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Metal−Organogermanate Frameworks Built by Two Kinds of Infinite Ge−O Chains with High Thermostability and Luminescent Properties

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A bifunctional metalloligand with metal−C (Ge−C) bonds, bis(carboxyethylgermanium) sesquioxide ($H_2E_2Ge_2O_3$, where E = $-CH_2CH_2COO^-$), has been used to make metal−organometallic frameworks (MOMFs) $Cd_{1.5}(E_3Ge_3O_5)$ (**1**) and $Pb(E_2Ge_2O_3)$ (**2**). In the structures, the inorganic Ge_2O_3 cores of the metalloligands polymerize to form two kinds of infinite Ge−O chains, and the organic carboxyls induce the Cd and Pb ions to produce Cd−O and Pb−O chains. Further, the Ge−O chains link the Cd−O/Pb−O chains via $-CH_2CH_2-$ groups to result in two novel MOMFs, showing high thermostability and blue-violet emission.

Hybrid materials are of great interest because of their fascinating structures and potential applications in catalysis, adsorption, nonlinear optics, and luminescent properties.[1] Most of the work has so far focused on modification of the building blocks and control of the assembled motifs for requiring products via the selection of different organic ligands. So, a careful selection of ligands is critical to making hybrid materials with intriguing structures and desired properties. Though hybrid materials based on metals and organic ligands containing O/N donors have been well-established, the analogous chemistry of metalloligands with metal−C bonds remains less developed.[2]

Recently, we focus our interest on making metal−organometallic frameworks (MOMFs) and cluster−organic frameworks by using bis(carboxyethylgermanium) sesquioxide, $(HOOCCH_2CH_2)_2Ge_2O_3$ ($H_2E_2Ge_2O_3$, where E = $-CH_2CH_2COO^-$; Scheme 1), as the bifunctional metalloligand. Since the structure of $H_2E_2Ge_2O_3$ was reported in 1976,[3] no systematic investigation has been carried out on its coordination chemistry. Lately, we made two types of cluster−organic frameworks built by $\{Ln_8Ge_{12}\}/\{Ln_{11}Ge_{12}\}$ cage cluster units.[2] Now we extend the reaction system from lanthanide to transition/main-group metals for making metal−organogermanate frameworks (MOGeFs). Here, the flexible $H_2E_2Ge_2O_3$ has two functional parts: one is the Ge_2O_3 ($O{=}Ge{-}O{-}Ge{=}O$) core with two Ge=O bonds, which may polymerize to form Ge−O polymers when the Ge=O double bonds are opened; the other is two carboxyls, which can capture the second metal ions to form M−O aggregates. Further, the combination of the Ge−O polymers and the M−O aggregates may result in novel MOGeFs.

Accordingly, two MOGeFs, $Cd_{1.5}(E_3Ge_3O_5)$ (**1**) and $Pb(E_2Ge_2O_3)$ (**2**), containing transition metal Cd^{II} in **1** and main-group metal Pb^{II} in **2**, were successfully made. **1** shows a 3D framework (Figure 1a) based on the mixed $\{GeOCd\}_n$ layers and E linkers. The $\{GeOCd\}_n$ layer is built by alternately linking a Ge−O chain with double Ge_6 rings and a $\{CdO\}_n$ chain with Cd_4 rings (Figure 1b) linked by the O atoms from the opened Ge=O bonds. Framework **2** is constructed of two cross-linked infinite chains (Figure 1c), namely, the Ge−O chain with Ge_4 rings (Figure 1d) and the Pb−O zigzag chain via edge-shared PbO_6 polyhedra (Figure 1e). Notice that the Ge−O chains are different from each other in **1** and **2**.

Colorless prismatic crystals of **1** or **2** were made by the hydrothermal reaction of $H_2E_2Ge_2O_3$ and CdO or $Pb(OH)_2$ in water in the presence of HNO_3 (pH 3).[4] X-ray structure analyses reveal that **1** and **2** crystallize in the space groups $C2/c$ and $P\bar{1}$, respectively.[5] In the asymmetric unit of **1**, there are two independent Cd atoms and one unique $E_3Ge_3O_5^{3-}$ group. Each Cd atom has octahedral geometry: $Cd(1)O_6$ with six O_{COO} atoms of six carboxyls and $Cd(2)O_6$ with five O_{COO} atoms and one O atom of the adjacent GeO_3C unit (Figure S1 in the Supporting Information, SI). In the $E_3Ge_3O_5^{3-}$ unit, the carboxyls with three different coordination modes bond eight

