CrystEngComm

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

A Family of Germanates Constructed from Ge_7 Clusters Co-templated by Metal Complexes and Organic/Inorganic Species

Xiaoyan Ren,[b] Qinhe Pan,[a,*] Jiancong Liu,[b] Yi Li,[b] Fuxiang Wang,[a]
Jiyang Li,[b,*] Yan Xu,[b] Li Li[b]

[a] *Ministry of Education Key Laboratory of Advanced Materials of Tropical Island Resources, Department of Materials and Chemical Engineering, Hainan University, Haikou 570228, PR China*

[b] *State Key of laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China*

CrystEngComm Accepted Manuscript

---

*Corresponding author. E-mail: panqinhe@163.com. Fax: +86-898-66193342.

To ***CrystEngComm*** as an article

Abstract

A series of germanates $[Ni(DETA)_2]_2 \cdot Cl \cdot [Ge_7O_{13}(OH)_2F_3)]$ (DETA = diethylenetriamine, **JLG-3**), $[Ni(1,2\text{-}PDA)_3] \cdot [Ge_7O_{14}F_2(OC_2NH_7)] \cdot 0.5H_2O$ (1,2-PDA = 1,2-propanediamine, **JLG-6**), $[Ni_2(TETA)_3]_{0.5} \cdot [Ge_7O_{14}F_2(OC_2NH_7)] \cdot H_2O$ (TETA = triethylenetetramine, **JLG-7**), and $|(NH_3CH_2CH_2OH)_2|[Ni_2(TEPA)_2(en)][Ge_7O_{14}F_3]_2 \bullet H_2O$ (en = ethylenediamine, TEPA = tetraethylenepentamine, **JLG-8**) have been synthesized. All these compounds are co-templated by metal complexes and organic/inorganic species in solvothermal system. Their structures are built up from Ge_7X_{19} (Ge_7, X = -O, -OH, -F or - OC_2NH_7) clusters connected in two different manners: T^2 linkage mode to form 1-D chain-like structure **JLG-3**, and T^4 linkage mode to form 2-D layered structures **JLG-*n*** (*n* = 6, 7, 8). It is interesting that all the layers of **JLG-*n*** (*n* = 6, 7, 8) are comprised of a pair of chains, which can be found separately in the structure of **JLG-3**. Considering such chains or layers as SBUs, we can design numerous hypothetical 2-D layered and 3-D open-framework germanates, based on the concept of "Scale Chemistry".

CrystEngComm Accepted Manuscript

Introduction

Open-framework materials represented by zeolites or molecular sieves have shown widespread applications in catalysis, ion exchange, and separation.[1] Recently, there has been considerable interest in the design and synthesis of open-framework oxide materials based on specific structure building units (SBUs). Germanates have attracted great attentions since the first discovery of organically templated germanates by Xu *et al*. in 1991.[2] Compared to tetrahedrally coordinated silicon, germanium atom represents rich coordination modes, such as four (tetrahedron), five (trigonal bipyramid or square pyramid), and six (octahedron) coordinations, and favors to form large and complicated clusters. Typical clusters in the germanates are found as Ge_7X_{19} (Ge_7),[3] Ge_9X_{26-m} (Ge_9),[4] and $Ge_{10}X_{27}$ (Ge_{10}) clusters[5] (X = O, OH, F; m = 0-1). These clusters can be further linked with each other to build various open-framework structures with large pores and low-framework densities, as predicted by G. Férey on the basis of the concept of “Scale Chemistry”.[6] Notable examples are ASU-12 (16-rings),[3a] ASU-16 (24-rings)[3b] and SU-12 (24-rings)[3c] constructed from Ge_7 clusters; ASU-14 (10-rings),[4a] $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ (16-rings)[4b] and FDU-4 (24-rings)[4c] built from Ge_9 clusters; and SU-M (30-rings)[5a] and SU-61 (26-rings)[5b] built from Ge_{10} clusters. Moreover, Ge_7 clusters can also connect with other larger clusters such as Ge_9 and Ge_{10} clusters to construct extra-large germanates. Such examples include SU-8 (16-rings) and SU-44 (18-rings)[7] built from Ge_7 and Ge_9 clusters, and chiral germanate SU-MB (30-rings)[5a] built from Ge_7 and Ge_{10} clusters. Recently, we synthesized a novel germanate JLG-12[8] built from Ge_7 and Ge_9 clusters with pores extending to the mesoporous range (21.4Å), and a silicogermanate SU-JU-14[9] built from $[(Ge,Si)_7]$ clusters and silica double chains $[(Ge,Si)_4O_8]$ with extended 24-ring channels. This suggests that many more open-framework germanate structures can be built from Ge_n (n = 7, 9, 10) clusters.

Open-framework oxide materials are usually synthesized by using various organic amines as the templates or structure-directing agents (SDAs) under the hydrothermal or solvothermal conditions. It is of vital importance to choose suitable

CrystEngComm Accepted Manuscript

templates to direct the formation of desired framework structures. In contrast to alkali-metal cations or organic amines, metal complexes have shown some advantages in the synthesis of novel open-framework compounds, due to various charges, rigid spatial configurations and abundant hydrogen-bonds with the host framework. Our previous works have shown that a chiral metal complex can transfer its chirality to the inorganic framework through the H-bonding of the host framework and guest molecules.[10] The compounds synthesized by using metal complexes as SDAs are usually found in metalphosphates,[11,12] however, the successful examples in the open-framework germanates are limited. Only few reported compounds are known as $Ge_7O_{14}F_3 \cdot 0.5[In(DETA)_2] \cdot 0.5H_3DETA \cdot 2H_2O$,[13] ICMM-2,[14] FJ-1,[15] FJ-6,[16] and JLG-4[3d]. Recently, two gallogermanate zeolites induced by chiral metal complexes, $[Ni(en)_3][Ga_2Ge_4O_{12}]$[17] with 10-ring channels and $|(Ni(C_3H_{10}N_2)_3)_{36}Ni_{4.7}|[Ga_{81.4}Ge_{206.6}O_{576}]$[18] with 11-ring channels have been reported.

Furthermore, the co-templating synthesis has also been proven to be an effective route to prepare open-framework compounds. In this way, zeolites SSZ-25 (MWW),[19] SSZ-32X (MTT),[20] SSZ-47B,[21] ferrierite (FER),[22] aluminophosphate AFI[23] and JIS-1[24], silicoaluminophosphates SAV and KFI,[25] and germanate ICMM-5[26] have been successfully discovered. Recently, our efforts on the co-templating synthesis have yielded three germanates: 2-D layered JLG-2[27] cotemplated by diprotonated piperazine cation and ammonium ion, 1-D tubular JLG-4[3d] cotemplated by $[Ni(1,2\text{-}PDA)_3]^{2+}$ cation and 3-amino-1-propanol, and 1-D tubular JLG-5[3e] cotemplated by $(H_2O)_{16}$ cluster and 1-methylpiperazine.

Herein, we present a family of germanates based on Ge_7 clustersco-templated by metal complexes and organic/inorganic species. These compounds are $[Ni(DETA)_2]_2 \cdot Cl \cdot [Ge_7O_{13}(OH)_2F_3)]$ (DETA = diethylenetriamine, **JLG-3**), $[Ni(1,2\text{-}PDA)_3] \cdot [Ge_7O_{14}F_2(OC_2NH_7)] \cdot 0.5H_2O$ (1,2-PDA = 1,2-propanediamine, **JLG-6**), $[Ni_2(TETA)_3]_{0.5} \cdot [Ge_7O_{14}F_2(OC_2NH_7)] \cdot H_2O$ (TETA = triethylenetetramine, **JLG-7**), $|(NH_3CH_2CH_2OH)_2|[Ni_2(TEPA)_2(en)][Ge_7O_{14}F_3]_2 \cdot H_2O$ (en = ethylenediamine, TEPA = tetraethylenepentamine, **JLG-8**). In this paper, we will describe the syntheses, structures, and structural correlations of these germanate compounds.

Experimental section

CrystEngComm Accepted Manuscript

Synthesis: All the materials GeO_2, $NiCl_2\cdot 6H_2O$, ethanolamine, diethylenetriamine (DETA), 1,2-propanediamine (1,2-PDA), triethylenetetramine (TETA), tetraethylene-pentamine (TEPA), HF and other reagents were purchased and used without from commercial sources without any purification.

Compounds **JLG-*n*** (n = 3, 6, 7, 8) have been synthesized in the system of GeO_2–$NiCl_2\cdot 6H_2O$–organic amine–ethanolamine–H_2O–HF at 180°C for 4 days. The detailed molar ratios of compositions are listed in Table 1. The synthesis method is similar, and **JLG-6** is taken as an example to describe their synthesis. Typically, GeO_2 (0.156g) and $NiCl_2\cdot 6H_2O$ (0.15g) were dissolved in the mixture solution of ethanolamine (5.0mL) and water (1.0mL) at Teflon beaker, and then 1, 2-PDA (2.0 mL) was added to the mixture drop wise. Finally, HF acid (40 wt%, 0.12mL) was added. The reaction mixture was stirred continuously at room temperature until it was homogeneous, subsequently transferred to 15 mL Teflon-lined stainless-steel autoclave and heated at 180°C for 4 days under autogenous pressure. After the reaction time, the autoclave was cooled to room temperature, and then the product was filtered, washed with water for several times, and dried at 80°C. All the products are pure phases, except **JLG-7** mixed with an unknown phase. Hence, only single crystal X-ray diffraction analysis had been done for **JLG-7** due to the impurity.

