB-1 (24-MR), ND-1 (24-MR), VSB-5 (24-MR), NTHU-1 (24-MR), FDU-4 (24-MR), ASU-16 (24-MR), and SU-12 (24-MR), have been made.[2] Recently, the replacement of framework O^{2-} with S^{2-} (Se^{2-}, Te^{2-}) anions has resulted in a new class of porous materials with giant cavities and channels.[3] In general, the cations and anions of the above frameworks are linked to each other by T-X-T linkage modes, while framework containing T-M-T linkages are unexplored so far (where T and M are cations, and X anions).

Chiral metal complex (CMC) templates have shown great advantages in the synthesis of unusual open-framework materials, because the CMCs not only have unique spatial configurations, various charges, different flexibilities, and hydrogen-bonding sites, but can also induce a chiral environment in the host framework.[4] Metal phosphates templated by an optically pure CMC or a racemic mixture of CMCs have been reported for AlPOs,[4a,5] GaPOs,[6] ZnPOs,[4b,c,7] and BPO.[8] Lately, the synthesis of open-framework germanates has made great progress,[2h–j] but to our knowledge little attention has been paid to the possibility of using CMCs as

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[*] Z.-E. Lin, Prof. Dr. J. Zhang, S.-T. Zheng, C.-Y. Pan, G.-M. Wang,
Prof. Dr. G.-Y. Yang
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, Fujian 350002 (P. R. China)
Fax: (+86) 591-8371-0051
E-mail: ygy@fjirsm.ac.cn

Prof. Dr. J.-T. Zhao
State Key Lab of High Performance Ceramics and Superfine
Microstructure
Shanghai Institute of Ceramics
Chinese Academy of Sciences
Shanghai 200050 (P. R. China)

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templates in the synthesis of germanates.[9] To introduce CMCs into germanates and understand their role in determining the frameworks, we focused on the synthesis of germanates templated by CMCs and obtained the chainlike germanate $[Ge_7O_{13}(OH)_2F_3]^{3-}\cdot 2\,[Ni(dien)_2]^{2+}$ (dien = diethylene triamine).[9d] As a continuation of this work, by using a racemic mixture of a $[NiCl_2(L)_3]$ complex [L = ethylenediamine (en), 1,2-diaminopropane (enMe)] as template, we have made two novel germanate frameworks $Ni@Ge_{14}O_{24}(OH)_3\cdot 2\,Ni(L)_3$ (L = en/enMe, denoted FJ-1a/FJ-1b), in which chiral $[Ni@Ge_{14}O_{24}(OH)_3]^{4-}$ ($Ni@Ge_{14}$) clusters (Figure 1 a,b) containing Ni–Ge bonds are connected to each other to form a three-dimensional (3D) framework with 24-ring windows (Figure 1 c,d). FJ-1 is the first example of porous materials having T-M-T linkages (where T-M-T = Ge-Ni-Ge).

