A New Open Metal-Organic Framework $[Zn_8(GeO_4)(C_8H_4O_4)_6]_n$, Constructed by Heterometallic Cluster $Zn_8(GeO_4)$ Secondary Building Units

Jinxi Chen,* Zhicheng Liu, Ting Yu, Zhenxia Chen, Jinyu Sun, Linhong Weng, Bo Tu, and Dongyuan Zhao*
Molecular Catalysis and Innovative Materials Lab., Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

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A new interpenetrating three dimensional open metal–organic framework $[Zn_8(GeO_4)(C_8H_4O_4)_6]_n$, constructed by $Zn_8(GeO_4)$ secondary building units is reported. It is a rare example of metal–organic frameworks based on the heterometallic cluster secondary building units. Thermogravimetric analysis shows that it is thermally stable up to 320 °C.

The recent upsurge in open metal–organic frameworks (MOFs) is caused by their potential applications in shape or size selective catalysis, gas storage, nonlinear optical devices, and magnetism.[1–7] The most efficient construction strategy for these compounds is expansion and decoration of the topological networks of some inorganic dense materials.[4] The process termed decoration is replacement of a vertices of a framework net by a group of vertices, such as metal cluster. One of the recent trends has been to design and synthesize MOF employing metal cluster as secondary building units (SBUs) and linking them with suitable multidentate organic ligands into three dimensional (3D) structures.[4] This approach has afforded structures with unprecedented porosity.[4,8] However, so far most of the frameworks were built with homometallic cluster as SBUs, the open metal–organic frameworks containing heterometallic cluster is much less well explored. The later may create much richer structural variations and still maintain chemical thermal stability. In our effort to seek heterometallic cluster as SBUs, we noticed the fact that the Zn(II) ion in tetrahedral geometry can match well the germanate anion. In this paper, we describe a new interpenetrating 3D open framework germanium/zinc 1,4-benzenedicarboxylate, $[Zn_8(GeO_4)(C_8H_4O_4)_6]_n$ **1**.

The compound **1** was prepared under hydrothermal condition: 1,4-benzenedicarboxylic acid (1,4-H_2BDC) (0.083 g, 0.5 mmol), GeO_2 (0.006 g, 0.05 mmol), and NaOH (0.080 g, 2 mmol) were dissolved in 8 mL of water. The pH value was adjusted to about 7.0 by 1 M HNO_3. Then to the above solution was added $Zn(NO_3)_2 \cdot 6H_2O$ (0.147 g, 0.5 mmol). Finally 3 mL of cyclohexanol was added. The mixture was heated to 180 °C in a Teflon-coated stainless-steel autoclave and held at that temperature for 120 h and then cooled to room temperature. The colorless crystals of **1** suitable for X-ray diffraction analysis were collected after washing by H_2O, which was stable in air and insoluble in water and common organic solvent.

Elemental analysis (%) calcd. for $C_{48}H_{24}O_{28}GeZn_8$: C, 35.03; H, 1.46; found: C, 34.46; H, 1.89%. The infrared spectra show two strong bands at 1623 and 1556 cm^{-1}, which could be ascribed to carboxylate anions (CO_2^-) stretching modes. The absence of absorption bands at 1730–1690 cm^{-1}, where the –COOH is expected to appear, is indicative of the complete deprotonation of H_2BDC.[9]

A single crystal X-ray diffraction study[10] reveals that **1** is isostructural to $[Zn_8(SiO_4)(C_8H_4O_4)_6]_n$[11] and made up of two fold interpenetrating three dimensional framework (Figure 1) with a cubic $Zn_8(GeO_4)$ cluster core (Figure 2) and 1,4-BDC anion building unit. The asymmetric unit of **1** with atom-numbering scheme is show in Figure 3. This unit consists of one Ge, two Zn atoms, two oxygen, three BDC^{2-} anions. In the $Zn_8(GeO_4)$ core, the germanate anion, located in the center of the unit with each oxygen atom of the germanate anion bridging two zinc(II) atoms in a μ_2 bridging mode, forms a distorted cubic core. Each zinc(II) atom occupying one apex of the cube. Two zinc(II) atoms at each edge of the core are then capped by a carboxylate group of 1,4-BDC, thus six faces of the $Zn_8(GeO_4)$ cube is spanned by six pairs of 1,4-BDC to form a 6-connected $Zn_8(GeO_4)(C_8H_4O_4)_{12}$ cluster. Each zinc(II) atom is four-coordinated by three oxygen atoms from three different 1,4-BDC and one oxygen atom from the germanate anion to complete a tetrahedral geometry. The bond lengths of $Zn–O_{carboxylate}$ are in the range of 1.921(7)–1.947(7) Å. The bond lengths of $Zn–O_{germanate}$ range from 1.934(6) to 1.946(6) Å. The bond angles of $O_{carboxylate}–Zn–O_{carboxylate}$, $O_{carboxylate}–Zn–O_{germanate}$, and O–Ge–O in the germanate anion are in the ranges of 106.8(4)–110.4(3)°, 103.(3)–121.8(3)°, and 107.6(3)–112.0(4)°, respectively, indicating that the germanate anion matches well the ZnO_4 geometry.