Please insert Table 1 here

Characterization: X-ray powder diffraction (XRD) data was collected on a Siemens D5005 diffractometer with CuKα radiation (λ = 1.5418 Å). For **JLG-*n*** (n = 3, 6, 8), the experimental XRD patterns agree well with the simulated ones generated on the basis of single-crystal structural analysis (Fig.S1-S3, Supporting Information).

Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. The elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyser. The content of fluorine ions was measured on a fluoride ion selective electrode. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of 10 °C/min (Fig. S4, Supporting Information).

CrystEngComm Accepted Manuscript

JLG-3: ICP analysis calcd (wt%): Ge 37.03, Ni 8.55; found: Ge 37.48, Ni 8.90. Elemental analysis calcd (wt%): C 14.00, N 12.24, H 3.97; found: C 13.55, N 12.47, H 3.53. Fluorine content calcd (wt%): 4.16, found: 4.02.

JLG-6: ICP analysis calcd (wt%): Ge 45.32, Ni 5.24; found: Ge 45.70, Ni 4.79. Elemental analysis calcd (wt%): C 11.78, N 8.75, H 3.42; found: C 11.34, N 8.60, H 3.75. Fluorine content calcd (wt%): 3.36, found: 3.30.

JLG-8: ICP analysis calcd (wt%): Ge44.64, Ni 5.16; found: Ge 45.30, Ni 4.60. Elemental analysis calcd (wt%): C 11.61, N 8.862, H 3.19; found: C 11.45, N 8.86, H 3.25. Fluorine content calcd (wt%): 5.01, found: 5.16.

X-ray Crystallography: Suitable single crystals with **JLG-*n*** (*n* = 3, 6, 7, 8) were selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073Å). The structures were solved by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL97. The Ge and Ni atoms were determined directly, and F, O, C and N atoms were found in the difference Fourier map. In **JLG-3**, H atoms attached to the metal complexes and O7 atom were placed geometrically and refined using a riding model. In **JLG-6**, H atoms attached to the organic species and the metal complexes were placed geometrically and refined using a riding model, and H atoms attached to the water were not added. In **JLG-7**, residual electron density peaks were found with a largest Fourier peak of 5.539 e/Å (0.9182 0.3234 0.4123), which is near to Ni atom (0.86996 0.306987 0.460646) with the distance of 1.219 Å. H atoms attached to the organic species and the metal complexes were placed geometrically and refined using a riding model, and H atoms attached to the water were not added. In **JLG-8**, it gave an formula of $\{[Ni_2(TEPA)_2(en)][Ge_7O_{14}F_3]_2{\bullet}H_2O\}_n^{2n-}$. However, the remaining charge balancing organic species cations were disordered and assigned as eight protonated ethanolamine cations per unit cell, which were determined by TGA and elemental analysis, which could not be located properly in the void region. The contributions of these disordered protonated ethanolamine cations to the scattering values have been

CrystEngComm Accepted Manuscript

removed by using the PLATON SQUEEZE program. H atoms attached to the metal complexes were placed geometrically and refined using a riding model, and H atoms attached to the water were not added. All non-hydrogen atoms of all structures were refined anisotropically. Experimental details for the structure determination were presented in Table 2.

Please insert Table 2 here

Results and Discussion

Germanates **JLG-*n*** (*n* = 3, 6, 7, 8) have been synthesized in the system of GeO_2–$NiCl_2·6H_2O$–organic amine–ethanolamine–H_2O–HF. Many synthetic factors influenced the formations of **JLG-*n*** (*n* = 3, 6, 7, 8). First, the organic amines used were crucial for the resulting products. **JLG-*n*** (*n* = 3, 6, 7, 8) were all prepared in the presence of ethanolamine and H_2O as the mixed solvents, but using different organic amines including DETA, 1,2-PDA, TETA, and TEPA, respectively. In the synthesis process, these organic amines and the Ni-complexes are formed in-situ acting as structure-directing agents to direct the formation of **JLG-*n***. If 3-amino-1-propanol was used as the solvent in the presence of 1,2-PDA as template, JLG-4[3b] would be obtained. Second, the nickel source played an important role in the synthesis of **JLG-3**. If using $Ni(NO_3)_2·6H_2O$ or $Ni(CH_3COO)_2·4H_2O$ as the Ni source, a chain-like germanate $|[Ni(DETA)_2]_3(H_2O)_3|[Ge_7O_{13}F_5]_2$[28] was obtained. However, little effect of the Ni source on the formation of other germanates **JLG-*n*** (*n*= 6, 7, 8) has been found. Finally, the use of HF was essential for the formation of these germanates. Only amorphous phases were obtained in the absence of HF.

Structures: The structures of germanates **JLG-*n*** (*n* = 3, 6, 7, 8) are all built up from the Ge_7X_{19} cluster (Ge_7, X = -O, -OH, -F or - OC_2NH_7) (Fig.1),. The idealized Ge7 cluster has 2*mm* symmetry, which consists of seven Ge atoms with mixed coordinations: one GeX_6 octahedron, two GeX_5 trigonal bipyramids and four GeX_4 tetrahedra. In the center of Ge_7 cluster, there is a tri-coordinated oxygen atom, which links one GeX_6 octahedron and two GeX_5 trigonal bipyramids. The other Ge atoms are tetrahedrally coordinated to four bridging oxygen atoms. The different connection of Ge_7 clusters through O atoms results in various open-framework structures of

CrystEngComm Accepted Manuscript

JLG-*n* (*n* = 3, 6, 7, 8). Their detailed structures will be discussed in the following text.

Please insert Figure 1 here

Structure of JLG-3: The asymmetric unit contains one half $[Ge_7O_{13}(OH)_2F_3]^{3-}$ moiety, two half $[Ni(DETA)_2]^{2+}$ moieties, and one crystallographically distinct Clsite. The Ni(1) lie on a twofold axis and Ni(2) locate on an inversion centre, and that O(1)-Ge(1)-F(1) atoms of the $[Ge_7O_{13}(OH)_2F_3]^{3-}$ moiety also lie on a twofold axis. The $[Ge_7O_{13}(OH)_2F_3]^{3-}$ anion with the symmetry of *C*2, and consists of seven germanium atoms: one octahedral $Ge(1)O_5F$ [Ge-O :1.875(4)-1.999(6)Å; Ge(1)-F(1) : 1.807(5)Å], two trigonal bipyramidal $Ge(2)O_4F$ [Ge-O : 1.772(4)-1.984(4) Å; Ge(2)-F(2) : 1.817(4) Å], and four tetrahedra $Ge(4)O_4$ and $Ge(3)O_4$ [Ge-O : 1.719(4)-1.754(5) Å]. The Ge_7 cluster has two terminal hydroxy groups and three terminal fluorine atoms (Fig. S5a), which prevent the Ge_7 clusters further connections to 3-D framework. Therefore, Ge_7 cluster can only be connected by μ_2-O atoms to form a chain-like structure with the symmetry of *C*2 (Fig. 2). It is noted that the structure of **JLG-3** is composed of a pair of enantiomorphic chains (named R- and L-chains), due to the connection of Ge_7 clusters in different orientations.

Please insert Figure 2 here

In **JLG-3**, there is two half independent $[Ni(DETA)_2]^{2+}$ cations in one asymmetric unit. Each Ni atoms are coordinated by six N atoms of two DETA ligands to form a distorted octahedral environment (Fig. 3a). It is known that $Ni(DETA)_2^{2+}$ possesses *s-fac*, *u-fac*, *mer*-configurations, while the latter two are chiral. Intersetingly, there are two isomers found in **JLG-3**: *s-fac*-$Ni(DETA)_2^{2+}$ and *mer*-$Ni(DETA)_2^{2+}$, which are seperated alternatively in the voids of adjacent chains. The **JLG-3** has the same structure with that of FJ-6, but they have been synthesized under different conditions. [16] The metal complexes $[Ni(DETA)_2]^{2+}$ of **JLG-3** are formed in-situ with ethanolamine as the solvent, while the metal complexes $Ni(DETA)_2Cl_2$ of FJ-6 are directly used as the templates with ethylene glycol as the solvent.

CrystEngComm Accepted Manuscript

Apart from $Ni(DETA)_2^{2+}$ cations, the Cl^- ions resided between the chains, also play an important role in the formation of **JLG-3** because it cannot be obtained without Cl^- anion. When $Ni(NO_3)_2 \cdot 6H_2O$ or $Ni(CH_3COO)_2 \cdot 4H_2O$ is used as the Ni source without Cl^- ions involved, germanate $|[Ni(DETA)_2]_3(H_2O)_3|[Ge_7O_{13}F_5]_2$ (denoted as **JU-85**)[28] is obtained. The structures of **JLG-3** and **JU-85** are analogous, but having different $Ge_7/[Ni(DETA)_2]^{2+}$ ratio. Moreover, the interactions among the Ge_7 chains and $[Ni(DETA)_2]^{2+}$ cations are different in **JLG-3** and **JU-85**, as shown in Fig. S6, causing different assembly of such chains. It is believed that the complicated cooperative effect of metal complex cations and inorganic ions is the reason causing the formation of **JLG-3**.