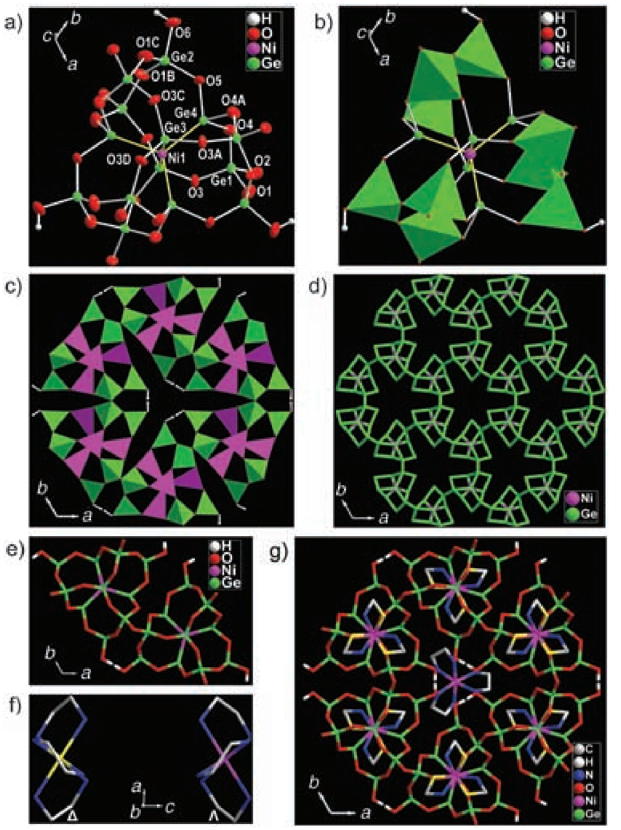

Figure 1. a) View of the coordination environments of the Ni and Ge atoms in the $Ni@Ge_{14}$ cluster (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ni1–Ge3 2.251(2), Ni1–Ge4 2.317(2); Ge3-Ni1-Ge3A 180, Ge3-Ni1-Ge4 90, Ge4-Ni1-Ge4A 120. b) Polyhedral and ball-and-stick view of the $Ni@Ge_{14}$ unit. GeO_4, green. c) View of the 24-ring channel constructed from three pairs of enantiomers of adjacent $Ni@Ge_{14}$ motifs in FJ-1a. d) Topological framework of FJ-1a showing the 24-ring channels and the $Ni@Ge_{14}$ motif. e) View of one pair of enantiomers for adjacent $Ni@Ge_{14}$ motifs with Δ and Λ configurations in the *ab* plane in FJ-1a. f) The chiral octahedral $[Ni2(en)_3]^{2+}$ complexes with Δ and Λ configurations arranged along the *c* axis (Δ, Ni2 yellow; Λ, Ni2 purple). g) View of the orderly separation of chiral $[Ni2(en)_3]^{2+}$ complexes in the center of the 24-ring channel and achiral trigonal prismatic $[Ni3(en)_3]^{2+}$ complexes occluded between the same chiral structural motifs along the *c* axis (N2 blue, N2′ yellow). The H atoms of C and N atoms are omitted for clarity.

Yellow hexagonal crystals of FJ-1a/FJ-1b (see the Supporting Information) were obtained by the solvothermal reaction of $[NiCl_2(L)_3]\cdot 2\,H_2O$ and GeO_2 in mixed solvents of ethylene glycol and L at 170 °C. X-ray crystal analysis revealed that FJ-1a and FJ-1b are isostructural and crystallize in the high-symmetry hexagonal space group $P\bar{6}2c$. Therefore, only the structure of FJ-1a is described in detail. The $Ni@Ge_{14}$ unit consists of one Ni^+ and five Ge^{2+} ions reduced from Ni^{2+} and Ge^{4+} by amine under solvothermal conditions, nine Ge^{4+} ions, and three H and 27 O atoms (Figures 1 a and Supporting Information). The Ni1 atom is located in the center of the $Ni@Ge_{14}$ unit and is bonded to five Ge^{2+} (three Ge4 and two Ge3) atoms to yield a trigonal-bipyramidal $\{Ni@Ge_5\}$ core (Figures 1 a,b and Supporting Information). The Ni^+–Ge^{2+} distances vary in the range 2.251(2)–2.317(2) Å, which is close to the sum of covalent radii for these elements and similar to the Ni^0–Ge^{2+} bonds (2.206–2.291 Å) in nickel germylene complexes,[10] but considerably shorter than a normal Ge–Ge bond or twice the covalent radius of Ge (2.44 Å).[11] Thus, it is reasonable to identify the central atom of $Ni@Ge_{14}$ as Ni. The Ge:Ni ratio obtained from electron probe microanalysis agrees with this assignment. Of the fourteen Ge atoms, five Ge3/Ge4 atoms around Ni1 are tetrahedrally coordinated by one μ_5-Ni1 and three O atoms (Ge–O 1.803(9)–1.849(7) Å). The 4s electron lone pair of Ge^{2+} permits five Ge^{2+} atoms to function as novel ligands to the Ni1 atom with unusual Ge-Ni-Ge linkages. The remaining nine Ge1/Ge2 atoms are typical Ge^{4+} ions and are bonded to four O atoms; the Ge–O distances (1.722(10)–1.766(7) Å) and O-Ge-O angles (99.3(4)–115.3(6)°) are in agreement with those of four-connected germanates.[12] Assuming the valences of nine Ge1/Ge2, five Ge3/Ge4, one Ni1, two Ni2/Ge3, twenty-seven O, and three H to be +4, +2, +1, +2, −2, and +1, respectively, in $Ni@Ge_{14}O_{24}(OH)_3\cdot 2\,Ni(L)_3$, the framework stoichiometry of $[Ni@Ge_{14}O_{24}(OH)_3]^{4-}$ creates a net framework charge of −4, which can just be balanced by two $[Ni(L)_3]^{2+}$ complex cations, that is, the low-valent Ni^+ and Ge^{2+} ions indeed exist in the $\{Ni@Ge_5\}$ core, as is further confirmed by magnetic and luminescence measurements (see below). In FJ-1a, three GeO_4 tetrahedra are linked together by sharing vertices to form a trimer (Ge_3O_{10}). Three trimers are linked alternately to three $Ge(4)O_3Ni$ tetrahedra around the Ni1 atom in the *ab* plane to form a $NiGe_{12}O_{24}(OH)_3$ cluster that is further capped by two Ge3 atoms above and below the *ab* plane to form a novel $Ni@Ge_{14}$ unit (Figure 1 b). Each $Ni@Ge_{14}$ building block is bridged to six others through O2 atoms to yield a 3D open framework with 24-ring channels (Figures 1 c,d and Supporting Information) with dimensions of about 8.3 × 13.6 Å (see Supporting Information), which intersect with two 12-ring channels running along the *a* and *b* axes (see Supporting Information). The construction of 24-ring channels can also be understood as shape-controlled synthesis templated by octahedral $[Ni2(en)_3]^{2+}$ complex. The propellane-like shape of the 24-ring channel around the $[Ni2(en)_3]^{2+}$ templates is delimited by eighteen GeO_4 and six GeO_3Ni tetrahedra (Figures 1 c,d and Supporting Information), which matches the shape of the $[Ni2(en)_3]^{2+}$ complex and is unique and different from that of known porous materials templated by amines.[2]