It is worth noting that the typical M–O–M angles in germanates are smaller than in silicates, the former offers greater op-

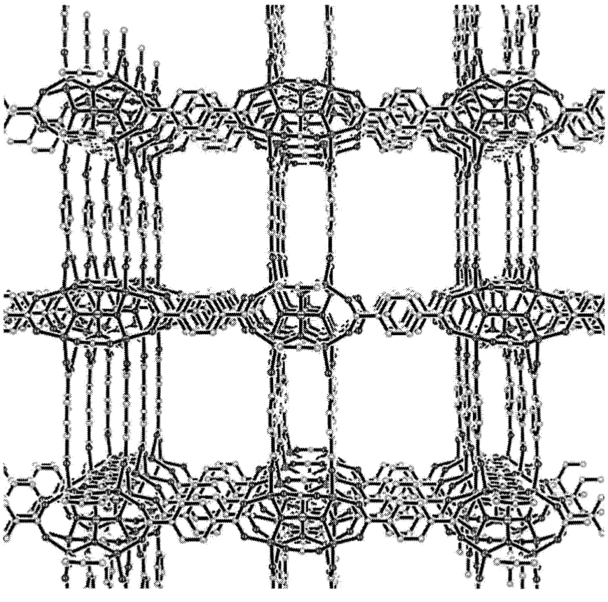

Figure 1. ORTEP (hydrogen atoms are omitted for clarity) view of one lattice set of the networks in **1** along the *b* axis.

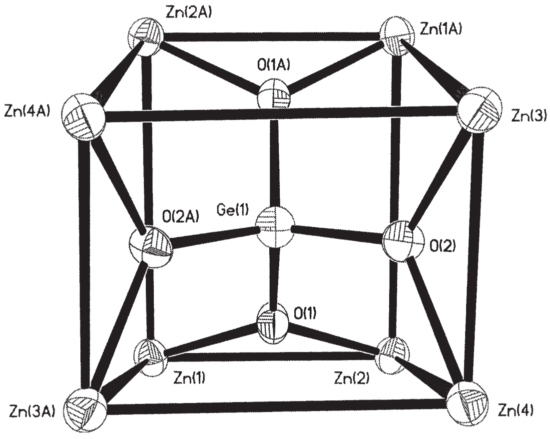

Figure 2. Perspective of the distorted cubic core of $Zn_8(GeO_4)$ in **1**.

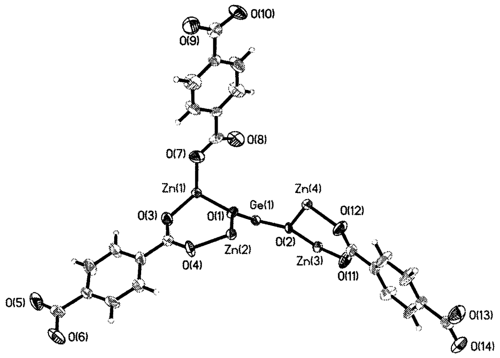

Figure 3. View of the asymmetric unit showing the atom numbering scheme. Thermal ellipsoids are 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

portunities for the formation of cluster aggregates. The larger cluster aggregate could be used to substitute the GeO_4 core in the germanium/zinc heterometallic cluster. By systematic variation of the size of the cluster aggregate, a variety of open MOFs containing heterometallic cluster core could be obtained.

Thermogravimetric analysis (TGA) was carried out on a polycrystalline sample under a flow of air. Below 120 °C, a slight weight loss is probably due to departure of the adsorbed water molecules. No further weight loss steps occurred below 320 °C, which indicates the compound **1** is thermally stable up to 320 °C.

In conclusion, A new two fold interpenetrating 3D open metal–organic framework $[Zn_8(GeO_4)(C_8H_4O_4)_6]_n$, constructed by heterometallic cluster, $Zn_8(GeO_4)$ secondary building units has been hydrothermally prepared. This work opens the way using heterometallic cluster as SBU in the construction of MOFs.

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10 Single crystal X-ray data was collected on a Bruker Smart Apex diffractometer at room temperature. Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXTL Version 5.10), and refined by full-matrix least-squares on F^2. All nonhydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were treated as idealized contributions. Crystal data for **1**. $C_{48}H_{24}GeO_{28}Zn_8$ (293 K). $M_r = 1644.22$, monoclinic, space group $C2/c$, $a = 19.658(7)$ Å, $b = 14.108(5)$ Å, $c = 19.540(6)$ Å, $\beta = 90.407(4)°$, $V = 5419(3)$ Å^3, $Z = 4$, $D_{calcd.} = 2.015$ g/cm^3, absorption coefficient = 4.114 mm^{-1}, total reflections collected 11104, unique 4780 ($R_{int} = 0.0676$), GOF = 1.098, $R1 = 0.0619$, $R_w = 0.1004$ ($I > 2\sigma(I)$). Crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 201425. Copies of the data can be obtained free of charge in application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk)

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