Please insert Figure 3 here

Structure of JLG-6: The structure of **JLG-6** consists of a new macro-anionic sheet $[Ge_7O_{14}F_2(OC_2NH_7)]_n^{2n-}$, and the charge neutrality is achieved by $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations. The inorganic sheet is constructed by $[Ge_7O_{14}F_2(OC_2NH_7)]^{2-}$ anions with an ethylammonium group connected to conventional Ge_7 cluster to form a derivate of Ge_7 cluster, shown in Fig. 1b. The Ge_7 cluster anion contains seven crystallographically distinct Ge atoms (Fig. S5b): one $Ge(1)O_5F$ octahedron, two trigonalbipyramids $Ge(2)O_4F$ and $Ge(3)O_5$, and four GeO_4 tetrahedra. The Ge-O bond lengths are in the range of 1.715(6) to 2.041(5) Å, and the bond lengths of Ge(1)-F and Ge(2)-F are 1.819(5) Å and 1.808(5) Å, respectively. Germanates with organic amines covalently-bonded to germanium atoms are rarely reported. Such examples are only known as SU-21[30] and ICMM-9[31], where the Ge atoms are connected to the nitrogen atoms of 1,2-diaminopropane and 1,6-diaminocyclehexane, respectively. However, to our best knowledge, this Ge_7 derivate is first observed in germanate compounds.

Except two terminal fluorine atoms and one terminal ethylammonium group, the remaining oxygen atoms of the GeO_4 tetrahedra link to four neighbouring Ge_7 clusters, thus forming the inorganic sheet $[Ge_7O_{14}F_2(OC_2NH_7)]_n^{n-}$ with 10-rings window, and the hanging ethylammonium groups pointing into the 10-rings windows (Fig.4a). In

CrystEngComm Accepted Manuscript

addition, the layers of **JLG-6** are built from the chains of **JLG-3** with the same chirality. Adjacent chains are related by a rotation of 180º with the axes parallel *a* direction through O(6) atoms, and then connected each other alternatively through the oxygen atoms to form the layer of **JLG-6** parallel to the *ab* plane, with the symmetry of *C*2.

Fig. 4b shows the stacking of inorganic layers along the *a* axis in an ABAB sequences, resulting in the framework structure of **JLG-6**. The $[Ni(1,2\text{-}PDA)_2]^{2+}$cations (Fig.3b) are located between two adjacent layers, and interact with the inorganic layers through H-bonds to form the supramolecular structure. The nickel complexes, together with the coordinated ethanolamine molecules, act as SDAs to direct the formation of **JLG-6**.

Structure of JLG-7: The structure of **JLG-7** contains a macro-anionic sheet $[Ge_7O_{14}F_2(OC_2NH_7)]_n^{n-}$, metal complex $[Ni_2(TETA)_3]^{4+}$ cation, and H_2O molecule. The macro-anionic sheet is same with that of **JLG-6**, so it isn't discussed in detail. The Ge-O bond lengths are in the range of 1.712(7) to 2.088(7) Å, and the bond lengths of Ge(1)-F and Ge(2)-F are 1.804(6) Å and 1.800(8) Å, respectively, which are all in reasonable scopes.

Fig. 4c shows the packing of the inorganic sheets along *a* axis. The metal cations $[Ni_2(TETA)_3]^{4+}$ reside between the layers and balance the negative charge of the sheets. Notably, the metal complex is dual-core and possesses a peculiar dumbbell-like configuration (Fig.3c). It contains three TETA molecules with two different coordination modes. One binds to one Ni atom though four N atoms; the other connects two Ni atoms together. The metal complexes interact with the inorganic layers through H-bonds to form a supramolecular structure.

Please insert Figure 4 here

Structure of JLG-8: Single-crystal X-ray diffraction analysis showed that the stoichiometry of an formula $\{[Ni_2(TEPA)_2(en)][Ge_7O_{14}F_3]_2\cdot H_2O\}_n^{2n-}$. However, the remaining charge balancing organic species cations were disordered and assigned as

CrystEngComm Accepted Manuscript

eight protonated ethanolamine cations per unit cell, which were determined by TGA and elemental analysis, which could not be located properly in the void region.

The inorganic sheet is constructed by $[Ge_7O_{14}F_3]^{2-}$ clusters composed by one Ge(1)O_5F octahedron, two trigonal bipyramids Ge(2)O_4F and Ge(3)O_4F, and four GeO_4tetrahedra. The range of Ge-O bond lengths is 1.725(2) to 2.091(2) Å, and the bond lengths of Ge(1)-F(1), Ge(2)-F(2), and Ge(3)-F(3) are 1.796(2) Å, 1.791(2) Å, and 1.804(2)Å, respectively (Fig. S5c). The connection of Ge_7 clusters through oxygen atoms results in a novel 2-D layered structure with 10-ring window parallel to the *ab* plane, as shown in Fig.5a. In other words, the layer of **JLG-8** can be considered as being constructed from both enantiomorphic chains found in **JLG-3**. The neighbouring a pair of enantiomorphic chains mirrored the plane through O11 atoms to form a double chain, and then adjacent double chains are related by a rotation of 180º with the axes parallel *a* direction through O(15) atoms. Such a connection gives rise to a novel 2-D layered structure different from those observed in **JLG-6** and **JLG-7**.

Please insert Figure 5 here

Fig. 5b shows the packing of the inorganic layers along the [100] direction. The $[Ni_2(TEPA)_2(en)]^{4+}$ cations lie in the void spaces of the framework. The metal complex contains two Ni atoms, two TEPA molecules and one en molecule, with a twofold axis along the centre of the en C-C bond, which possesses a special dumbbell-like configuration (Fig. 3d). The TEPA molecules located between the adjacent layers bind to Ni atoms through five N atoms. The en molecules, which are the decomposition product of TEPA, connect the two Ni atoms in an end-to-end manner (Ni-N-C-C-N-Ni) and pass through the 10-ring window. Disorder protonated ethanolamine cations are dispersed in the void region to balance the negative charge of the inorganic sheets together with metal complex. Protonated ethanolamine cations and metal complexes $[Ni_2(TEPA)_2(en)]^{4+}$ act as co-templates in the crystallization of **JLG-8**.

CrystEngComm Accepted Manuscript

Discussion: Several structural features are commonly observed in the structures of **JLG-*n*** (*n* = 3, 6, 7, 8). First, in all compounds, metal complexes are found along with organic/inorganic cations in all structures as co-template. Second, all the structures are constructed from Ge_7 clusters. It appears that the synthetic system involving ethanolamine and metal complexes may be favourable for the formations of Ge_7 clusters, although the crystallization mechanism is unclear. Third, these germanate compounds all possess low-dimensional framework, *i.e.* 1-D chain and 2-D layer structures, likely owing to the abundant terminal hydroxyl groups and fluorine atoms of the host framework. Fourth, these compounds are structurally related with each other. Such correlation will be discussed in the following text. Furthermore, new 3-D open-framework germanates have been designed based on the 2-D layers of **JLG-6** and **JLG-8**.

The connection of Ge_7 clusters in JLG-*n* (*n* = 3, 6, 7, 8): According to our previous work,[3d] Ge_7 cluster may exhibit many different ways of linkage with adjacent clusters to form various open frameworks. Seven known types of linkage modes of Ge_7 cluster are proposed and denoted as T^2, T^2P^2, T^4, T^4P, T^4O, T^4P^2, T^4PO, and T^4P^2O (T = tetrahedron, P = trigonal bipyramid, O = octahedron; the superscript means the coordination number of polyhedra and 1 is omitted). The various ways of connection of Ge_7 clusters in germanates may give rise to different structures. The linkage of Ge_7 clusters in **JLG-3** is T^2 mode which results in 1-D chain-like germanate. While the Ge_7 clusters in other three compounds adopt T^4 linkage modes which result in 2-D layered germanates **JLG-*n*** (*n* = 6, 7, 8). The reported examples of 2-D layered germanates constructed by Ge_7 clusters in T^4 linkage mode are also found as ASU-20,[32] SU-22, SU-23,[33] and $Ge_7O_{14}F_3\cdot0.5[In(DETA)_2]\cdot0.5H_3DETA\cdot2H_2O$.[13]

The structural relationship among JLG-*n* (*n* = 3, 6, 7, 8): Previously mentioned, there is a pair of chains in **JLG-3**. It is interesting that such chains can also be found in the structures of other compounds **JLG-*n*** (*n* = 6, 7, 8). In other to better illustrate the structural relationship among them, we assume such R- and L-chains as Δ and Λ, respectively. And named as ∇ and V configuration to the chains

CrystEngComm Accepted Manuscript

rotated 180° of Δ and Λ configuration around the axes along the chains direction., . By using these configurations of chains as SBUs and considering four chains as a cycle, we can design numerous possible 2-D sheets, such as ΔΔΛΛ, ΔΔVV, ΔΔ∇∇, ΔΛΔΛ, ΔVΔV, ΔΛ∇V, ΔV∇Λ.