Interestingly, there are two types of chiral Ni@Ge_{14} motifs and two types of $[Ni(en)_3]^{2+}$ complexes (Figure 1 e,g) in FJ-1a. The $[Ni2(en)_3]^{2+}$ template located in the center of the 24-ring is chiral (Figures 1 g and Supporting Information). The enantiomers of $[Ni2(en)_3]^{2+}$ complexes are alternately arranged as Δ and Λ configurations in the 24-ring channels along the *c* axis (Figures 1 f and Supporting Information), and further interact with chiral Ni@Ge_{14} motifs through H-bonding interactions (N1···O6, 3.072(16 Å). The Δ-$[Ni2(en)_3]^{2+}$ complex forms hydrogen bonds to six adjacent Ni@Ge_{14} motifs with both Δ and Λ configuration, or vice versa (see Supporting Information), while the $[Ni3(en)_3]^{2+}$ cations residing in the 12-ring channels (see Supporting Information) are achiral and separated by Ni@Ge_{14} motifs along the *c* axis. Adjacent $[Ni3(en)_3]^{2+}$ complexes in the *ab* plane exhibit different orientations (Figures 1 g and Supporting Information). The $[Ni3(en)_3]^{2+}$ complex also interacts with the Ni@Ge_{14} motifs through hydrogen-bonding interactions (N2···O3 3.142(18) and N2′···O3/O4 3.144(9)–3.167(20) Å, see Supporting Information).