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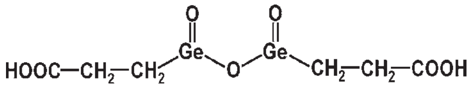
(4) Synthesis of **1**: A mixture of $H_2E_2Ge_2O_3$ (0.085 g, 0.25 mmol), CdO (0.032 g, 0.25 mmol), HNO_3 (0.33 mL, 8.4 wt %), and H_2O (6 mL) was stirred for about 2 h (pH 3) and then heated at 150 °C for 5 days. Colorless crystals were isolated by filtration (65% yield based on $H_2E_2Ge_2O_3$). Elem anal. Calcd for $C_9H_{12}Cd_{1.5}Ge_3O_{11}$: C, 15.82; H, 1.76. Found: C, 15.81; H, 1.80. Synthesis of **2**: Solid **2** was obtained using the same procedure as that for **1** but substituting $Pb(OH)_2$ (0.060 g, 0.25 mmol) for CdO (0.032 g, 0.25 mmol). The yield was 53% based on $H_2E_2Ge_2O_3$. Elem anal. Calcd for $C_6H_8Ge_2O_7Pb$: C, 13.22; H, 1.47. Found: C, 13.32; H, 1.38.

Scheme 1. Structural Scheme of $H_2E_2Ge_2O_3$ ($E = -CH_2CH_2COO^-$)


$HOOC-CH_2-CH_2-Ge(=O)-O-Ge(=O)-CH_2-CH_2-COOH$

Cd atoms to form the $\{CdO\}_n$ chain with Cd_4 rings (Figure S2 in the SI); the $\{Ge_3O_5\}$ group is formed by the Ge_2O_3 core of $H_2E_2Ge_2O_3$ and the $\{GeO_2\}$ unit derived from in situ decomposition of $H_2E_2Ge_2O_3$ via cleavage of the Ge−O bond under hydrothermal conditions and further polymerize to form an infinite $\{GeO\}_n$ chain with double Ge_6 rings built by GeO_3C tetrahedra (Figure S3 in the SI). As a result, a layer based on the alternate linkages of the $\{GeO\}_n$ and $\{CdO\}_n$ chains by O atoms is formed (Figure 1b), which are further linked by E units to form a 3D pillared-layer CdOGeF (Figure 1a). **1** is a new type in the pillared-layer frameworks: (1) In **1**, the bimetallic layer is built by two distinct chains, the $\{GeO\}_n$ chains polymerized by the inorganic part of the ligands and the $\{CdO\}_n$ chains induced by the organic part of the ligands; there is no such characteristic in the bimetallic layer.[6] (2) The pillars in **1** are from the organic parts of the bifunctional metalloligands, while the pillars in other pillared-layer frameworks are either the organic ligands or the linkers containing organic ligands and metal ions/clusters.[7] (3) The bonding modes between the pillars and layers in **1** contain not only coordination bonds but also metal−C (Ge−C) bonds, while only coordination bonds exist in other pillared-layer frameworks.

The main-group element Pb is an important industrial material and has been widely used in paints, storage batteries, and nuclear industry, although it is an environmental pollutant. In the area of coordination chemistry and photochemistry, it also has a tendency to form novel compounds with stable frameworks and luminescent properties. The intrinsic features of Pb^{II} reported, the presence of a $6s^2$ outer electron configuration and a large radius and which are relatively rare, inspire our interest. So, by the replacement of CdO with $Pb(OH)_2$ in the reaction system of **1**, crystals of **2** were obtained. In the asymmetric unit of **2**, there is one independent $E_2Ge_2O_3^{2-}$ unit and one unique Pb atom. The Ge centers are of tetrahedral geometry, while the Pb center adopts a hemidirected[8] configuration built by six O_{COO} atoms (Figure S4 in the SI). To bifunctional $E_2Ge_2O_3^{2-}$, the inorganic Ge_2O_3 core polymerizes to form a novel Ge−O chain with Ge_4 rings (Figure 1d), which differs from the Ge−O chain with Ge_6 rings in **1**; the two carboxyls of E groups have different coordination modes: one only chelates to one Pb atom; the other bonds to three Pb atoms via chelate and monodentate modes (Figure S5 in the SI), resulting in a Pb−O zigzag chain edge-shared by PbO_6 polyhedra (Figure 1e). The Ge−O chains and Pb−O zigzag chains are further cross-linked by the E groups to form a novel 3D PbOGeF (Figure 1c), which is the first 3D framework made by two kinds of chainlike building blocks via metal−C (Ge−C) bonds.