Fig. 6 shows four designed layered structures, named H-1, H-2, H-3, and H-4. H-1 with Δ∇Δ∇ arrangement corresponds to the structure of **JLG-6** and **JLG-7**. H-2 with ΔΛV∇ arrangement and H-3 with ΔΔΔΔ arrangement are consistent with **JLG-8** and $Ge_7O_{14}F_3 \cdot 0.5[In(DETA)_2] \cdot 0.5H_3DETA \cdot 2H_2O$,[13] respectively. H-4 is a hypothetical structure, which has not been synthesized so far.

Please insert Figure 6 here

Furthermore, it is noted that the 3-D framework structure of ASU-12 also consists of such chains.[3a] Compared to **JLG-*n***, the connection mode of Ge_7 clusters in ASU-12 is T^4P, and the fifth connection node (P) is a penta-coordinational germanium atom, which connects 2-D sheet into a 3-D open framework. Based on this idea, if the fifth connection could hypothetically be introduced into the structure of **JLG-*n***, they would extend into 3-D framework structures. Fig. 7 shows two hypothetical structures generated by changing the connection mode of the Ge_7 clusters in **JLG-6** and **JLG-8** to T^4P. By using energy optimization of Material Studio software,[34] the hypothetical framework **H-F1** crystallized in space group $P2_1/c$ with a = 8.829 Å, b = 16.632 Å, c = 19.470 Å, β = 109.99° has 16-ring channels running along the [100] direction, and 10-ring channels along the [010] direction (Fig.7a). The 16-ring channel has free diameter of 4.3 × 5.5 Å^2. The hypothetical framework **H-F2** is found in space group *Pmna* with a = 31.246 Å, b = 8.814 Å, c = 23.446 Å. It has 24- and 8-ring channels running along the [100] direction, and 10-ring channels along the [010] and [001] directions (Fig.7b). The 24-ring channel has free diameter of 7.3 × 14.2 Å^2. Based on the powerful concept of "Scale Chemistry",[6] various 3-D novel germanate frameworks could be designed resulting from different arrangement of the Ge_7 clusters. These hypothetical structures would be synthesized under suitable conditions.

CrystEngComm Accepted Manuscript

Please insert Figure 6 here

Conclusion

Four novel germanates **JLG-*n*** (*n* = 3, 6, 7, 8) have been prepared using metal complexes and organic amines cations/inorganic anions as co-templates under solvothermal conditions. Four different metal complexes are self-assembled by $NiCl_2 \cdot 6H_2O$ and organic amines in the solvothermal system. Although germanates synthesized by metal complexes as SDAs is limit, it provides a new synthetic strategy to obtain novel open-framework germanates. These compounds are all built up from Ge_7 clusters and classified into two structural types according to the dimensionality: **JLG-3** is 1-D chain-like structure with T^2 connection manner of Ge_7 cluster, which consists of one pair of chains; **JLG-*n*** (n = 6, 7, 8) are 2-D layered structures with T^4 connection manner of Ge_7 clusters. Additionally, the structure of **JLG-7** is similar to that of **JLG-6**, but using different metal complexes as SDA. The structures of **JLG-6** and **JLG-8** shows several features: 1) The configurations of metal complexes are different; 2) Though Ge_7 clusters possess same configurations, the rotation and arrangement of Ge_7 clusters are different, which is possibly relative to the different configurations of metal complexes; 3) The packing way of layer is different; 4) The structures of **JLG-6** and **JLG-8** can be viewed as being constructed by chain-1 and chain-2, respectively, which are found in **JLG-3**. Using chain-1 and chain-2 as SBUs, we can design numerous 2-D layered structures by different arrangements of these chains. In addition, we also design two 3-D frameworks of **H-F1** (16-rings), **H-F2** (24-rings) on the basis of sheets of **JLG-6** and **JLG-8**, respectively, with the connection of Ge_7 clusters as T^4P mode. The Ge_7 clusters display various connection ways, it is destined to be effective to construct novel open-framework germanates. A series of 2-D, even 3-D structures of germanates can be designed using Ge_7 clusters as SBUs, based on the concept of “Scale Chemistry”. Further developing of synthetic strategies to obtain the hypothetical compounds is of great interest, and researches in this area are underway.

CrystEngComm Accepted Manuscript

Acknowledgements

This project is supported by the National Natural Science Foundation of China (No. 21271081, 21101047, 11204057), the State Basic Research Project of China (No. 2011CB808703), the Program for New Century Excellent Talents in University (NCET-11-0929, NCET-11-0197), the Natural Science Foundation of Hainan Province (211010).

Electronic supplementary information (ESI) available: Simulated and experimental XPRD (Fig. S1 to S3) and TGA (Fig S4) of JLG-3, 6 and 8. The cif files of hypothetical frameworks (H-F1 and 2). CCDC reference numbers 992864-992867 for JLG-3, 6, 7 and 8, respectively.

References

1 (a) Z. P. Wang, J. H. Yu and R. R. Xu, *Chem. Sov. Rev.*, 2012, **41**, 1729–1741; (b) J. H. Yu and R. R. Xu, *Chem. Sov. Rev.*, 2006, **35**, 593–604; c) M. E. Davis, *Nature,* 2002, **417**, 813-821; d) J. Sun, C. Bonneau, Á. Cantín, A. Corma, M. J. Díaz-Cabaňas, M. Moliner, D. Zhang, M. Li, X. Zou, *Nature,* 2009, 458, 1154 – 1157.

2 (a) J. Cheng, R. Xu and G. Yang, *J. Chem. Soc. Dalton Trans.*, 1991, 1537–1540; (b) J. Cheng and R. Xu, *J. Chem. Soc. Chem. Common.*, 1991, 483–485.

3 (a) H. Li, M. Eddaoudi, D. A. Richardson and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8567–8568; (b) J. Plévert, T. M. Gentz, A. Laine, H. Li, V. G. Young, O. M. Yaghi and M. O'Keeffe, *J. Am. Chem. Soc.*, 2001, **123**, 12706–12707; (c) L. Tang, M. S. Dadachov and X. Zou, *Chem. Mater.*, 2005, **17**, 2530–2536; (d) Q. Pan, J. Li, X. Ren, Z. Wang, G. Li, J. Yu and R. Xu, *Chem. Mater.*,2008, **20**,

CrystEngComm Accepted Manuscript

370–372; (e) Q. Pan, J. Li, K. E. Christensen, C. Bonneau, X. Ren, L. Shi, J. Sun, X. Zou, G. Li, J. Yu and R. Xu, *Angew. Chem. Int. Ed.*, 2008, **47**, 7868–7871.

4 (a) H. Li, M. Eddaoudi and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 1999, **38**, 653–655; (b) M. P. Attfield, Y. Al-Ebini, R. G. Pritchard, E. M. Andrews, R. J. Charlesworth, W. Huang, B. J. Masheder and D. S. Royal, *Chem. Mater.*, 2007, **19**, 316–322; (c) Y. Zhou, H. Zhu, Z. Chen, M. Chen, Y. Xu, H. Zhang and D. Zhao, *Angew. Chem. Int. Ed.*, 2001, **40**, 2166–2168.

5 (a) X. Zou, T. Conradsson, M. Klingstedt, M. Dadachov and M. O'Keeffe, *Nature*, 2005, **437**, 716–719; (b) K. E. Christensen, C. Bonneau, M. Gustafsson, L. Shi, J. Sun, J. Grins, K. Jansson, I. Sbille, B. Su and X. Zou, *J. Am. Chem. Soc.*, 2008, **130**, 3758–3759.

6 (a) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3–20; (b) G. Férey, *J. Solid State Chem.*, 2000, **152**, 37–48; (c) G. Férey, C. Mellot-Draznieks and T. Loiseu, *Solid State Sci.*, 2003, **5**,79–94.

7 K. E. Christensen, L. Shi, T. Conradsson, T. Ren, M. S. Dadachov and X. Zou, *J. Am. Chem. Soc.*, 2006, **128**, 14238–14239.

8 X. Ren, Y. Li, Q. Pan, J. Yu, R. Xu and Y. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 14128–14129.

9 L. Tang, X. Ren, A. K.Inge, T. Willhammar, D. Grüner, J. Yu and X. Zou, *Cryst. Growth Des.*, 2012, **12**, 3714–3719.

10 (a) J. Yu, Y. Wang, Z. Shi and R. Xu, *Chem. Mater.*, 2001, **13**, 2972–2978; (b) Y. Wang, J. Yu, M. Guo and R. Xu, *Angew. Chem. Int. Ed.*, 2003, **34**, 4089–4092; (c) Y. Wang, J. Yu, Y. Li, Z. Shi and R. Xu, *Chem. Eur. J.*, 2003, **9**, 5048–5055.