The chiral $[Ni2(en)_3]^{2+}$ complexes with regular octahedral and achiral $[Ni3(en)_3]^{2+}$ complex with rare trigonal-prismatic geometry in FJ-1a respectively have D_3 and D_{3h} symmetry (see Supporting Information), and the chiral Ni@Ge_{14} motif has C_3 symmetry (Figure 1 a and Supporting Information). It appears that the symmetry of the Ni@Ge_{14} motif is a good match with those of the chiral and achiral metal complex templates (Figures 1 g and Supporting Information). This suggests that the complex template can impose its individual symmetry constraint on the structural motifs,[4] which have a subgroup of point-group symmetry of the complex template.[4c] In addition, the configuration of the chiral Ni@Ge_{14} motif is also matched with that of the chiral $[Ni2(en)_3]^{2+}$ complex template (see Supporting Information). Furthermore, the orderly separation of chiral $[Ni2(en)_3]^{2+}$ and achiral $[Ni3(en)_3]^{2+}$ complexes in FJ-1a (Figures 1 g and Supporting Information) indicates that the host framework has molecular-recognition capability and stereospecificity for guest templates. From insight into the structure of FJ-1a and other metal phosphates templated by CMCs,[4–7] it is found that the CMCs are responsible for the formation of the chiral motif/framework in the crystallization process and can impart their chirality and symmetry to an inorganic motif/framework, as well as leading to the existence of stereospecificity and molecular recognition between the inorganic host and CMC guest, while the achiral metal complex only transfers its symmetry to the inorganic motif. It is believed that the hydrogen bonding between the complex template and the host is the origin of the above phenomena.[4–7]

Variable-temperature magnetic measurements on FJ-1a showed that the product of molar magnetic susceptibility and temperature $\chi_M T$ remains nearly constant down to 50 K and then rapidly decreases on further cooling (see Supporting Information). The magnetic data can be fitted well to the Curie–Weiss law with $\theta = -1.21$ K, which indicates weak antiferromagnetic coupling between metal centers. This is consistent with isolated Ni^{2+} centers and a long distance (10.71 Å) between Ni^{+} centers in adjacent Ni@Ge_{14} units. The high-temperature value of $\chi_M T$ is 1.74 $cm^3 K mol^{-1}$, much smaller than that calculated for two Ni^{2+} ($S = 1$, d^8 configuration) and one Ni^{+} ions ($S = 1/2$, d^9 configuration) without magnetic interaction (2.375 $cm^3 K mol^{-1}$, $g = 2$). This suggests that one Ni^{2+} ion should be in the nonmagnetic state, which might originate from the structural disorder of the trigonal-prismatic coordination of the $Ni3^{2+}$ ion. The experimental value of 1.74 $cm^3 K mol^{-1}$ is in good agreement with the spin-only value expected for one $Ni2^{2+}$ and one $Ni1^{+}$ ions with an average *g* value of 2.25 that is within the generally observed range for Ni^{2+} and Ni^{+} ions.[13,14] In view of the regular octahedral geometry around the $Ni2^{2+}$ ion, the zero-field splitting effect on the Ni^{2+} ion should be very small,[15] and the sharp decrease in $\chi_M T$ at low temperature could be attributed to a weak antiferromagnetic interaction between Ni^{+} ions.[16]

FJ-1a exhibits blue luminescence in the solid state at room temperature. On excitation at 200 nm, the luminescence of FJ-1a has two strong emission bands at 482 and 523 nm and one shoulder at 458 nm (see Supporting Information) that differ from those of reported open-framework phosphates and germanates, which usually show a single emission peak,[17] that is, a more complex mechanism is involved in FJ-1a. Unlike crystalline porous materials incorporating organic dyes or doped with metal activators,[18] the luminescence of phosphates and germanates is generally attributed to the presence of lattice defects.[17] For FJ-1a, apart from lattice defects, low-valent Ge^{2+} with s^2 configuration and $Ge^{2+}(4s) \rightarrow Ni^{+}(3d)$ metal–metal charge transfer in the Ni@Ge_{14} cluster should also make contributions to the luminescence.[19,20]

In summary, we have successfully made two novel germanate open frameworks with 24-MRs by using a metal complex as template under solvothermal conditions. The key points of the synthetic procedures have been well established. These are rare examples of metal–metal bonds in porous materials, and the presence of Ge-Ni-Ge linkages makes them different from other open-framework materials that only contain T-X-T linkages. This study may open up possibilities for the synthesis of novel frameworks with T-M-T linkages. FJ-1 exhibits stereospecificity and chiral molecular recognition between guest CMC and inorganic structural motif. The chirality and symmetry of the guest CMC template can induce that of the inorganic motif/framework. In addition, the symmetry of the achiral guest was transferred to the inorganic motif. These phenomena originate from hydrogen bonding between the guest and the inorganic motif/framework.