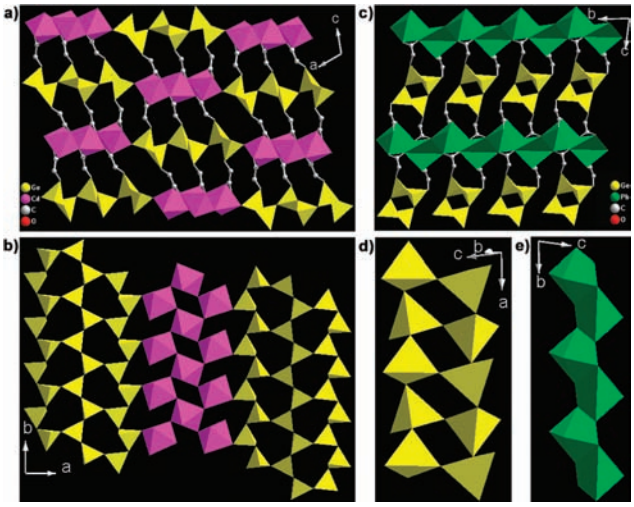


Figure 1. (a) Side view of the 3D framework **1** along the *b* axis. (b) Top view of the {GeOCd} layer in **1**. The C atoms are omitted for clarity. (c) Side view of the 3D framework **2** along the *a* axis. (d and e) View of the Ge−O double chain with Ge_4 rings and the Pb−O chain, respectively. Color code: GeO_3C, yellow; CdO_6, pink; PbO_6, green.

Notice that the Ge_2O_3 core of $H_2E_2Ge_2O_3$ can polymerize to the isolated cluster or polymer with different shapes in the presence of distinct metal ions, such as the trimeric Ge_6 wheel in a cage of $\{Ln_8Ge_{12}\}/\{Ln_{11}Ge_{12}\}$,[2] the infinite chain with Ge_6 and Ge_4 rings in **1** and **2**, respectively.

Both **1** and **2** exhibit not only new-type frameworks but also high thermal stability. Thermogravimetric analysis (TGA) of **1** and **2** was performed in a dry air atmosphere from 30 to 1000 °C at a heating rate of 10 °C min^{-1} (Figure S6 in the SI). The TGA curve of **1** indicates that the framework is stable up to 390 °C, and the one-step weight loss of 25.8% (calcd 26.1%) from 390 to 837 °C implies a departure of the organic parts via combustion. The residue is a mixture of CdO and GeO_2 (obsd 74.2%, calcd 73.9%). The TGA curve of **2** exhibits a higher thermal stability to 438 °C followed by a weight loss of 20.5% (calcd 20.8%) to 796 °C, due to the combustion of the organic parts. The remains are PbO and GeO_2 (obsd 79.5%, calcd 79.2%). Besides **1** and **2**, the thermal stability of the free $H_2E_2Ge_2O_3$ ligands has also been investigated, but it is only stable to 220 °C. Therefore, the thermal stabilities, 390 °C for **1** and 438 °C for **2**, are much higher than that of the free ligands. Furthermore, the difference between **1** and **2** could be attributed to the structural diversity and different metal ions.

The luminescent properties for **1**, **2**, and the free ligands in the solid state at room temperature have been studied (Figures 2 and S7 in the SI). Both **1** and **2** show emission bands similar to those of the free ligands when excited at 237 nm, indicating that luminescence is from the ligands or linker-based emissions. Thus, the observed emissions in **1** and **2** are neither metal-to-ligand charge transfer (MLCT) nor