11 (a) K. Morgan, G. Gainsford and N. Milestone, *J. Chem. Soc. Chem. Commun.*, 1995, 425–426; (b) D. A. Bruce and A. P. Wilkinson, *J. Chem. Soc. Chem. Commun.*, 1995, 2059–2060; (c) M. J. Grey, J. D. Jasper and A. P. Wilkinson, *Chem. Mater.*, 1997, **9**, 976–980; (d) K. R. Morgan, G. J. Gainsford and N. B. Milestone, *Chem. Commun.*, 1997, 61–62; (e) S. M. Stalder and A. P. Wilkinson, *Chem. Mater.*, 1997, **9**, 2168–2173; (f) J. D. Jasper and A. P. Wilkinson, *Chem. Mater.*, 1998, **10**, 1664–1667; (g) D. J. Williams, J. S. Kruger, A. F. McLeroy, A. P. Wilkinson and J. C. Hanson, *Chem. Mater.*, 1999, **11**, 2241–2249; (h) Y. Wang, P. Chen, J. Li, J. Yu, J. Xu, Q. Pan and R. Xu, *Inorg. Chem.*, 2006, **45**,

CrystEngComm Accepted Manuscript

4764–4768; (i) J. Liang, J. Li, J. Yu, P. Chen, L. Li and R. Xu, *J. Solid State Chem.*, 2006, **179**, 1977 – 1983; (j) G.-Y. Yang and S. C. Sevov,*Inorg. Chem.*, 2001, **40**, 2214–2215.

12 (a) Q. H. Pan, Q. Chen, W. Song, T. Hu and X.-H. Bu, *CrystEngComm.*, 2010, **12**, 4198–4204; (b) Q. H. Pan, J. Y. Li, Q. Chen, Y. D. Han, Z. Chang, W.-C. Song and X.-H. Bu, *MicroporousMesoporous Mater.*, 2010, **132**, 453–457; (c) Q. H. Pan, R. J. Tian, S.-J. Liu, Q. H. Wu, Y. Y. Zhu, Q. Chen, X. Y. Ren and T.-L. Hu, *Chin. Chem. L.*, 2013, **24**, 861–865; (d) Q. H. Pan, Q. Chen, Y.-D. Han, T.-L. Hu, X.-H. Bu, *Chem. J. Chin. Univ.*, 2011, **32**, 527-531.

13 G. Liu, H. Zhang, Z. Lin, S. Zheng, J. Zhang, J. Zhao,G. Wang and G. Yang, *Chem. Asian J.*, 2007, **2**, 1230–1239.

14 C. Cascales, E. Gutierrez-Puebla, M. Iglesias, M. A. Monge and C. Ruiz-Valero, *Angew. Chem. Int. Ed.*, 1999, **38**, 2436–2439.

15 Z. Lin, J. Zhang, J. Zhao, S. Zheng, C. Pan, G. Wang and G. Yang, *Angew. Chem. Int. Ed.*, 2005, **44**, 6881–6884.

16 H. Zhang, J. Zhang, S. Zheng and G. Yang, *Inorg. Chem.*, 2003, **42**, 6595–6597.

17 Y. Han, Y. Li, J. Yu and R. Xu, *Angew. Chem. Int. Ed.*, 2011, **50**, 3003–3005.

18 Y. Xu, Y. Li, Y. Han, X. Song and J. Yu, *Angew. Chem. Int. Ed.*, 2013, **52**, 5501–5503.

19 S. I. Zones, S. J. Hwang and M. E. Davis, *Chem. Eur. J.*, 2001, **7**, 1990–2001.

20 S. I. Zones, G. Zhang, K. R. Krishna, J. A. Biscardi, P. Marcantonio and E. Vittoratos, US Patent Appl. No. 2005/092651A1, **2005**.

21 A. W. Burton and S. I. Zones, US Patent No. 7,063,828, **2006**.

22 A. B. Pinar, L. Gómez-Hortigüela and J. Perez-Pariente, *Chem. Mater.*, 2007, **19**, 5617–5626.

23 L. Gómez-Hortigüela, C. Márquez-Álvarez, F. Corà, F. López-Arbeloa and J. Pérez-Pariente, *Chem. Mater.*, 2008, **20**, 987–995.

24 H. Xing, J. Li, W. Yan, P. Chen, Z. Jin, J. Yu, S. Dai and R. Xu, *Chem. Mater.*, 2008, **20**, 4179–4181.

25 M. Castro, R. Garcia, S. J. Warrender, A. M. Z. Slawin, P. A. Wright, P. A. Cox, A. Fecant and N. Bats, *Chem. Commun.*, 2007, 3470–3472.

26 M. E. Medina, M. Iglesias, M. A. Monge and E. Gutiérrez-Puebla, *Chem. Commun.*, 2001, 2548–2549.

CrystEngComm Accepted Manuscript

27 Q. Pan, X. Ren, Y. Xu and W. Yan, *Inorg. Chem. Commun.*, 2011, **14**, 1842–1845.

28 X. Ren, Y. Li, L. Shao, J. Yu and R. Xu, *Z. Anorg. Allg. Chem.*, 2012, **638**, 1345–1350.

29 J. Yu, Y. Wang, Z. Shi and R. Xu, *Chem.Mater.*, 2001, **13**, 2972–2978.

30 L. Tang and X. Zou, *MicroporousMesoporous Mater.*, 2007, **101**, 24–29.

31 F. Gándara, M. E. Medina, N. Snejko, B. Gómez-Lor, M. Iglesias, E. Gutiérrez-Puebla and M. A. Monge, *Inorg. Chem.*, 2008, **47**, 6791–6795.

32 J. Plévert, T. M. Gentz, T. L. Groy, M. O'Keeffe and O. M. Yaghi, *Chem. Mater.*, 2003, **15**, 714–718.

33 L. Shi, C. Bonneau, Y. Li, J. Sun, H. Yue and X. Zou, *Cryst. Growth Des.*, 2008, **8**, 3695–3699.

34 Materials Studio software 4.4, Accelry Inc.

CrystEngComm Accepted Manuscript

Table 1 The synthetic conditions of **JLG-*n*** (*n* = 3, 6, 7, 8).

GeO_2	$NiCl_2·6H_2O$	H_2O	Ethanolamine	Amine	HF	Products
1.0	0.5	37.04	55.46	18.42 DETA	1.86	JLG-3
1.0	0.5	37.04	55.46	15.47 1,2-PDA	1.86	JLG-6
1.0	0.5	37.04	55.46	13.46 TETA	3.71	JLG-7[a]
1.0	0.5	37.04	55.46	7.0TEPA	1.86	JLG-8

[a] the obtained products were impure, including JLG-7 and an unknown phase.

CrystEngComm Accepted Manuscript

Table 2 Crystal data and structure refinements for JLG-*n* (*n* = 3, 6, 7, 8).

Name	JLG-3	JLG-6	JLG-7	JLG-8
Empirical formula	$C_{16}H_{54}ClF_3Ge_7N_{12}Ni_2\ O15_3$	$C_{11}H_{38}F_2Ge_7N_7NiO_{15.5}$	$C_{11}H_{36}F_2Ge_7N_7NiO_{16}$	$C_{22}H_{72}F_6Ge_{14}N_{14}Ni_2O_{31}$
Formula weight	686.36	1121.32	1127.31	2276.62
Temperature	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system,	Momoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*P*2/*n*	*P*2(1)/*n*	*P*2(1)/*c*	*Pbcm*
Unit cell dimensions	*a* = 8.8785(7) Å, *α* = 90 º, *b* = 17.4501(14)Å, *β* = 101.292(2)º, *c* = 13.1922(11)Å, *γ* = 90º	*a* = 8.829(3) Å, *α* = 90°, *b* = 16.632(5) Å, *β* = 96.992(6) °, *c* = 20.933(6) Å, *γ* = 90°	*a* = 8.8029(18) Å, *α* =90°, *b* = 16.671(3) Å, *β* = 101.21(3)°, *c* = 21.293(4) Å, *γ* = 90°	*a* = 8.8089(18) Å, *α* = 90°, *b* = 22.436(5) Å, *β* = 90°, *c* = 31.193(6) Å, *γ* = 90°
Volume	2004.3(3) $Å^3$	3051.0(16) $Å^3$	3065.2(10) $Å^3$	6165(2) $Å^3$
Z	2	4	4	4
Calculated Density	2.275 Mg/m^3	2.441 Mg/m^3	2.443Mg/ m^3	2.453 Mg/m^3
Absorption coefficient	6.244 mm^{-1}	7.489 mm^{-1}	7.457 mm^{-1}	7.419 mm^{-1}
F(000)	1356	2188	2196	4432
Crystal size	0.08 × 0.08 ×0.04 mm	0.40 × 0.30 × 0.25 mm	0.20 × 0.20 ×0.10 mm	0.25 × 0.25 ×0.15 mm
Theta range for data collection	1.17 to 26.35 º	1.57 to 26.35º	1.56 to 26.35 º	1.31 to 26.35 º
Limiting indices	-11≤h≤9, -21≤k≤21, -13≤l≤16	-10≤h≤11, -16≤k≤20, -25≤l≤25	-10≤h≤10, -20≤k≤18, -26≤l≤13	-11≤h≤11, -28≤k≤24, -36≤l≤38
Reflectionscollected/unique	11746/4088 [*R*(int) = 0.0782]	17507/6206 [*R*(int) = 0.0921]	17842/6232 [*R*(int) = 0.0533]	34855/6400 [*R*(int) = 0.0351]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4088/0/258	6206/36/427	6232/230/418	6400/0/369
GOF	1.032	0899	1.173	1.064
R_1/wR_2 [$I>2\sigma(I)$]	0.0410/0.0687	0.0474/ 0.1006	0.0688/0.1765	0.0296/ 0.0774
R_1/wR_2 (all data)	0.0806/0.0894	0.0947/0.1141	0.0955/0.1974	0.0355/0.0796