Experimental Section

Synthesis of FJ-1a/FJ-1b: GeO_2 (0.152 g) was dissolved in a mixture of water (0.5 mL), ethylene glycol (1.3 mL), and en/enMe (0.4 mL), followed by $[Ni(L)_3Cl_2]\cdot 2H_2O$ (L = en/enMe, 0.171 g). The clear solution was heated at 170 °C for 7 d in a Teflon-lined steel autoclave and then cooled to room temperature. Later, complex $[Ni(L)_3Cl_2]\cdot 2H_2O$ was replaced by $NiCl_2\cdot 2H_2O$ (0.170 g) and en/enMe (1.0 mL), and FJ-1a/FJ-1b was also obtained as a pure phase. The single yellow crystals with hexagonal shape were recovered by filtration, washed by distilled water and ethanol, and air-dried without further separation (17%/15% yield based on Ge for FJ-1a/FJ-1b). Elemental analysis (%) calcd for $C_{12}N_{12}H_{51}Ge_{14}Ni_3O_{27}$ (FJ-1a): C 7.25, H 2.59, N 8.46; found: C 7.34, H 2.39, N 8.26; calcd for

$C_{18}N_{12}H_{63}Ge_{14}Ni_3O_{27}$ (FJ-1b): C 10.43, H 3.06, N 8.11; found: C 10.15, H 2.87, N, 7.92.

Electron-probe microanalysis (EPMA) was performed on a Shimadzu electron microprobe EPMA-8705QH$_2$ to analyze Ge and Ni contents. Different points were selected, both from different areas of the same crystal and from different crystals. The Ge:Ni ratio obtained by EPMA are in agreement with the formula of FJ-1a obtained from the structure refinement (obsd Ge:Ni = 1:0.208, calcd Ge:Ni = 1:0.214).

Crystal data for FJ-1a: $Ni@Ge_{14}O_{24}(OH)_3{\cdot}2Ni(en)_3$, $M_r = 1988.04$, hexagonal, space group $P\bar{6}2c$, $a = 13.5567(4)$, $c = 14.6138(5)$ Å, $V = 2325.96(13)$ Å^3, $Z = 2$, $\rho = 2.839\ \mathrm{g\,cm^{-1}}$, $\mu = 10.173\ \mathrm{cm^{-1}}$, $F(000) = 1910$, GOF = 1.171. $\theta_{max} = 25.01°$. A total of 5454 reflections (1417 independent, $R_{int} = 0.0418$) were measured at 293 K. Final agreement indices were $R1$ ($wR2$) = 0.0405 (0.0829) for 120 parameters and 1288 reflections $[I > 2\sigma(I)]$.

Crystal data for FJ-1b: $Ni@Ge_{14}O_{24}(OH)_3{\cdot}2Ni(enMe)_3$, $M_r = 2072.19$, hexagonal, space group $P\bar{6}2c$, $a = 13.6681(8)$, $c = 14.5642(7)$ Å, $V = 2356.3(2)$ Å^3, $Z = 2$, $\rho = 2.921\ \mathrm{g\,cm^{-1}}$, $\mu = 10.049\ \mathrm{cm^{-1}}$, $F(000) = 2006$, GOF = 1.047. $\theta_{max} = 27.53°$. A total of 9190 reflections (1861 independent, $R_{int} = 0.1042$) were measured at 293 K. Final agreement indices were $R1$ ($wR2$) = 0.0741 (0.1684) for 103 parameters and 1422 reflections $[I > 2\sigma(I)]$.

Data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed with the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXTL97 program package. All non-hydrogen atoms (except N1, N2, N2′, C1, C2, C3, C4 in FJ-1b) were refined anisotropically. The unique N atoms coordinated to Ni3 in FJ-1a and FJ-1b occupy two split positions (N2, N2′) and have occupancies of 0.5. The C2 and C4 (methyl group of enMe) atoms of FJ-1b have occupancies of 0.5. The positions of H atoms (except those on C2 in FJ-1a and N1, N2, N2′, C1, C3 in FJ-1b) were placed geometrically and refined in a riding model. CCDC-277021/280327 (FJ-1a/FJ-1b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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