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(5) Crystal data for **1**: $M_r = 682.56$, monoclinic, space group $C2/c$, $a = 24.577(4)$ Å, $b = 4.9372(3)$ Å, $c = 27.131(5)$ Å, $\beta = 110.943(9)°$, $V = 3074.6(8)$ Å^3, $Z = 8$, $\rho = 2.949$ g cm^{-3}, $\mu = 7.904$ cm^{-1}, $F(000) = 2576$, GOF = 1.075. Of 11 387 total reflections collected, 3536 were unique ($R_{int} = 0.0279$). R1/wR2 = 0.0276/0.0570 for 223 parameters and 3013 reflections [$I > 2\sigma(I)$]. Crystal data for **2**: $M_r = 544.54$, triclinic, space group $P\bar{1}$, $a = 4.935(6)$ Å, $b = 7.272(8)$ Å, $c = 15.003(17)$ Å, $\alpha = 81.37(2)°$, $\beta = 86.03(2)°$, $\gamma = 85.97(3)°$, $V = 530.1(11)$ Å^3, $Z = 2$, $\rho = 3.412$ g cm^{-3}, $\mu = 21.492$ cm^{-1}, $F(000) = 492$, GOF = 1.044. Of 4115 total reflections collected, 2413 were unique ($R_{int} = 0.0419$). R1/wR2 = 0.0452/0.1092 for 145 parameters and 2022 reflections [$I > 2\sigma(I)$]. CCDC 754604 and 754605 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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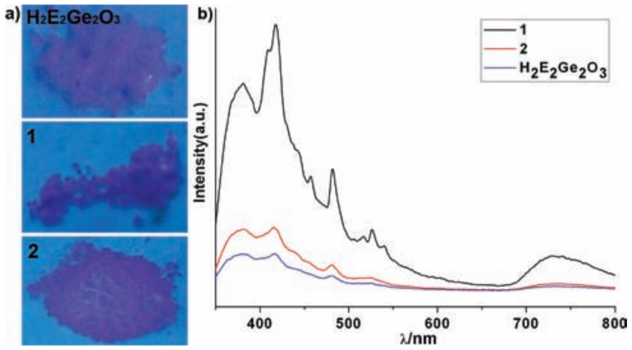

Figure 2. (a) Images of the powder samples of the $H_2E_2Ge_2O_3$ ligand, **1**, and **2** and their corresponding photoluminescence. (b) Emission spectra of **1**, **2**, and the $H_2E_2Ge_2O_3$ ligand (excited at 237 nm).

ligand-to-metal charge transfer (LMCT) in nature and can be mainly assigned to the intraligand fluorescent emission.[9]

As shown in Figure 2a, powder samples of the $H_2E_2Ge_2O_3$ ligand, **1**, and **2** display blue-violet photoluminescence when illuminated with near-UV light. As shown in Figure 2b, all emission spectra are very similar in shape and position among the three species, which indicates that the emission properties are dominated by linkers, i.e., the free ligands. **1** and **2** exhibit five clear emission bands at 380, 417, 481, 525, and 729 nm and one shoulder at 458 nm with an excitation maximum at 237 nm (Figures 2b and S7 in the SI). However, the luminescent mechanism for {GeO}-based materials is ambiguous at this stage because of very limited investigation. So far, the photoluminescence of germanates is often attributed to the presence of various kinds of lattice defects, such as oxygen vacancies. Such a defect mechanism is also possible for three species reported here. Some closely related {GeO}-based materials with luminescence have been observed. For example, UCSB-7GaGe/7AlGe exhibit efficient luminescence at 396 and 421 nm,[10] which resembles 380 and 417 nm in Figures 2b and S7 in the SI. For FJ-1a/1b, the blue luminescence in the solid state gives two strong emission bands at 482 and 523 nm and one shoulder at 458 nm,[11] which is very similar to that of Figures 2b and S7 in the SI. Recently, the luminescence of the as-deposited GeO_x films presents a broad band centered at 735 nm attributed to the Ge aggregates,[12] which is also observed at 729 nm in Figures 2b and S7 in the SI reported here.

In summary, we have successfully made two 3D MOGeFs by using the bifunctional metalloligand with Ge−C bonds under mild hydrothermal conditions, in which the linkages between two distinct building blocks through the flexible arms of the metalloligands result in 3D frameworks. The key points of the synthetic procedures have been well established, which indicates that this strategy offers a feasible and effective pathway for designing and making novel MOMFs. In addition, these results provide a perspective toward mixed-metal functional materials and confirm the potential for developing new structural classes of solid-state materials by using this bifunctional metalloligand as the linker. Further work is in progress for making novel functional MOGeFs.

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Supporting Information Available: X-ray crystallographic data in CIF format, physical measurements, different structural views of **1** and **2**, TGA curves, emission and IR spectra, and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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