*$R_1=\Sigma(\Delta F/\Sigma(F_o));wR_2=(\Sigma[w(F_o^2-F_c^2)])/\Sigma[w(F_o^2)^2]^{1/2},w=1/\sigma^2(F_o^2)$

CrystEngComm Accepted Manuscript

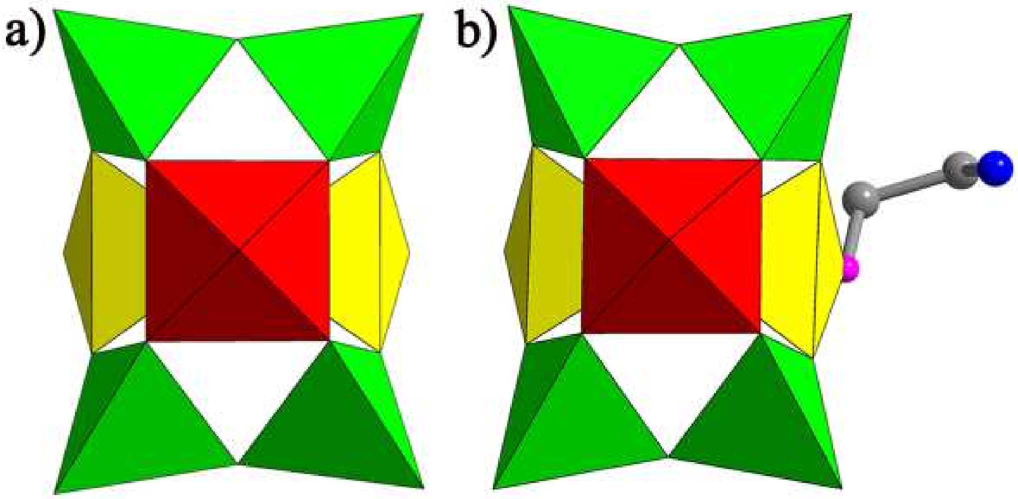


Fig. 1 Schematic diagram of (a) Ge_7 cluster; (b) the derivation of Ge_7 cluster in **JLG-6** and **JLG-7**. Color code: GeO_5X octahedron, red; GeO_4X trigonal bipyramid, yellow; GeO_4 tetrahedron, green; C, grey; N, blue; O, purple.

CrystEngComm Accepted Manuscript

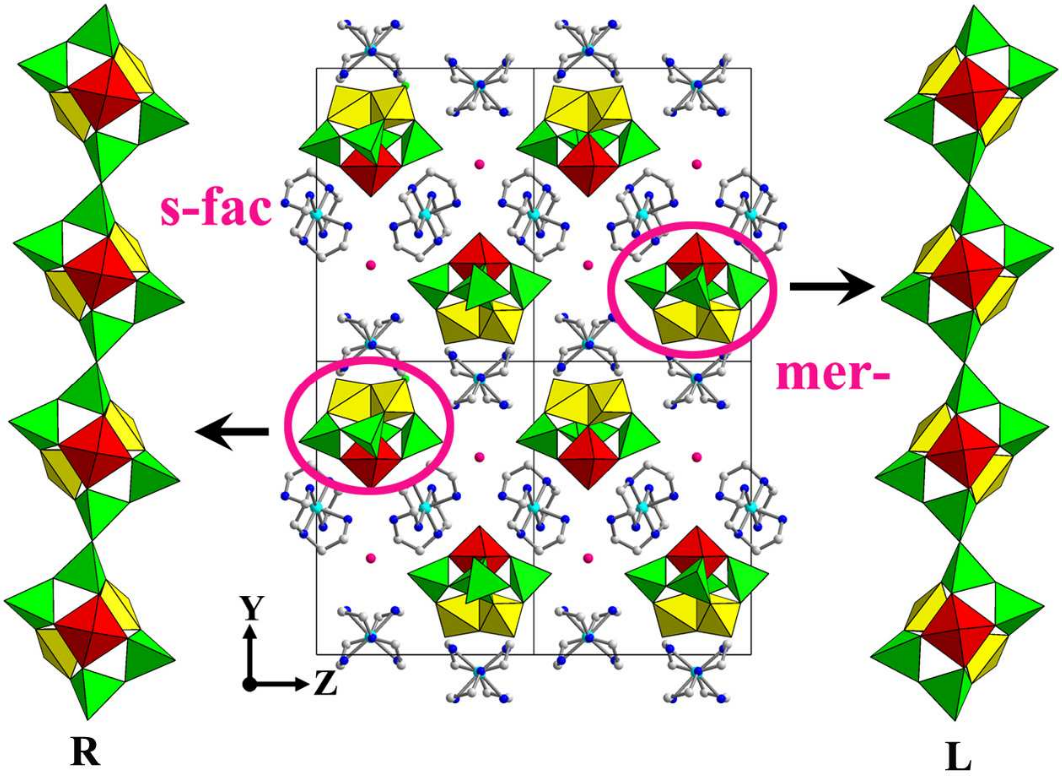


Fig. 2 The framework of JLG-3 viewed along the [100] direction. Color code: Ni, cyan; Cl, purple

CrystEngComm Accepted Manuscript

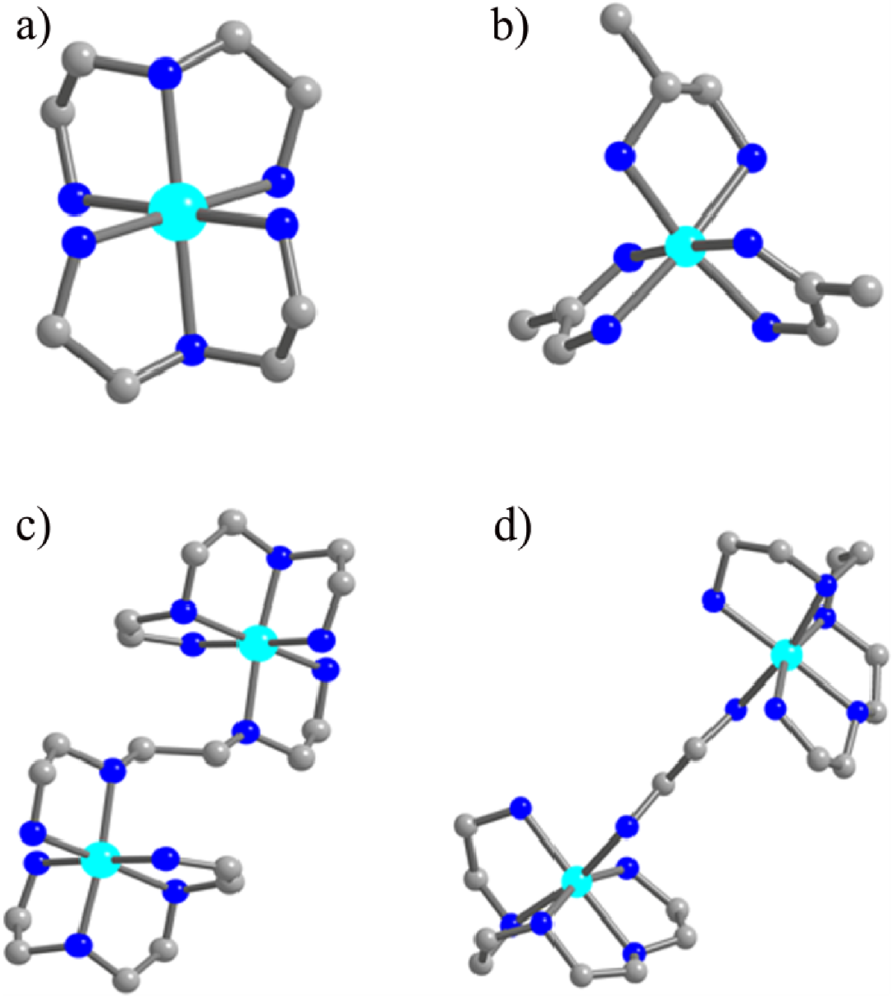


Fig. 3 The configurations of metal complexes used in the syntheses of germanates (a) **JLG-3**; (b) **JLG-6**; (c) **JLG-7**; (d) **JLG-8**, respectively.

CrystEngComm Accepted Manuscript

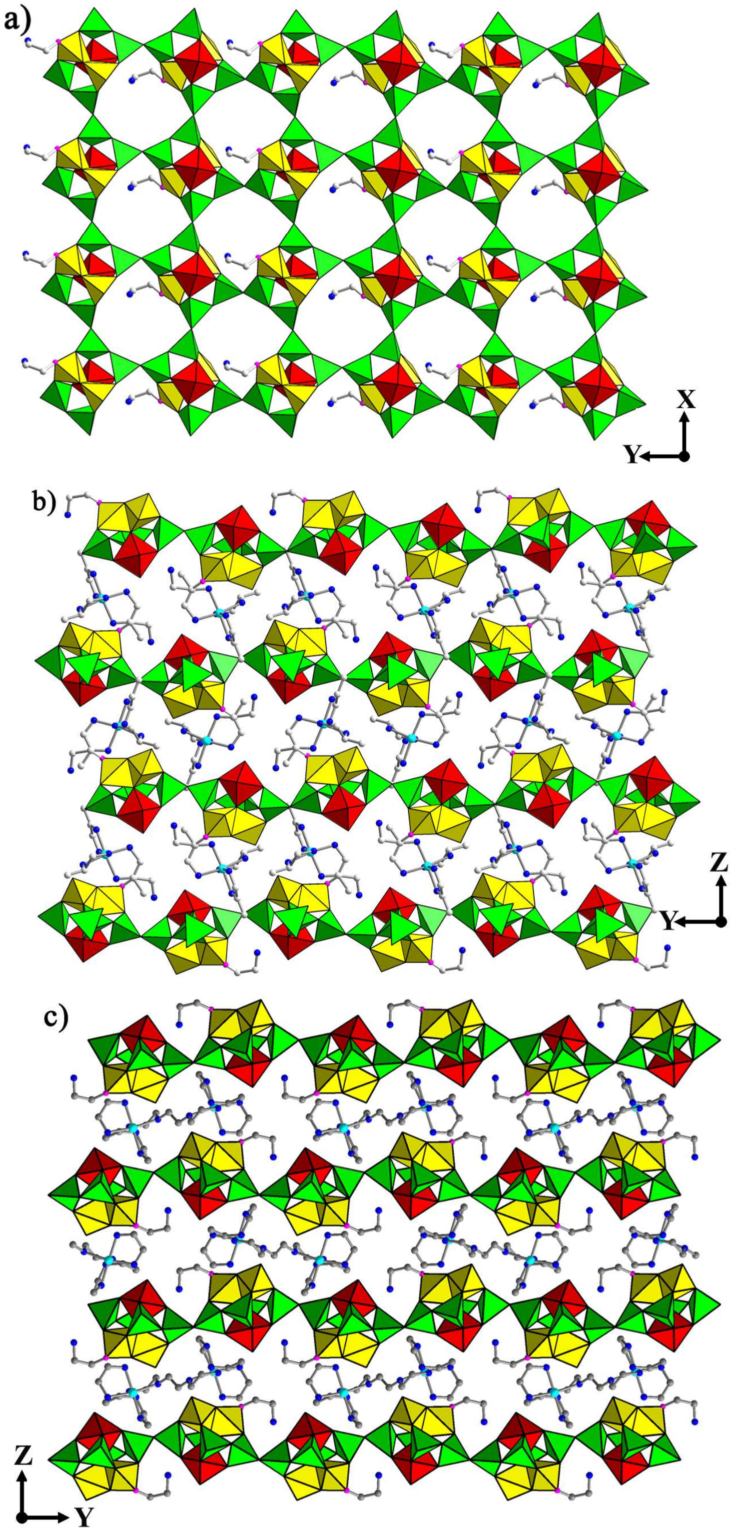


Fig. 4 (a) The layer structure of JLG-6 and JLG-7 projected down the [001] direction. (b) The stacking of the inorganic layers in JLG-6 along *a* axis. (c) The packing of the inorganic sheets in JLG-7 along *a* axis.

CrystEngComm Accepted Manuscript

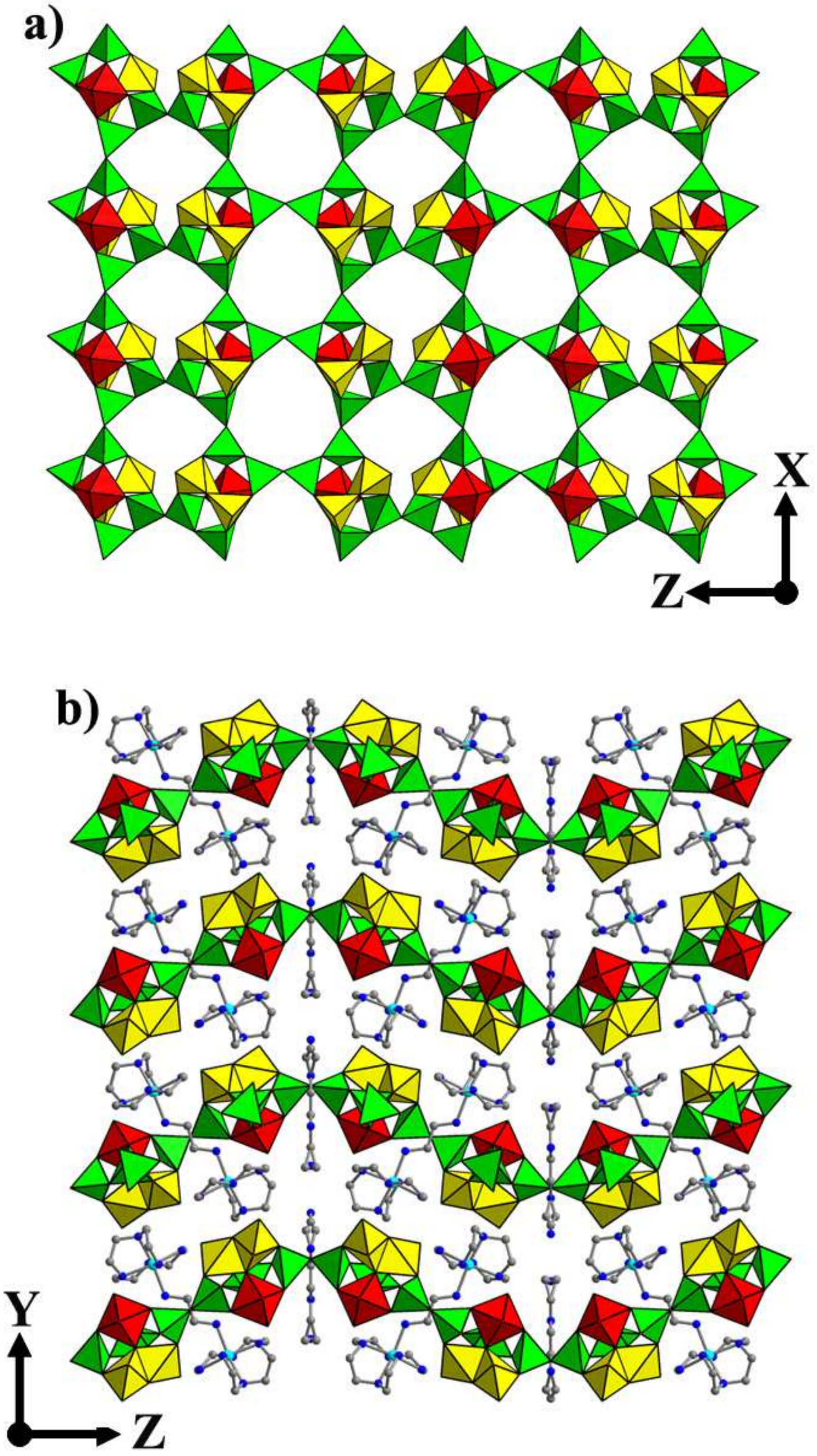


Fig. 5 (a) The layered structure of JLG-8 projected down the [001] direction. (b) The stacking of inorganic layers in JLG-8 along *a* axis.

CrystEngComm Accepted Manuscript

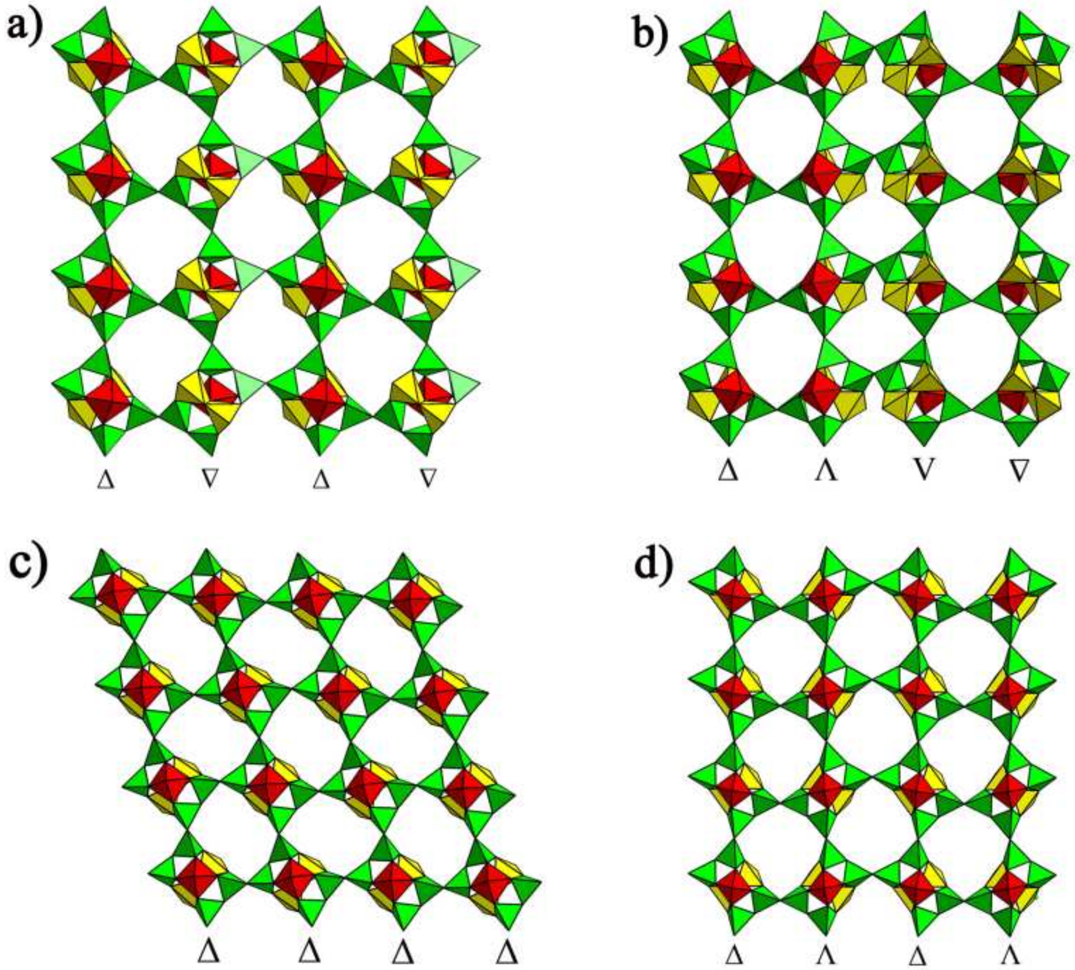


Fig. 6 Four designed layer structures of (a) H-1; (b) H-2; (c) H-3 and (d) H-4.

CrystEngComm Accepted Manuscript

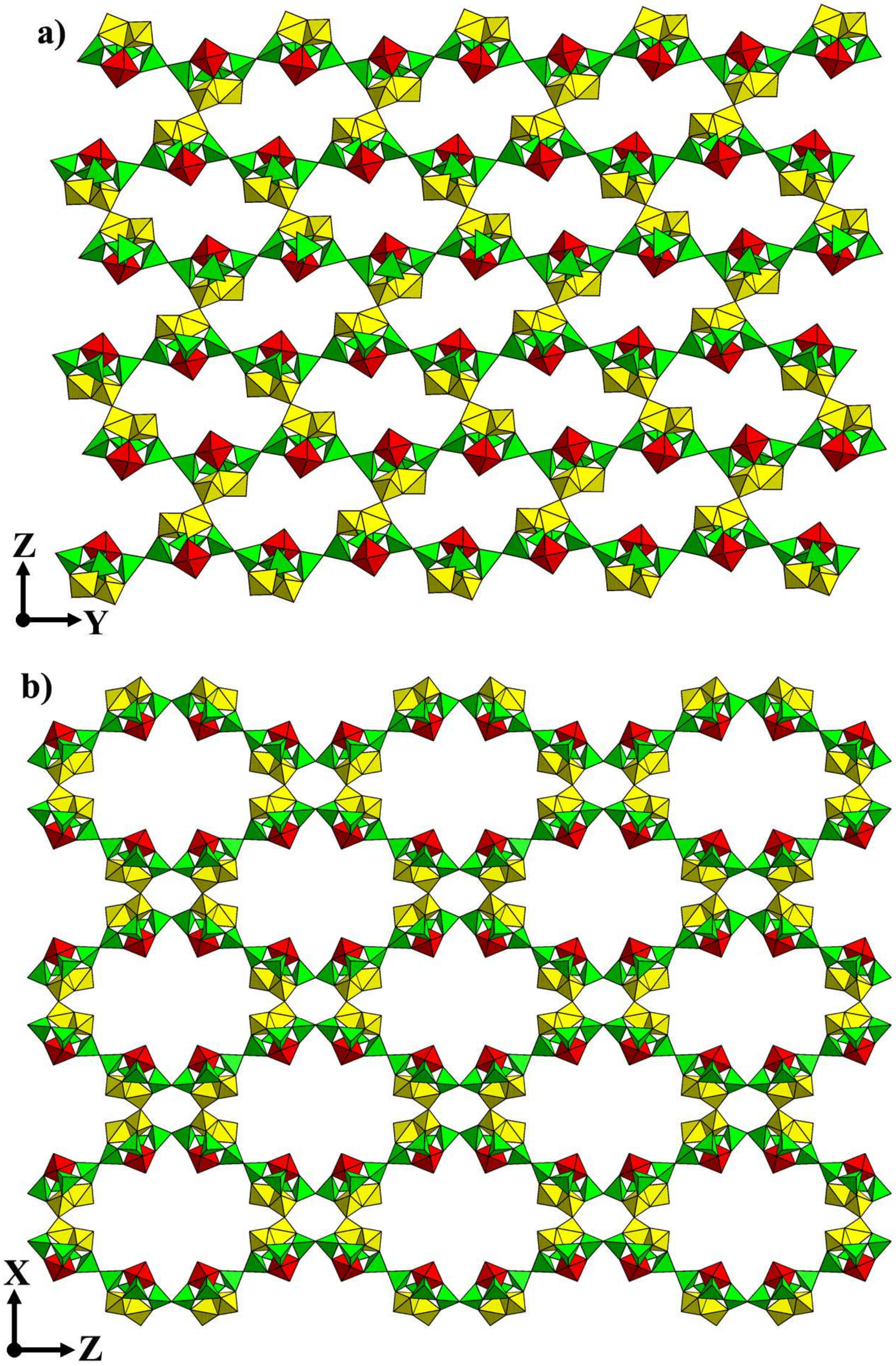
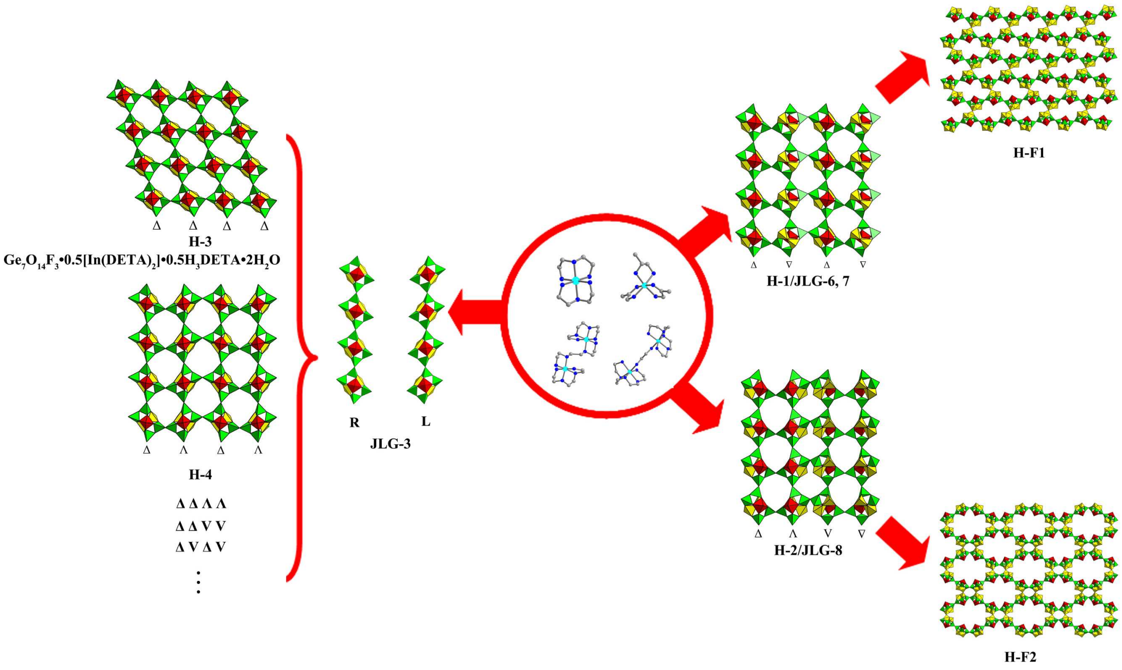


Fig. 7 Structures of two hypothetical 3-D germanates (a) H-F1 (16-rings) and (b) H-F2 (24-rings) viewed along the [100] direction.

CrystEngComm Accepted Manuscript



Graphical Abstract

By using metal complexes and organic amines cations/inorganic anions as co-templates, Four novel germanates **JLG-*n*** (*n* = 3, 6, 7, 8) have been prepared under solvothermal conditions. These compounds are all built up from Ge_7 clusters and classified into two structural types according to T^2 connection manner of Ge_7 cluster for **JLG-3** with chain-like structure and T^4 connection manner for **JLG-*n*** (n = 6, 7, 8) with 2-D layered structures. Then numerous 2-D layered structures were designed by different arrangements of R- and L- chains of **JLG-3**. In addition, two 3-D frameworks of **H-F1** (16-rings), **H-F2** (24-rings) were designed on the basis of sheets of **JLG-6** and **JLG-8**, respectively, with the connection of Ge_7 clusters as T^{4}P mode. The Ge_7 clusters display various connection ways, it is destined to be effective to construct novel open-framework germanates. A series of 2-D, even 3-D structures of germanates can be designed using Ge_7 clusters as SBUs, based on the concept of "Scale Chemistry".

CrystEngComm Accepted Manuscript